pendent on the cis porphyrin basicity. Differences in properties observed between cytochromes P_{450} and (*n*-butanethiolato)heme models could, in part, be accounted for in terms of trans ligand basicity.

Acknowledgment. This research was supported by a grant from the National Institutes of Health.

Registry No. Mesoheme thiolate, 102940-33-0; protoheme thiolate, 102940-34-1; 2-formyl-4-vinyldeuteroheme thiolate, 102940-35-2; diacetyldeuteroheme thiolate, 102940-36-3; dicyanodeuteroheme thiolate, 102940-37-4; mesoheme thiolate, CO complex, 102940-38-5; protoheme thiolate, CO complex, 102940-39-6; 2-formyl-4-vinyldeuteroheme thiolate, CO complex, 102940-40-9; diacetyldeuteroheme thiolate, CO complex, 102940-41-0; dicyanodeuteroheme thiolate, CO complex, 102940-42-1; CO, 630-08-0.

Contribution from the Department of Chemistry,
The University of British Columbia, Vancouver, BC, Canada V6T 1Y6

Magnetic and Spectroscopic Study of Pyrazine-Bridged Iron(II) Halide Complexes

John S. Haynes, John R. Sams,* and Robert C. Thompson*

Received March 11, 1986

The low-dimensional compounds $Fe(pyz)_2X_2$ (X = Cl, Br, I; pyz = pyrazine) and $Fe(pyz)Cl_2$ have been prepared and characterized by vibrational, electronic, and Mössbauer spectroscopies, by differential scanning calorimetry, and by magnetic susceptibility measurements between 300 and 4.2 K [and to 1.9 K for the mono(pyrazine) complex]. Although bidentate bridging pyrazine ligands are known to support magnetic exchange interactions in a number of other systems, including iron(II) complexes, no conclusive evidence for exchange coupling is found here.

Introduction

Pyrazine-bridged transition-metal complexes represent examples of materials that may exist as one-dimensional linear chains or two-dimensional lattices, with the possibility of magnetic exchange interactions being propagated through the bridging pyrazine ligand. The most extensive series of pyrazine complexes investigated have been derivatives of copper(II). Chloride and bromide complexes of copper(II) have been synthesized with a series of mono- and dimethyl-substituted pyrazine ligands,[1] and all exhibit a maximum in the magnetic susceptibility vs. temperature curve, indicative of antiferromagnetic interactions. Using a variety of substituted pyrazine ligands L in complexes of the type $CuL(NO_3)_2$, Richardson and Hatfield[2] elegantly demonstrated that the variation in the antiferromagnetic coupling constant J correlates with the energy of the π–π^* transition of the pyrazine ligand in the complex. Thus, the pyrazine π-system is implicated in the exchange mechanism. Another important factor in determining the nature of the magnetic exchange interactions in copper(II) pyrazine complexes has been found to be the overlap between the copper d orbitals and the pyrazine π-system.[3-5]

Investigations of the nickel(II) pyrazine halides, $Ni(pyz)_2X_2$ (X = Cl, Br, I),[6] revealed temperature-independent magnetic moments between 90 and 300 K. Similarly, the cobalt(II) derivatives $Co(pyz)_2X_2$ (X = Cl, Br)[7] showed no evidence of magnetic interactions over the temperature range 1.8–300 K, although subsequent heat capacity[8] and susceptibility[9] measurements to substantially lower temperatures show both these cobalt(II) complexes to be *xy* antiferromagnets with critical temperatures of 0.85 and 0.66 K, respectively.

Relatively little research has been undertaken on iron(II) complexes of pyrazine, a fact that may be due to the problems associated with the relative ease of oxidation of iron(II) to iron(III), and to the difficulties in analyzing magnetic susceptibility data for d^6 systems. Previous work on iron(II) pyrazine halides includes the preparation of $Fe(pyz)Cl_2$,[10] $Fe(pyz)_2Cl_2$,[11] and $Fe(pyz)_2Br_2$[12] and a hydrate, $Fe(pyz)_2Cl_2{\cdot}H_2O$.[12] Characterization of these complexes has included thermal studies,[11] infrared spectroscopy,[10,12,13] and room-temperature magnetic susceptibility measurements.[12] The pseudohalide complex, $Fe(pyz)_2(NCS)_2$,[14] has been reported, but no synthetic procedure was given and characterization was limited to susceptibility measurements in the 80–300 K temperature region.

