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Pressure-Induced Spin-State Phase Transitions in $Fe(dppen)_2Cl_2$ and $Fe(dppen)_2Br_2$

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The pressure-induced high-spin to low-spin transformation in solid $Fe(dppen)_2X_2$, where X = Cl or Br and dppen = *cis*-1,2-bis(diphenylphosphino)ethylene, has been studied by variable-pressure Mössbauer spectroscopy. It is found that the dichloro complex undergoes an abrupt first-order phase transition in the region of 7–9 kbar, while the dibromo complex undergoes a more gradual transition starting at approximately 60 kbar. The somewhat more gradual nature of the transformation in the dibromo case likely reflects a first-order phase transition influenced by defect structures. In neither compound is the transition complete: approximately 20% of the molecules remain in the high-spin state for each compound at the highest pressures studied (70 kbar for the dichloro complex and 111 kbar for the dibromo complex). The difference in transition pressures is discussed in terms of lattice cooperativity, in addition to ligand field and polarizability effects manifested with increasing pressure.

Introduction

There is considerable and growing interest in the study of spin-state interconversions in the solid state.[1-3] In part this reflects the observation of molecular tunneling for the spin-state interconversion in the solid state,[4] as well as the exciting light-induced excited state stabilization, the so-called LIESST effect.[3,5] In the latter case it has been shown that certain crystalline spin-crossover complexes can at low temperature be converted from low spin to high spin by simply shining a light on the crystalline sample. What is amazing is that these samples will persist for minutes to hours in the high-spin state providing the crystals are maintained at low (<50 K) temperatures.

In studies of iron(II) phosphine compounds, spin-crossover behavior has been shown to occur for complexes of the general formula *trans*-$Fe(dppen)_2X_2\cdot nS$, where X = Cl or Br and the solvate S = $(CH_3)_2CO$, CH_2Cl_2, or $CHCl_3$.[6-9] Techniques used to study the behavior of these systems include magnetic susceptibility,[6-9] Mössbauer spectroscopy,[6,8,9] solid-state NMR,[9] and differential scanning calorimetry (DSC).[9] Single-crystal X-ray diffraction data have also been obtained for both unsolvated complexes,[7,9] as well as the acetone solvate of the dichloro complex.[7] Although $Fe(dppen)_2Br_2$ does not exhibit a temperature-dependent singlet ↔ quintet equilibrium and the two isomorphs of $Fe(dppen)_2Cl_2$ display weak to no temperature dependence (forms I and II),[6,7] each of the solvated forms of $Fe(dppen)_2Cl_2$ undergoes a thermally driven spin-state phase transition in the region 150–240 K.[7]

The crystal structures of the acetone solvate obtained at 130 and 295 K reveal a substantial shortening of the Fe–P bond upon going from high spin to low spin, with an average change of ~0.3 Å for all four coordination sites. Very little change was observed in the Fe–Cl bond length: this has been rationalized in a related system in terms of electron–electron repulsion between metal and ligand electrons.[10] Other X-ray studies[10] have similarly shown an average Fe–P bond length of 2.25 Å for low-spin complexes with a P_4Cl_2 coordination sphere and 2.60 Å for analogous high-spin complexes with little variation in the Fe–Cl bond length. König and co-workers[8] have reported on the coupling of the spin-state transition in the acetone solvate to an order–disorder transition in the acetone molecules, implying a degree of cooperativity exists in the lattice.

Although the unsolvated forms of the two complexes do not exhibit temperature-induced spin crossover, it is possible that a pressure-induced transition may be observable by using Mössbauer spectroscopy. We report the results of such a study. It has been found that both $Fe(dppen)_2Cl_2$ and $Fe(dppen)_2Br_2$ do undergo high-spin to low-spin transitions in the solid state at pressures of approximately 8 and 60 kbar, respectively (1.0 kbar = 986.9 atm = 0.1 GPa).

Table I. Mössbauer Data for $Fe(dppen)_2Cl_2$

P, kbar		isomer shift, mm/s	ΔE_Q, mm/s	% area
3.5		0.812 (4)	2.464 (9)	100
6.0		0.762 (3)	2.500 (6)	100
8.7	HS	0.68 (4)	2.34 (8)	36.4
	LS	0.57 (4)	1.42 (8)	63.6
15.0	HS	0.68 (2)	2.63 (4)	22.4
	LS	0.398 (5)	0.778 (9)	77.6
30.0	HS	0.615 (1)	2.50 (3)	19.0
	LS	0.355 (2)	0.857 (4)	81.0
50.0	HS	0.55 (2)	2.36 (5)	15.6
	LS	0.311 (2)	0.962 (5)	84.4
70.0	HS	0.59 (5)	2.14 (9)	20.4
	LS	0.292 (2)	1.015 (4)	79.6