Very recently we have reported, inter alia, Mössbauer spectra of $Fe(pyz)_2(NCS)_2$ in the range 1.8–10 K.[15] The magnetic susceptibility of this complex exhibited a maxiumum at about 8 K, indicative of antiferromagnetic exchange coupling,[16] and Mössbauer spectroscopy revealed a magnetic phase transition at T_N = 9.1 K with substantial line broadening, due to relaxation effects, in the vicinity of T_N. Reiff et al.[17] have also reported briefly their low-temperature Mössbauer measurements on $Fe(pyz)_2Cl_2$ and $Fe(pyz)Cl_2$. Neither complex was found to show any sign of magnetic ordering in the zero field down to 0.5 K. No other information on these derivatives seems to be available.

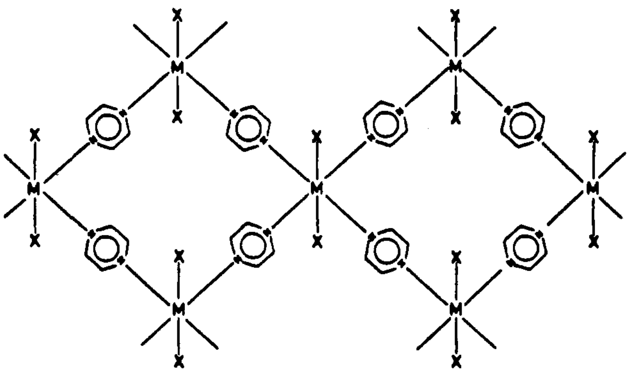
We report here the synthesis and characterization of the bis(pyrazine)halide complexes $Fe(pyz)_2X_2$ (X = Cl, Br, I) and also the mono(pyrazine) complex $Fe(pyz)Cl_2$. The bis(pyrazine) derivatives are proposed to have polymeric structures as found by X-ray crystallography for $Co(pyz)_2Cl_2$.[18] In this cobalt(II)

---

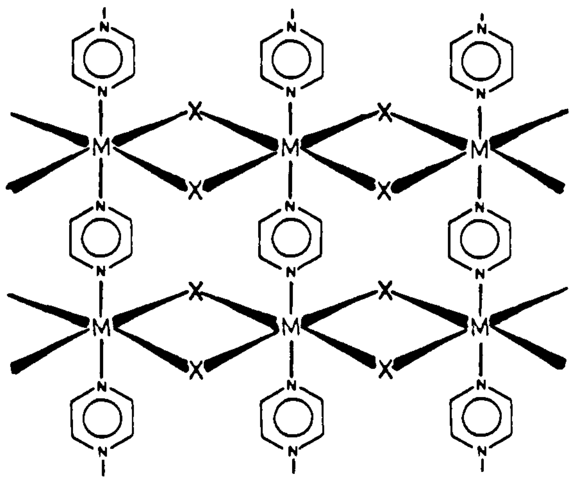
(1) Inman, G. W.; Hatfield, W. E. *Inorg. Chem.* **1972**, *11*, 3085.
(2) Richardson, H. W.; Hatfield, W. E. *J. Am. Chem. Soc.* **1976**, *98*, 835.
(3) Santoro, A.; Mighell, A. D.; Reimann, C. W. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1970**, *B26*, 979.
(4) Belford, R. C. E.; Fenton, D. E.; Truter, M. R. *J. Chem. Soc., Dalton Trans.* **1974**, 17.
(5) Richardson, H. W.; Wasson, J. R.; Hatfield, W. E. *Inorg. Chem.* **1977**, *16*, 484.
(6) Goldstein, M.; Taylor, F. B.; Unsworth, W. D. *J. Chem. Soc., Dalton Trans.* **1972**, 418.
(7) Inoue, M.; Kubo, M. *Coord. Chem. Rev.* **1976**, *21*, 1.
(8) Gonzalez, D.; Bartolome, J.; Navarro, R.; Greidanus, F.; De Jongh, L. J. *J. Phys. Colloq.* **1978**, *39*, 762.
(9) Carlin, R. L.; Carnegie, D. W.; Bartolome, J.; Gonzalez, D.; Floria, L. M. *Phys. Rev. B: Condens. Matter* **1985**, *32*, 7476.
(10) Child, M. D.; Foulds, G. A.; Percy, G. C.; Thornton, D. A. *J. Mol. Struct.* **1981**, *75*, 191.
(11) Beech, G.; Mortimer, C. T. *J. Chem. Soc. A* **1967**, 1115.
(12) Ferraro, J. R.; Zipper, J.; Wozniak, W. *Appl. Spectrosc.* **1969**, *23*, 160.
(13) Bayer, R.; Ferraro, J. R. *Inorg. Chem.* **1969**, *8*, 1654.
(14) Figgis, B. N.; Lewis, J.; Mabbs, F. E.; Webb, G. A. *J. Chem. Soc. A* **1967**, 442.
(15) Haynes, J. S.; Kostikas, A.; Sams, J. R.; Simpopoulos, A.; Thompson, R. C. Presented at the International Conference on Applications of the Mössbauer Effect, Leuven, 1985; Paper 3.44.
(16) Haynes, J. S. Thesis, University of British Columbia, 1985.
(17) Reiff, W. M.; Zhang, J. H.; Takacs, J.; Takacs, L. Presented at the International Conference on Applications of the Mössbauer Effect, Leuven, 1985; Paper 2.04.

0020-1669/86/1325-3740$01.50/0

complex, pyrazine acts as a bridging ligand between metal centers to form a two-dimensional lattice, with chloride anions above and below the plane, as in **1**. The mono(pyrazine) iron(II) complex $Fe(pyz)Cl_2$ is considered[16,17] to have a structure in which adjacent iron centers are bridged by chloride ions to provide linear chains, which are cross-linked by symmetrically bridging pyrazine ligands, **2**.



1



2

For none of the iron(II) pyrazine complexes have single crystals suitable for X-ray diffraction measurements been isolated. Thus, structural conclusions in the present study are based on a combination of electronic, vibrational, and Mössbauer spectroscopies. We have also measured the magnetic susceptibilities of the complexes from 4.2 to 300 K [and down to 1.9 K in the case of $Fe(pyz)Cl_2$].

In contrast to the lack on definitive structural information for the iron(II) pyrazine halides, the structures of the pyridine complexes $Fe(py)_nX_2$ ($n = 2$ or 4; X = Cl, Br, I) are well-known.[19-24] Where $n = 4$ these complexes are monomeric with trans halide ions, giving tetragonally distorted octahedral structures in which there is no pathway for superexchange. With $n = 2$, linear chain compounds obtain, the bridging halide ions offering the sole pathway for exchange coupling between metal centers. The present study therefore provides an interesting comparison between the magnetic and structural properties of the bis- and tetrakis(pyridine)iron(II) halides and the corresponding mono- and bis(pyrazine) derivatives.

Table I. Differential Scanning Calorimetry Results

compd	peak temp, K	ΔH, kJ mol^{-1}	wt loss, % calcd^a	wt loss, % obsd
$Fe(pyz)_2Cl_2$	477	70	28	34
	723	86	56	59
$Fe(pyz)_2Br_2$	508	75	21	23
	742	41	43	48
$Fe(pyz)_2I_2$	516	59	*b*	69
$Fe(pyz)Cl_2$	730	60		

[a] For explanation of calculated values see text. [b] See text for discussion of this complex.

Experimental Section

Materials. Anhydrous iron(II) chloride, iron(II)bromide, iron(II) iodide (Alfa Products), and pyrazine (Aldrich Chemical Co.) were used without further purification. Methanol and ethanol were dried by refluxing them in the presence of the corresponding magnesium alkoxide; diethyl ether was refluxed over sodium benzophenone ketyl. The iron(II) compounds were found to be slightly oxygen and moisture sensitive, and to prevent decomposition all manipulations were carried out either in a nitrogen-atmosphere glovebox or by the use of Schlenk techniques.

Syntheses. Bis(pyrazine)iron(II) Chloride, $Fe(pyz)_2Cl_2$. The synthesis of $Fe(pyz)_2Cl_2$ has been described previously,[11] although few details were given. In the present study the product was obtained by the addition of an ethanolic solution (20 mL) of $FeCl_2$ (0.503 g, 3.97 mmol) to a solution of pyrazine (3.54 g, 44.3 mmol) in ethanol (10 mL). A deep red solid formed immediately, and the mixture was stirred for 0.5 h. The product was isolated in 62% yield after filtration and being washed with small amounts of ethanol followed by diethyl ether. Anal. Calcd for $C_8Cl_2FeH_8N_4$: C, 33.49; H, 2.81; N, 19.53. Found: C, 33.28; H, 2.89; N, 19.65.

Bis(pyrazine)iron(II) Bromide, $Fe(pyz)_2Br_2$. The preparation of this complex was briefly described in an earlier report.[12] The following method was used in this work. Anhydrous iron(II) bromide (0.490 g, 2.27 mmol) was dissolved in methanol (15 mL). The resulting solution was filtered into a solution of pyrazine (0.80 g, 10 mmol) in methanol (5 mL). A red precipitate started to form after several minutes; the solution was left to stand for 3 h, and subsequently the product was isolated by filtration and washed with portions of methanol and finally diethyl ether (yield 74%). Anal. Calcd for $Br_2Cl_8FeH_8N_4$: C, 25.57; H, 2.15; N, 14.91. Found: C, 26.06; H, 2.41; N, 14.51.