Experimental Section

Sample Preparation. ^{57}Fe-enriched (>98% ^{57}Fe) samples of $Fe(dppen)_2Cl_2$ and $Fe(dppen)_2Br_2$ were synthesized according to the method of Cecconi,[2] using $^{57}FeX_2$ (X = Cl, Br) prepared from 10 mg of ^{57}Fe powder and the appropriate acid halide under an Ar atmosphere.[6,8] The sample preparation gave form II of the dichloro complex. Structural analyses of form II of $Fe(dppen)_2Cl_2$ and $Fe(dppen)_2Br_2$ indicate that the two compounds are isomorphous.[7,10]

Mössbauer Spectroscopy. The high-pressure system used in this study has been previously described.[11] The diamond-anvil cell was filled with the maximum amount of sample possible to provide a maximum signal for data collection. A small amount of mineral oil was added onto each sample prior to cell loading to ensure hydrostatic pressure during the collection of data. A typical run, involving the collection of data at 7–10 different pressures and ambient temperature, lasted approximately 3–4 weeks. At no time during the run was there any evidence of cell leakage or loss of pressure.

Mössbauer spectra were recorded in the constant acceleration mode by using a Ranger Scientific MS-900 Mössbauer spectrometer interfaced to an Apple IIe personal computer. The source used was a 20 mCi ^{57}Co point source diffused into a Rh matrix (Amersham Corp.). All Mössbauer parameters are referenced to iron foil at 300 K. Data were

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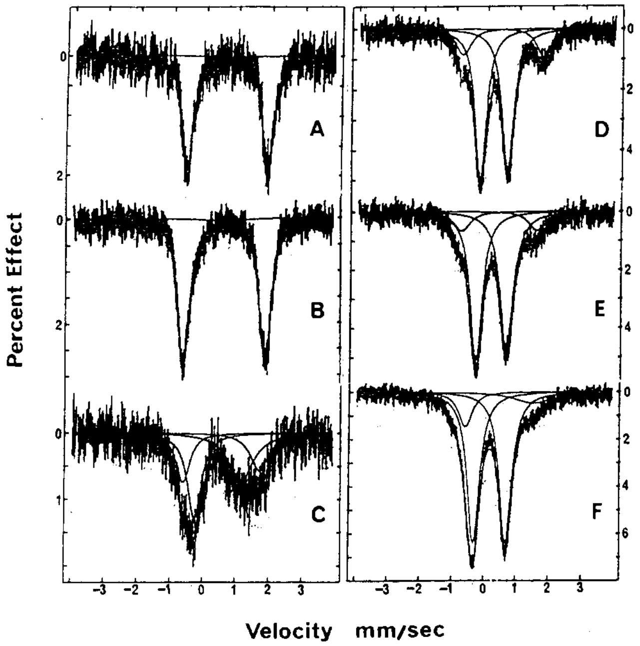

Figure 1. Selected Mössbauer spectra for Fe(dppen)$_2$Cl$_2$ at various pressures: (A) 3.5 kbar; (B) 6.0 kbar; (C) 8.7 kbar; (D) 30 kbar; (E) 50 kbar; (F) 70 kbar.

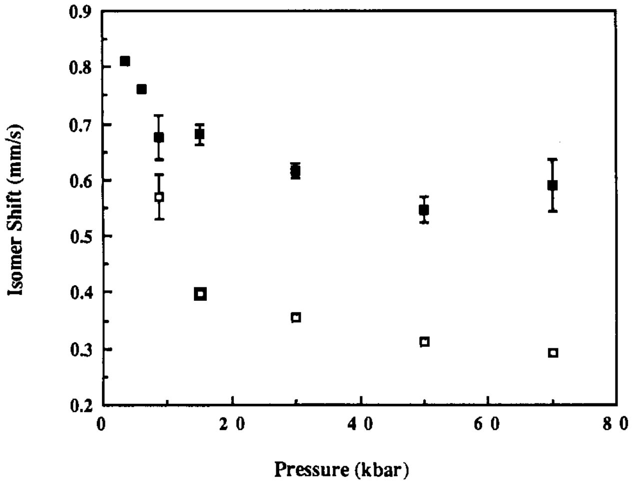

Figure 2. Plot of isomer shift versus pressure for Fe(dppen)$_2$Cl$_2$: (□) low-spin signal; (■) high-spin signal. (Error bars are present for all data points. Where bars are not visible, error lies within the dimension of the square.)