Bis(pyrazine)iron(II) Iodide, $Fe(pyz)_2I_2$. Iron(II) iodide (0.524 g, 1.69 mmol) was dissolved in methanol (10 mL) and filtered into a methanolic solution (10 mL) of pyrazine (0.62 g, 7.75 mmol). The solution first turned yellow and then orange, and after 5 min an orange cloudiness appeared. Overnight, a lustrous maroon solid formed; the product was isolated by filtration and washed with methanol followed by diethyl ether (yield 44%). Anal. Calcd for $C_8FeH_8I_2N_4$: C, 20.45; H, 1.72; N, 11.92. Found: C, 20.41; H, 1.75; N, 12.09.

Mono(pyrazine)iron(II) Chloride, $Fe(pyz)Cl_2$. The synthesis of this complex has been described previously[10] and involved the addition of a solution of pyrazine to an iron(II) chloride solution in 1:1 mole ratio. We have found that the mono(pyrazine) complex can be prepared simply by thermolysis of $Fe(pyz)_2Cl_2$. The procedure used was to heat the bis(pyrazine) derivative at 380 K in an Aberhalden drying pistol, in vacuo and in the presence of phosphorus(V) oxide. After the compound was heated for 3 days no further change in the infrared spectrum of the product was noted, and analytical data indicated the formation of $Fe(pyz)Cl_2$. Anal. Calcd for $C_4Cl_2FeH_4N_2$: C, 23.23; H, 1.95; N, 13.54. Found: C, 23.15; H, 1.99; H, 13.36.

Physical Measurements. Infrared and electronic spectra and differential scanning calorimetry data were obtained by using equipment and procedures previously described.[25] ^{57}Fe Mössbauer spectra were recorded at 78 and 293 K in transmission mode on a constant-acceleration spectrometer of conventional design. The samples were sealed in nylon sample holders with epoxy resin. The Doppler velocity scale was calibrated with an iron foil absorber, and isomer shifts are quoted relative to the centroid of the iron foil spectrum.

The Gouy technique was used for magnetic susceptibility measurements between 80 and 300 K.[25] Between 1.9 and 130 K a vibrating sample magnetometer was employed.[26] Magnetic susceptbitilities were

---

(18) Carrack, P. W.; Goldstein, M.; McPartlin, E. M.; Unsworth, W. D. *J. Chem. Soc., Chem. Commun.* **1971**, 1634.

(19) Little, B. F.; Long, G. J. *Inorg. Chem.* **1978**, *17*, 3401.

(20) Long, G. J.; Clarke, P. J. *Inorg. Chem.* **1978**, *17*, 1394.

(21) Long, G. J.; Whitney, D. L.; Kennedy, J. E. *Inorg. Chem.* **1971**, *10*, 1406.

(22) Reiff, W. M.; Frankel, R. B.; Little, B. F.; Long, G. J. *Inorg. Chem.* **1974**, *13*, 2153.

(23) Foner, S.; Frankel, R. B.; Reiff, W. M.; Little, B. F.; Long, G. J. *Solid State Commun.* **1975**, *16*, 159.

(24) Foner, S.; Frankel, R. B.; Reiff, W. M.; McNiff, E. J.; Little, B. F.; Long, G. J. *AIP Conf. Proc.* **1975**, *No. 24*, 363.

(25) Haynes, J. S.; Sams, J. R.; Thompson, R. C. *Can. J. Chem.* **1981**, *59*, 669.

Table II. Vibrational Spectra[a]

compd	IR frequencies, cm^{-1}							
pyrazine[b]	3066 w 2973 w	1490 s 1418 vs	1178 m 1148 vs 1125 w 1110 m	1067 vs 1048 vw 1032 vw 1022 m 1006 w	926 vw	823 vw 804 vs	789 w 752 vw 700 vw	597 w 417 m
$Fe(pyz)_2Cl_2$	3104 w 3093 vw	1483 m 1415 sh 1411 s	1163 m 1154 s 1120 s 1114 s	1086 vw 1052 s	993 w 990 w	822 s 819 m 812 s		473 s 470 s
$Fe(pyz)_2Br_2$	3095 vw 3085 w	1480 w 1412 s	1155 m 1119 m	1087 vw 1054 s	989 w	875 vw 816 s		474 s 470 s
$Fe(pyz)_2I_2$	3096 vw 3075 w	1485 w 1414 sh 1410 s	1152 m 1118 m	1089 w 1056 s	988 m	817 s		472 s
$Fe(pyz)Cl_2$	3100 m 3040 w	1485 m 1418 s	1168 s 1119 s	1089 w 1054 s			794 s	475 s

[a] Abbreviations: s, strong; m, medium; w, weak; v, very. [b] From ref 29.

also measured at room temperature at three different values of $H(dH/dx)$ with a Faraday magnetic balance.[27] No field dependence was observed. Molar magnetic susceptibilities were corrected for the diamagnetism of the metal ion and ligands. Corrections used were as follows (in units of 10^{-6} cm^3 mol^{-1}): Fe^{2+}, −13; $C_4H_4N_2$, −45; Cl^-, −26; Br^-, −36; I^-, −52.

Results and Discussion

Thermal Studies. Differential scanning calorimetry measurements were made on all the compounds, and the results are summarized in Table I. Thermal analysis of $Fe(pyz)_2Cl_2$ has been reported in a previous study,[11] and the peak temperatures and ΔH values reported here are in reasonable agreement with those in the earlier work. The DSC curves for $Fe(pyz)_2Cl_2$ and $Fe(pyz)_2Br_2$ are qualitatively very similar, and in both cases two endothermic events are observed. In the previous study of the chloride complex[11] a combination of DSC-TGA analysis suggested that the events were associated with the stepwise loss of the neutral ligand. Our results support this interpretation for both the chloride and the bromide, and knowledge of this behavior for the chloride was utilized in devising the synthetic procedure described in the present work for the preparation of $Fe(pyz)Cl_2$.

In contrast, the thermogram of $Fe(pyz)_2I_2$ shows only a single endothermic event with a weight loss of 69%. This figure is considerably higher than expected for the loss of both neutral ligands from the complex. The gravimetric measurements, together with the observation of a brown ring around the pin hole in the aluminum crucible after the compound was heated to 340 K, indicate the loss of iodine and suggest more extensive sample decomposition in this compound.

Infrared Spectra. Because of the different symmetry of unidentate terminal and bidentate bridging pyrazine groups (C_{2v} vs. D_{2h}) the infrared and Raman activity of pyrazine vibrations has been used to diagnose the mode of ligand coordination.[6,28] In the present study the intense color of the complexes has precluded the use of Raman spectroscopy; however, infrared spectra have yielded valuable information concerning the pyrazine coordination mode. Typical spectra over the 1600–400 cm^{-1} frequency range are shown in Figure 1.

The absorption bands in the 250–4000-cm^{-1} region arise from internal vibrations of the pyrazine ligand and are listed in Table II for the complexes studied in this work. The absorptions given for free pyrazine are those of Lord et al.[29] Our results for $Fe(pyz)Cl_2$, $Fe(pyz)_2Cl_2$, and $Fe(pyz)_2Br_2$ are in reasonable agreement with those reported in earlier studies.[10-12] It is observed that most of the pyrazine absorptions are shifted from those of the free ligand. The band most sensitive to coordination, at 417 cm^{-1} in the free ligand,[29] is shifted to considerably higher frequency (~470 cm^{-1}) upon complex formation. Small splittings of some of the pyrazine vibrations are observed upon coordination, and this may arise from interactions between adjacent pyrazine rings, as has been proposed for pyridine complexes.[30] Another possible cause of the splittings is that different orientations of the pyrazine rings about their N–N axes may result in different environments for these groups.

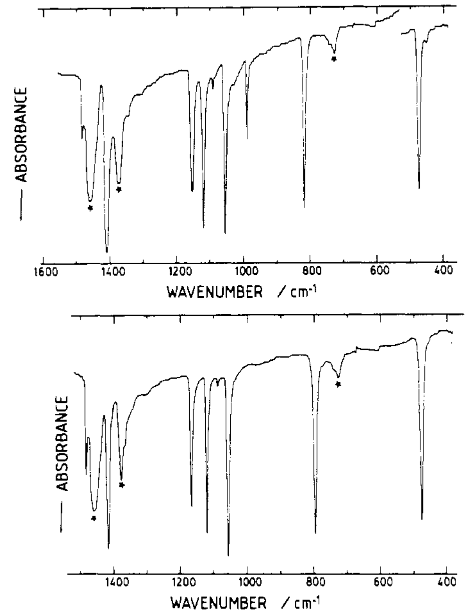


Figure 1. Infrared spectra of $Fe(pyz)_2I_2$ (top) and $Fe(pyz)Cl_2$ (bottom). The stars indicate Nujol absorptions.

The infrared spectrum of the mono(pyrazine) complex $Fe(pyz)Cl_2$ is relatively simple (see Figure 1), and there is no evidence of band splitting. This particularly simple spectrum may result from the fact that there is only one distinct type of pyrazine ligand and also that pyz–pyz interactions are not present.