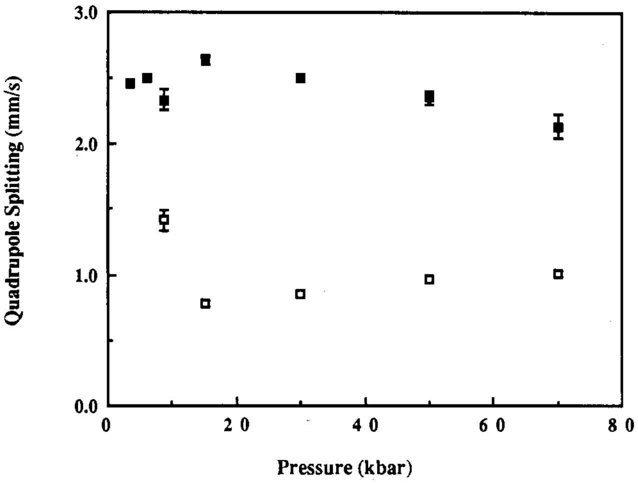

Figure 3. Plot of quadrupole splitting versus pressure for Fe(dppen)$_2$Cl$_2$: (□) low-spin species; (■) high-spin species.

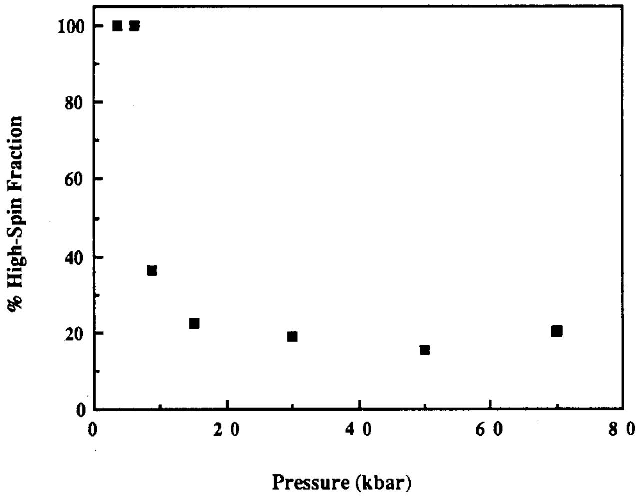

Figure 4. Plot of percent high-spin fraction as a function of pressure for Fe(dppen)$_2$Cl$_2$.

Table II. Mössbauer Data for Fe(dppen)$_2$Br$_2$

P, kbar		isomer shift, mm/s	ΔE_Q, mm/s	% area
4.1		0.780 (5)	2.465 (9)	100
24.7		0.593 (5)	2.462 (9)	100
45.0		0.672 (6)	2.66 (1)	100
58.9		0.603 (5)	2.56 (1)	100
62.7	HS	0.53 (1)	2.37 (2)	70.2
	LS	0.39 (2)	1.12 (6)	29.8
69.2	HS	0.51 (1)	2.40 (4)	49.2
	LS	0.36 (2)	1.14 (4)	50.8
71.0	HS	0.52 (1)	2.41 (3)	35.0
	LS	0.37 (1)	1.18 (2)	65.0
74.0	HS	0.47 (2)	2.36 (5)	40.2
	LS	0.32 (1)	1.10 (3)	59.8
91.0	HS	0.41 (3)	2.11 (6)	46.6
	LS	0.30 (2)	1.02 (4)	53.4
111.0	HS	0.38 (4)	2.30 (7)	19.8
	LS	0.32 (2)	1.18 (4)	80.2

fitted to Lorentzian peaks with a modified version of a previously published computer program.[12]

Results

Mössbauer spectra at pressures in the range 4–70 kbar were collected for Fe(dppen)$_2$Cl$_2$. At pressures of 3.5 and 6.0 kbar there is only one doublet (all high spin), whereas at higher pressures each spectrum was fit with two doublets (HS/LS). Fitting parameters for these data are given in Table I, along with the percent high-spin fraction present at each pressure as determined by peak area ratios. Selected spectra are given in Figure 1. Plots of isomer shift and quadrupole splitting (ΔE_Q) as functions of pressure are given in Figures 2 and 3, respectively. For both the high-spin and low-spin components, the isomer shift is found to decrease with increasing pressure. This is consistent with what has been observed previously.[13-16] It is interesting to note that the profile for this decrease in isomer shift is different for the two spin states. The decrease occurs fairly monotonically with pressure the case of the high-spin fraction, whereas there exists an apparent discontinuity for the low-spin fraction at approximately 10 kbar, just above the pressure at which the low-spin form is first evident.