The infrared activity of the pyrazine vibrational modes in these complexes is similar to that observed in known pyrazine-bridged complexes, for example $M(pyz)_2X_2$[6] (M = Co, Ni; X = Cl, Br, I) and $Sn(pyz)X_4$,[28] but is markedly different from that of $Sn(pyz)_2X_4$[28] (X = Cl, Br), in which pyrazine coordinates in a unidentate fashion. The infrared spectra of complexes containing unidentate pyrazine groups and the Raman spectrum of free pyrazine[29] exhibit bands at approximately 1230, 920 and 750 cm^{-1}. For the complexes studied here there are no bands in these regions,

---

(26) Haynes, J. S.; Oliver, K. W.; Rettig, S. J.; Thompson, R. C.; Trotter, J. *Can. J. Chem.* **1984**, *62*, 891.

(27) Herring, F. G.; Landa, B.; Thompson, R. C.; Schwerdtfeger, C. F. *J. Chem. Soc. A* **1971**, 528.

(28) Goldstein, M.; Unsworth, W. D. *Spectrochim. Acta, Part A* **1971**, *27A*, 1055.

(29) Lord, R. C.; Marston, A. L.; Miller, F. A. *Spectrochim. Acta* **1957**, *9*, 113.

(30) Clark, R. J. H.; Williams, C. S. *Inorg. Chem.* **1965**, *4*, 350.

Table III. Electronic Spectra

compd	abs max, cm^{-1}		
$Fe(pyz)_2Cl_2$	19000	11800	
$Fe(pyz)_2Br_2$	19000	11200	
$Fe(pyz)_2I_2$	16100	11000	7350
$Fe(pyz)Cl_2$	16700	11400	

Table IV. Mössbauer Parameters[a]

compd	temp	ΔE_Q	δ	Γ_1	Γ_2
$Fe(pyz)_2Cl_2$	293	3.19	0.98	0.31	0.30
	78	3.33	1.08	0.33	0.34
$Fe(pyz)_2Br_2$	293	3.17	0.98	0.39	0.40
	78	3.47	1.09	0.39	0.33
$Fe(pyz)_2I_2$	293	2.01	0.97	0.41	0.35
	78	2.50	1.08	0.39	0.33
$Fe(pyz)Cl_2$	293	1.72	1.04	0.46	0.39
	78	2.52	1.15	0.48	0.45

[a] Temperatures are in K; quadrupole splittings, isomer shifts and line widths are in mm s^{-1}.

indicating that the pyrazine ligand retains D_{2h} symmetry upon complex formation by acting as a symmetrical bidentate bridge between metal centers.

Electronic Spectra. Spectra in the near-infrared region show broad absorptions with maxima in the range 11000–12000 cm^{-1} for all complexes (Table III). In addition, the iodide derivative has a second, less intense, band in this region centered at 7350 cm^{-1}. These spectra are typical of pseudooctahedral iron(II) complexes and result from transitions from a ground electronic state derived from $^5T_{2g}$ to excited states derived from ^5E_g in O_h symmetry.[19] The low symmetry environment in these complexes results in a splitting of the ^5E_g level, the degree of which is large enough in the case of $Fe(pyz)_2I_2$ to give rise to two distinct band maxima. The ligand field spectra of these complexes are comparable to those of the analogous pyridine derivatives $Fe(py)_4X_2$,[19] although the absorptions in the pyrazine complexes are consistently at higher energies. This suggests a slightly stronger ligand field for the latter species, a consequence possibly of stabilization of the iron $^5T_{2g}$ levels by the better π-acceptor properties of pyrazine compared to pyridine.

An interesting difference between the bis(pyrazine) and tetrakis(pyridine) complexes is that the latter are pale yellow whereas the former are all intensely red-brown. This difference is reflected in the visible spectra of the two types of complexes. The pyrazine derivatives exhibit intense bands in this region (in the range 16100–19000 cm^{-1}), which are presumably a consequence of charge-transfer transitions. Charge-transfer spectra have been observed in other iron(II) complexes,[31] and in view of the relative ease of oxidation of iron(II) to iron(III), it has been suggested that these transitions are predominantly metal-to-ligand in character. Previously in metal pyrazine complexes, charge transfer has been proposed to be from the metal to a low-lying vacant π^*-antibonding orbital of the pyrazine moiety,[32] and this is probably the case here. From the pale yellow color of the tetrakis(pyridine) complexes the metal-to-ligand charge-transfer band presumably occurs at higher energy in the ultraviolet region. These results are again consistent with pyrazine being a better π-acceptor than pyridine.

^{57}Fe Mössbauer Spectra. Mössbauer parameters are given in Table IV. At room and liquid-nitrogen temperatures all the complexes show symmetric quadrupolar doublets, with isomer shifts and quadrupole splittings consistent with their formulation as hexacoordinate high-spin iron(II) compounds.