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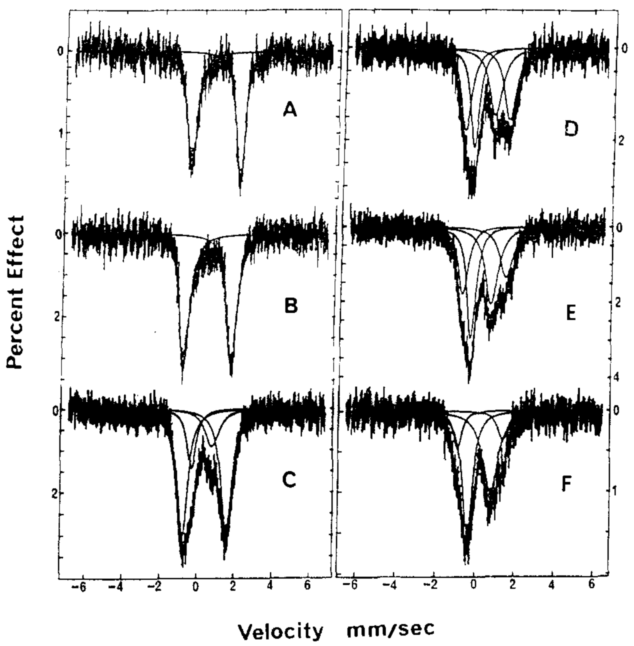

Figure 5. Selected Mössbauer spectra for Fe(dppen)$_2$Br$_2$ at various pressures: (A) 4.1 kbar; (B) 58 kbar; (C) 62 kbar; (D) 69 kbar; (E) 74 kbar; (F) 111 kbar.

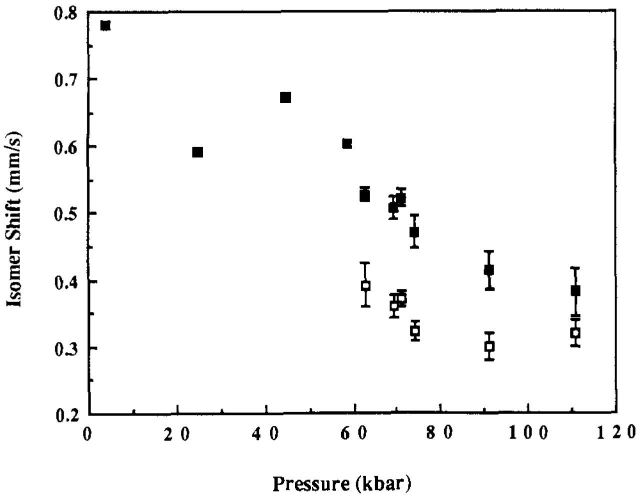

Figure 6. Plot of isomer shift versus pressure for Fe(dppen)$_2$Br$_2$: (□) low-spin signal; (■) high-spin signal.

Figure 3 illustrates the variation in ΔE_Q with increasing pressure for both spin-state fractions of Fe(dppen)$_2$Cl$_2$. For the high-spin fraction, ΔE_Q increases slightly and then begins to decrease monotonically with pressure above 15 kbar. ΔE_Q for the low-spin component increases monotonically above 15 kbar. As was the case with the isomer shift, a discontinuity is apparent around 10 kbar with the appearance of the low-spin species. The break is more pronounced in the low-spin data, but is suggested in the ΔE_Q variation for the high-spin species as well. The plot of percent high-spin fraction as a function of pressure given in Figure 4 indicates that approximately 20% of the sample remains in the high-spin form even at 70 kbar. However, approximately 80% of the total conversion in this system occurs at or around 8.7 kbar.

The corresponding least-squares fitting Mössbauer parameters for Fe(dppen)$_2$Br$_2$ are given in Table II and illustrated in Figures 6–8. Selected spectra are shown in Figure 5. As in the case of the dichloro complex, the decrease in the isomer shift with increasing pressure (Figure 6) occurs fairly monotonically for the high-spin fraction in the range 4–111 kbar. However, there is no marked discontinuity in the value of the isomer shift at the point where the low-spin species becomes evident. Similarly, this characteristic is absent in Figure 7, a plot of ΔE_Q versus pressure for the dibromo complex. When the profiles for the isomer shift and ΔE_Q variation of both compounds are compared, it is apparent that subtle differences exist. In particular, while the value of the isomer shift for the high-spin component of each compound decreases with increasing pressure, the decrease is greater for a given increment of pressure in the case of Fe(dppen)$_2$Br$_2$. Additionally, although the high-spin form of Fe(dppen)$_2$Br$_2$ exhibits an increase in ΔE_Q prior to the onset of the low-spin form, as in the dichloro complex, the subsequent decrease in the value of ΔE_Q with increasing pressure is much less pronounced.

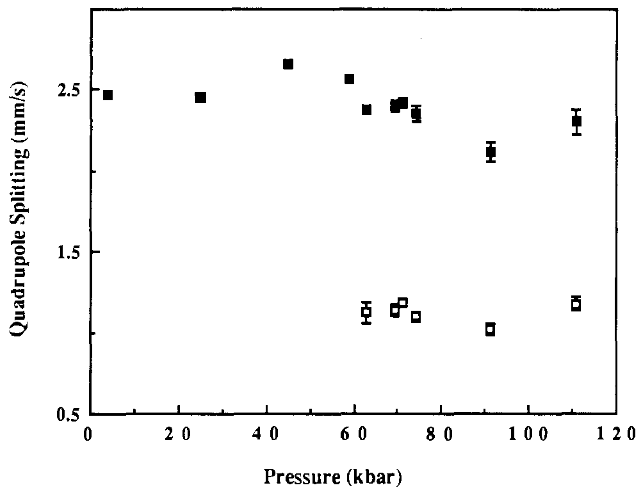

Figure 7. Plot of quadrupole splitting versus pressure for Fe(dppen)$_2$Br$_2$: (□) low-spin species; (■) high-spin species.

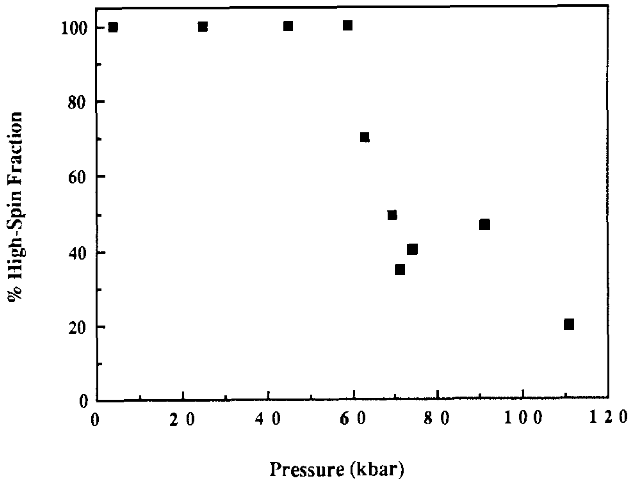

Figure 8. Plot of percent high-spin fraction as a function of pressure for Fe(dppen)$_2$Br$_2$.

A plot of the percent high-spin fraction as a function of pressure for Fe(dppen)$_2$Br$_2$ is given in Figure 8. Fe(dppen)$_2$Br$_2$ undergoes a fairly abrupt conversion at 60 kbar, with an increase of low-spin content of about 30% over 4 kbar. A comparison of this plot with Figure 4, however, reveals that the overall spin-state conversion is more gradual for the dibromo complex than for the dichloro complex. In addition, the high-spin fraction does not attain a constant nonzero level as was the case with Fe(dppen)$_2$Cl$_2$. The profile of the high-spin fraction does appear to begin to flatten out somewhat above 80 kbar, suggesting that a steady-state value might be attained at sufficiently high pressure.

Discussion

There are several important aspects of the results mentioned above that need to be addressed. Fe(dppen)$_2$Cl$_2$ undergoes an abrupt spin-state transition at or around 8 kbar, whereas the somewhat more gradual transition in the corresponding dibromo complex occurs at approximately 60 kbar. The plots of percent high-spin fraction versus pressure for both compounds indicate that the pressure-driven spin-state conversion is occurring as a phase transition in the solid. Clearly the abruptness of the conversion for the dichloro complex (Figure 4) indicates that the phase transition in this case is of first order. The conversion in the case of Fe(dppen)$_2$Br$_2$ does appear (Figure 8) to be less abrupt. However, it is likely that this conversion is occurring in a first-order phase transition as well. The transformation for the dibromo complex probably occurs more gradually due to greater amounts of crystal imperfections, grain boundaries, dislocations, surfaces, etc. generated while the pressure is being increased even in a quasihydrostatic medium.

As is true with any phenomenon where pressure is the variable, the thermodynamics of the system is essentially governed by $\partial G/\partial P$, which corresponds to volume. At what point does increasing pressure dictate thermodynamically that a volume change for a crystal system must occur? For the systems under consideration, the transition from a high-spin to a low-spin ferrous compound has with it an associated decrease in molecular volume. Therefore, the pressure at which the spin-state transition occurs corresponds to that point at which the inter- and intramolecular forces that dictate a high-spin form at ambient pressure are outweighed by $\partial G/\partial P$ and the necessity of a volume change. It is not just the free energy of individual complexes but the free energy of the crystal that is to be considered.