The $Fe(pyz)_2X_2$ complexes exhibit no appreciable differences in isomer shifts. This is somewhat unexpected in view of the different σ-donor abilities of the halide anions. For the $Fe(py)_4X_2$ complexes, small changes in isomer shift values have indeed been correlated with differences in the σ-donating properties of the anionic ligands.[19] The difference between the two series of complexes is probably related to the better π-acceptor ability of pyrazine. As discussed above, the observation of charge-transfer bands in the visible region suggests a rather facile charge-transfer process in the pyrazine series that is not available to the pyridine derivatives. Thus, variations in σ-donation from the halides are reflected in different s-electron densities at the iron nucleus in the latter, while in the pyrazine complexes increased σ-donation from the anion can be compensated for by a transfer of electron density onto the neutral ligand.

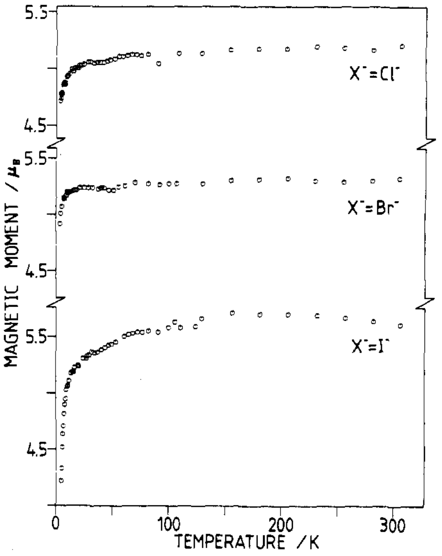


Figure 2. Magnetic moment as a function of temperature for the $Fe(pyz)_2X_2$ complexes.

At 78 K the quadrupole splittings of all four pyrazine complexes are substantially greater than 2 mm s^{-1}. This is indicative of a nondegenerate $^5B_{2g}$ ground state.

In view of the very recent report of Reiff et al.[17] that both chloride derivatives are still paramagnetic at 0.5 K, a temperature considerably lower than those accessible in our laboratory, we have not extended out Mössbauer measurements down to the pumped helium range.

Magnetic Susceptibility. Magnetic susceptibility data are given in Table V,[33] and the temperature dependence of the magnetic moments of the bis(pyrazine) compounds is shown in Figure 2. $Fe(pyz)_2Cl_2$ and $Fe(pyz)_2Br_2$ have magnetic moments that remain fairly constant down to approximately 50 K and then decrease more significantly, especially at temperatures below 20 K. At room temperature the magnitudes of the moments are in the order I > Br > Cl, and of the three compounds, $Fe(pyz)_2I_2$ shows the largest temperature dependence: the magnetic moment passes through a broad maximum at approximately 160 K before falling to 4.2 μ_B at 4.2 K. The susceptibility vs. temperature plots for the three compounds imply Curie–Weiss behavior, and the absence of maxima in these plots indicates a lack of any strong magnetic exchange interactions. Presumably, the decrease in moment at low temperatures results primarily from zero field splitting effects, although a small contribution from magnetic exchange cannot be ruled out.

The room temperature magnetic moment of $Fe(pyz)_2Br_2$ has been reported[12] as 4.4 μ_B, which does not compare well with the value of 5.3 μ_B found here. Ferraro et al.[12] surmized that the low magnetic moment was a result of exchange interactions, but from the more extensive data obtained here this appears unlikely. The reason for this large discrepancy is not fully understood. Corrections for packing errors, which were not applied to the Gouy measurements of Ferraro et al.,[12] may be one source, but are not likely to be large enough to account for all the disagreement.

The temperature dependence of the magnetic moments of the polymeric bis(pyrazine) halides may be compared with data for

---

(31) Lever, A. B. P. *J. Chem. Educ.* **1974**, *51*, 612.

(32) Lever, A. B. P.; Lewis, J.; Nyholm, R. S. *J. Chem. Soc.* **1964**, 4761.

(33) Supplementary material.

the corresponding monomer tetrakis(pyridine) complexes, studied by Little and Long[19] over the temperature range 20–300 K. The moments of both groups of compounds show a similar temperature dependence; i.e., for the $Fe(py)_4X_2$ species the moment remains fairly constant down to about 60 K and then decreases slightly. The implication of this similarity is that magnetic exchange interactions in the bis(pyrazine) complexes, if present at all, are of a very weak nature. This is consistent with the observation of Reiff et al.[17] that the zero field Mössbauer spectrum of $Fe(pyz)_2Cl_2$ is a symmetric doublet at 0.52 K. However, these authors also noted that the application of a transverse magnetic field of only 0.1 T induced substantial Zeeman splitting at this temperature, possibly suggesting approach to a magnetically ordered state.

Although $Fe(pyz)_2Cl_2$ and $Fe(pyz)Cl_2$ have almost the same value of the magnetic moment at about 50 K, the decrease at lower temperature is much more pronounced for the latter, and its moment at 1.86 K is only 1.98 μ_B (Table V). This very low moment is consistent with the presence of weak exchange interactions in $Fe(pyz)Cl_2$, but as the magnetic susceptibility has not passed through a maximum at the lowest temperature available, conclusive evidence for magnetic exchange is lacking.

The weak nature (or absence) of exchange interactions in $Fe(pyz)Cl_2$ is unexpected in view of the findings that both $Fe(pyz)(NCO)_2$ and $Fe(pyz)(CF_3SO_3)_2$ show spontaneous antiferromagnetic ordering with Neel temperatures of 27.05 and 3.8 K, respectively.[15,16] Moreover, the linear chain complexes $Fe(py)_2X_2$ (X = Cl, NCS, NCSe) are all spontaneously ordered ferromagnets at 4.2 K (although $Fe(py)_2Br_2$ is still paramagnetic at 1.1 K).[19] We would expect the structures of the mono(pyrazine)iron(II) chloride and cyanate derivatives to be similar. Spectroscopic evidence suggests that both complexes possess an FeN_2X_4 chromophore and that bridging anionic ligands as well as bridging pyrazine groups are present. Indeed, there are numerous examples of complexes in which bridging halide anions act as efficient agents for the propagation of magnetic exchange interactions,[34] and it is surprising that such interactions are not more strongly manifested in $Fe(pyz)Cl_2$.

We also note that at 2 K there is only a modest difference between the magnetic moments of $Fe(pyz)Cl_2$ and $Fe(pyz)(CF_3SO_3)_2$, viz. 2.05 and 1.59 μ_B, respectively (Table V and ref 16). In view of the fact that the trifluoromethanesulfonate derivative is antiferromagnetically ordered at 2 K,[16] a magnetic phase transition in the chloride might have been expected near this temperature; however, Reiff *et al.*[17] report the complex to be a fast relaxing paramagnet down to 0.5 K. It is possible that different preparative routes could lead to somewhat different magnetic properties for our material and that studied by Reiff et al.,[17] who gave no details of their preparative procedure.

In the $Fe(pyz)_2X_2$ complexes it seems clear that the existence of the Fe–pyz–Fe pathway is not a sufficient condition for magnetic superexchange. Thus, none of the three halide derivatives we have described here shows long-range order at 4.2 K (and the chloride is still paramagnetic at 0.52 K),[17] whereas the pseudohalide complex $Fe(pyz)_2(NCS)_2$ has a Neel point of 9.1 K.[15] An interesting feature of the latter complex is that the angle θ, defining the orientation of the internal hyperfine field to V_{zz}, the z axis of the electric field gradient (EFG) tensor, is 41°. As the EFG in this complex is axially symmetric,[15] the obvious choice of axis system is with V_{zz} normal to the FeN_4 plane. Thus, the hyperfine field might be expected to lie in the xy plane, while in fact it is significantly canted out of this plane. The most likely explanation is that the observed angle arises from a canting of the pyrazine rings out of the xy plane in order to maximize overlap between the pyrazine π-system and the appropriate iron d orbitals for propagation of the magnetic exchange. The orientation of the pyrazine rings to the xy plane has been found to be important in determining the nature of the exchange in such systems,[3-5] and in $Cu(pyz)_2(ClO_4)_2$[35] and $Co(pyz)_2Cl_2$,[18] the canting angles are 66 and 44°, respectively. It may be that in the $Fe(pyz)_2X_2$ (X = Cl, Br, I) complexes, this angle is unfavorable for a facile exchange mechanism, although in the absence of detailed X-ray structural information this suggestion must be considered speculative.

Acknowledgment. J.S.H. thanks the U.B.C. Graduate Scholarship Committee for scholarship awards. Financial support from the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

Registry No. $Fe(pyz)_2Cl_2$, 18040-57-8; $Fe(pyz)_2Br_2$, 99294-47-0; $Fe(pyz)_2I_2$, 99294-48-1; $Fe(pyz)Cl_2$, 35015-81-7.

Supplementary Material Available: Listings of magnetic data (Table V) (1 page). Ordering information is given on any current masthead page.

---

(34) Smith, D. W. *Coord. Chem. Rev.* **1976**, *21*, 93.

(35) Darriet, J.; Haddad, M. S.; Deusler, E. N.; Hendrickson, D. N. *Inorg. Chem.* **1979**, *18*, 2679.