In order to evaluate the role of intermolecular forces, the previously reported crystal structures of the complexes were compared.[7,10] Both Fe(dppen)$_2$Br$_2$ and form II of Fe(dppen)$_2$Cl$_2$ crystallize in the triclinic space group $P\bar{1}$. The volumes of the unit cells for these compounds are essentially identical (1082 Å^3 for Fe(dppen)$_2$Cl$_2$ and 1086 Å^3 for Fe(dppen)$_2$Br$_2$). This strongly suggests that the crystal packing for these isostructural molecules is identical. Unfortunately, crystallographic coordinates were not given in the literature reports[7,10] for either of the complexes. Thus, it is not possible to describe the packing arrangement for these two complexes. From a qualitative standpoint, we may infer that increasing pressure will have a similar effect on intermolecular spacing in the lattice for both complexes. We suggest, therefore, that differences in cooperativity are likely to be important in determining the pressure at which the spin transition occurs, but that differences in the effect increasing pressure has on the unit cell, e.g., inducing volume changes, will be minimal between the two complexes.

On the basis of these conclusions, intramolecular differences between the two compounds were examined. Specifically, we examined (a) the greater polarizability of Br$^-$ versus Cl$^-$ and (b) differences in the electronic structures of the compounds manifested with increasing pressure. A third factor, that of the steric effects associated with the larger bromide ligand, was not deemed significant based on an examination of the molecular structures of the two compounds. Previous work on the effects of pressure on tetrahedral Ni^{II} and Co^{II} complexes[17] has shown that polarizability and modification of the ligand field are not necessarily uncorrelated. However, ligand field effects aside, the greater polarizability of bromide compared to chloride could be a factor simply because the electron cloud of a bromide ion is more readily deformed than that of a chloride ion. This would allow the dibromo system to "absorb" more pressure prior to a spin-state change, since the bromide ion can respond to the increasing pressure by deformation of its electron cloud more readily than the chloride ion.

Correlated to the polarizability of the ligand are ligand field effects, which we believe to be of primary importance in determining the transition pressure. Stated simply, Br$^-$ is a weaker field ligand than Cl$^-$. For a low-spin d^6 ion in strictly O_h symmetry, ΔE_Q is zero. Deviation from O_h symmetry results in a nonzero value for ΔE_Q due to the asymmetry in the ligand field, and ΔE_Q will increase as the asymmetry of the field becomes more pronounced. Both Fe(dppen)$_2$Cl$_2$ and Fe(dppen)$_2$Br$_2$ have P$_4$L$_2$ coordination spheres and may be considered to possess D_{4h} symmetry. Phosphines, such as dppen, are strong field ligands. The nonzero value for ΔE_Q of the low-spin form of both compounds indicates that the halides impart a weaker ligand field on the Fe^{II} center than do the phosphines; the larger value of ΔE_Q for Fe(dppen)$_2$Br$_2$ compared to Fe(dppen)$_2$Cl$_2$ indicates that this difference in ligand-field strengths is greater for the dibromo complex; hence, the bromide is a weaker field ligand.

The weaker ligand field strength of Br$^-$ implies that it is a better π-donor than Cl$^-$. This is consistent with the notion that the 4p π-orbitals of Br$^-$ are larger than the 3p orbitals of Cl$^-$ and can overlap better with the 3d orbitals of the iron center. This overlap results in an unfavorable interaction between the filled π-system of the halide and the occupied t$_{2g}$ orbitals of iron (assuming O_h symmetry for the sake of this discussion). In the high-spin state, there are four electrons in the t$_{2g}$ set; in the low-spin form, the t$_{2g}$ set is completely filled with six electrons. Di Vaira and co-workers[10] have suggested that this difference in electron–electron repulsion between the low-spin and high-spin states is responsible for stabilization of the high-spin state in a closely related phosphine, Fe(dme)$_2$Cl$_2$, where dme is 1,2-bis(dimethylphosphino)ethane. It is our belief that the better π-donor characteristics of bromide relative to chloride, i.e., stronger interaction with the t$_{2g}$ orbitals, greatly contributes to the increased destablization of the low-spin state for the dibromo complex. These effects are magnified with increasing pressure (vide infra).

Zahner and Drickamer[18] have discussed the effect of pressure on crystal field energies in transition-metal complexes. They found that the Racah parameter B, which reflects the interelectronic repulsion of the d electrons, decreases with increasing pressure. This was interpreted as an increase in covalency at high pressure. In related work, Stephens and Drickamer[17] found a strong correlation between a decrease in the Racah B parameter and the polarizability of the ligands. From their data, they concluded that the order of polarizability was Cl$^-$ < Br$^-$, implying that increasing pressure has a greater effect upon increasing the covalency of the metal–ligand interaction in the case of bromide than for chloride. As covalency increases, so too will the interactions between ligand and metal electrons.

This increased covalent interaction is evident from the isomer shift data for these molecules (see Figures 2 and 5). For both complexes, the isomer shift is found to decrease with increasing pressure. This is consistent with previous observations.[15,16] A decrease in the isomer shift corresponds to an increase in the s electron density present at the nucleus. Since the 3d electrons tend to shield s electrons from the nucleus, the decrease in the isomer shift may equivalently be correlated to a decrease in d electron density close to the metal center.[13,14] Specifically, Drickamer and co-workers describe the effect by stating that increased interaction with the ligands as pressure is increased leads to a spreading of the 3d orbitals and, consequently, higher s electron densities at the nucleus. A comparison of Figures 2 and 5 reveals that, for the high-spin form of each complex, the decrease in isomer shift for Fe(dppen)$_2$Br$_2$ is greater in a given pressure increment than that for Fe(dppen)$_2$Cl$_2$. This indicates that, as the pressure is increased, there is a larger interaction between the metal and ligand orbtials in Fe(dppen)$_2$Br$_2$ than in the dichloro complex. This will result in a greater destabilization of the low-spin form of Fe(dppen)$_2$Br$_2$ relative to Fe(dppen)$_2$Cl$_2$ and is consistent with the higher HS → LS transition pressure found for the dibromo complex.

Concluding Comments

Pressure-driven first-order spin-state phase transitions have been found at ~8 kbar for Fe(dppen)$_2$Cl$_2$ and at ~60 kbar for Fe(dppen)$_2$Br$_2$. The transition for the dibromo complex is somewhat less abrupt than that for the dichloro complex probably because the higher pressure for the phase transition produces more defect structures in the dibromo case. The weaker ligand field strength associated with the Br$^-$ ligand compared to the Cl$^-$ ligand is the main origin of the fact that Fe(dppen)$_2$Br$_2$ requires a higher pressure in order to undergo the spin-state phase transition.

The application of pressure may well be a more facile way of studying phase transitions in spin-crossover complexes than by

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the variable-temperature techniques commonly employed. The full range of pressures would lead to more complexes converting from high spin to low spin than have been observed by the temperature range ~4–500 K. The goal in the study of these spin-state phase transitions is to understand the mechanism of the phase transitions. What is the nature of the cooperativity? In a general sense the goal is to discover the universality class or classes[19] that characterize the phase transitions in these complexes. To determine the universality class it is necessary to determine two things: the dimensionality of the lattice and the dimensionality of the order parameter. In the first case it is important to determine from the packing diagram of the complex or by other means whether the intermolecular interactions dictate a one-, two-, or three-dimensional lattice of spin-crossover complexes. Are there stacks or layers of complexes? The dimensionality of the order parameter refers to the nature of the pairwise interactions of complexes. Are these interactions of a Heisenberg, Ising, or XY type? Pressure should be a useful variable in this endeavor.

Finally, it must be noted that increasing the pressure does not have the same effect on a spin-crossover complex as decreasing the temperature. As the temperature is decreased, intermolecular interactions probably change little. Decreasing the temperature changes Boltzmann populations and reduces the thermal energy available to drive nucleation and growth processes. On the other hand, increasing the pressure could dramatically increase intermolecular interactions and also affect intramolecular energetics.

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Registry No. Fe(dppen)$_2$Cl$_2$, 58031-48-4; Fe(dppen)$_2$Br$_2$, 58031-47-3.

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Dirhenium Complexes Containing Pairs of Bridging Acetate and Bis(diphenylphosphino)amine Ligands. Cis and Trans Isomers of the Type $[Re_2(O_2CCH_3)_2X_2(Ph_2PNHPPh_2)_2]^{n+}$ (X = Cl, Br; n = 0, 1)

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The reactions of dirhenium(III) carboxylates of the type $Re_2(O_2CCH_3)_2X_4(H_2O)_2$ (**1**, X = Cl, Br) with bis(diphenylphosphino)amine (dppa) in hot ethanol afford reduced, mixed-halide–phosphine complexes with two, one, or zero bridging acetate ligands. Yellow $Re_2(O_2CCH_3)X_4(dppa)_2$ (**2**) is produced in reactions of very short duration (ca. 3 min), while longer reaction times (ca. 15 min) favor yellow *trans*-$[Re_2(O_2CCH_3)_2X_2(dppa)_2]X$ (**3**). After several days, under these same reaction conditions, *cis*-$Re_2(O_2CCH_3)_2X_2(dppa)_2$ (**4**) is produced. While **2** can undergo reductive decarboxylation to give $Re_2X_4(dppa)_2$ (**5**), the latter species does not appear to be an important precursor to **4**, as it is in an analogous system involving reactions of **1** with bis(diphenylphosphino)methane (dppm) (see: *J. Am. Chem. Soc.* **1988**, *110*, 5024). The most important reaction pathway to **4** is via the sequence **1** → **2** → **3** → **4**. The complex **4** (X = Cl) reacts with the one-electron oxidant $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ to produce paramagnetic *cis*-$[Re_2(O_2CCH_3)_2Cl_2(dppa)_2]PF_6$ (**6**). The redox properties of **2**–**6** have been studied by the cyclic voltammetric technique. The pair of complexes **4** and **6** (X = Cl) were characterized structurally by X-ray crystallography. Crystal data for **4** at 19 °C: monoclinic space group $P2_1/c$, a = 14.267 (2) Å, b = 15.831 (4) Å, c = 23.824 (3) Å, β = 100.163 (9)°, V = 5296 (3) Å^3, Z = 4. The structure was refined to R = 0.034 and R_w = 0.049 for 5026 data with $F^2 > 3.0\sigma(F^2)$. Crystal data for **6** at −100 °C: monoclinic space group $C2/c$, a = 34.539 (5) Å, b = 14.015 (4) Å, c = 26.018 (5) Å, β = 103.83 (2)°, V = 12229 (9) Å^3, Z = 8. This structure was refined to R = 0.047 and R_w = 0.065 for 6311 data with $F^2 > 3.0\sigma(F^2)$.

Introduction

Metal–metal-bonded dimetal complexes that contain two bridging bidentate phosphine ligands of the type $R_2PCH_2PR_2$ are well-known.[1-3] However, systems in which these complexes exist in cis and trans isomeric forms are very rare. We recently encountered a set of such examples in the case of the cis and trans isomers of $[Re_2(O_2CR)_2X_2(dppm)_2]^{n+}$ (R = CH_3, C_2H_5, C_6H_5; X = Cl, Br; dppm = $Ph_2PCH_2PPh_2$; n = 0, 1),[4,5] and in seeking to expand this chemistry, we have extended our studies to include several related systems that contain the bis(diphenylphosphino)amine ligand (abbreviated dppa). In the course of this work we have structurally characterized the redox pair *cis*-$Re_2(O_2CCH_3)_2Cl_2(dppa)_2$ and *cis*-$[Re_2(O_2CCH_3)_2Cl_2(dppa)_2]PF_6$ and describe herein the full details of this study.

Experimental Section

Starting Materials. The compounds $Re_2(O_2CCH_3)_2X_4(H_2O)_2$ (X = Cl, Br),[6] were prepared by using established literature procedures. Bis(diphenylphosphino)amine (abbreviated dppa) was prepared by the procedure of Nöth et al.[7] All solvents were obtained from commercial sources and were used as received.

Reaction Procedures. Syntheses were performed in an atmosphere of drying nitrogen, and solvents were deoxygenated prior to use. Some reactions were carried out in the presence of a pine boiling stick to promote crystal formation.

A. Synthesis of $Re_2(O_2CCH_3)X_4(dppa)_2$ (2). (i) X = Cl. A mixture of $Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$ (0.100 g, 0.150 mmol) and dppa (0.350 g,

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(1) Puddephatt, R. J. *Chem. Soc. Rev.* **1983**, 99.

(2) Cotton, F. A. *Polyhedron* **1987**, *6*, 667.

(3) Chaudret, B.; Delavaux, B.; Poilblanc, R. *Coord. Chem. Rev.* **1988**, *86*, 191.

(4) Cutler, A. R.; Derringer, D. R.; Fanwick, P. E.; Walton, R. A. *J. Am. Chem. Soc.* **1988**, *110*, 5024.

(5) An interesting example of isomerization has also been encountered in the case of the diplatinum(II) complex $Pt_2(C{\equiv}CMe)_4(depm)_2$ (depm = $Et_2PCH_2PEt_2$), but in this instance there is no metal–metal bond present. See: McLennan, A. J.; Puddephatt, R. J. *Organometallics* **1985**, *4*, 485.

(6) Chakravarty, A. R.; Cotton, F. A.; Cutler, A. R.; Walton, R. A. *Inorg. Chem.* **1986**, *25*, 3619 and references cited therein.

(7) Nöth, H.; Meinel, L. *Z. Anorg. Allg. Chem.* **1967**, *349*, 225.