

Pressure Effect on Spin Crossover in [Fe(phen)₂(NCS)₂] and [CrI₂(depe)₂]V. Ksenofontov,[†] A. B. Gaspar,[†] G. Levchenko,[‡] B. Fitzsimmons,[†] and P. Gülich^{*,†}*Institut für Anorganische Chemie und Analytische Chemie, Johannes Gutenberg Universität, Staudinger Weg 9, D-55099 Mainz, Germany, and Donetsk Physical-Technical Institute, National Academy of Science of Ukraine, R. Luxemburg Strasse 72, Donetsk, 83114 Ukraine**Received: February 3, 2004; In Final Form: March 30, 2004*

In the present article, we discuss the results of investigations of the influence of hydrostatic pressure (up to 1.2 GPa) on the spin transition behavior in [Fe(phen)₂(NCS)₂] polymorph II and [CrI₂(depe)₂]. It is demonstrated that pressure effect studies are very helpful in elucidating the mechanism of cooperative dynamic electronic structure phenomena accompanied by significant volume changes. Application of hydrostatic pressure serves as a tool for modifying the ligand field strength in a controlled manner.

Introduction

The miniaturization of components for the construction of useful devices, which is an essential feature of modern technology, is currently pursued in different branches of molecular science. Electronic and photonic technologies require functional materials exhibiting bistability behavior at a molecular scale.^{1–2} The reversible change between low-spin (LS) and high-spin (HS) states driven by a variation of temperature and/or pressure or also by light irradiation, mainly observed in pseudo-octahedral iron(II) complexes, is one of the most attractive examples of molecular bistability.³ Indeed, in the area of functional materials research such classes of compounds are promising particularly for applications in memory and display devices as well as molecular switches.^{4–5}

The first experiments to study the effect of applied pressure on the spin crossover (SCO) phenomenon date back more than 40 years and have been performed in solution by Ewald et al. with a family of Fe(III) dithiocarbamate complexes.⁶ It was soon realized that the temperature dependent thermal equilibrium between ²T₂ ↔ ⁶A₁ states is strongly influenced by pressure. The low spin (LS) ²T₂ state has a smaller molecular volume than the high spin (HS) ⁶A₁ state and becomes favored as pressure increases. König⁷ pointed out that the strong dependence of the ligand-field strength on the metal-donor atom distances and the resulting large difference in metal–ligand bond lengths between the two spin states leads to the change of entropy, which is the genuine driving force for the thermal spin transition. Indeed, the underlying reason for the pressure influence on the spin transition process is the large difference in the metal-donor atom bond lengths, $\Delta r_{\text{HL}} = r_{\text{HS}} - r_{\text{LS}} \approx 0.1$ and 0.2 \AA , for Fe(III) and Fe(II) spin crossover molecules, respectively. A schematic representation of the pressure influence on the LS and HS potential wells of Fe(II) is shown in Figure 1: application of pressure increases the relative vertical displacement of the potential wells; the additional minor relative horizontal displacement of the potential wells due to a slight decrease in bond length accompanying an increase in pressure has been neglected in this scheme. Increasing the pressure favors the LS state of the molecule, thus shifting the spin transition to

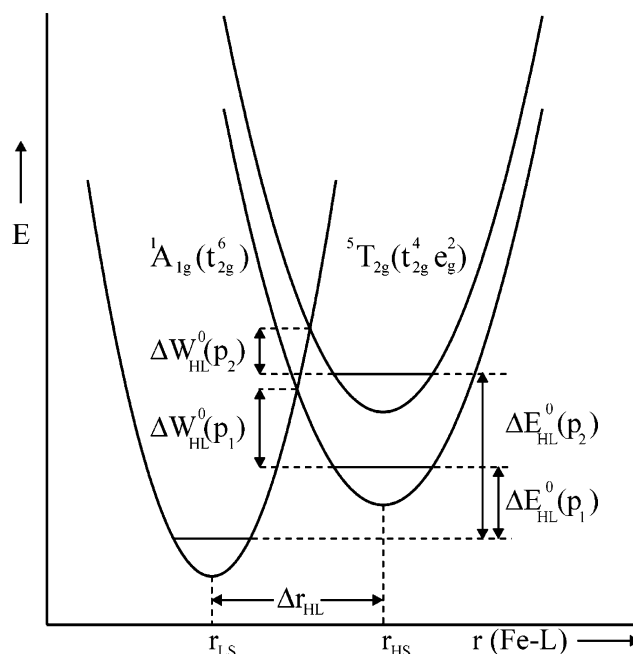


Figure 1. Schematic representation of the pressure influence ($p_2 > p_1$) on the LS and HS potential wells of Fe(II). The minor change in bond lengths Δr_{HL} under pressure is not considered.

higher temperatures because pressure increases the zero-point energy difference ΔE_{HL}^0 by the work term $p\Delta V_{\text{HL}}^0$ and decreases the activation energy ΔW_{HL}^0 , favoring the LS state.

Although the spin crossover phenomenon is essentially a property of the isolated complex molecule due to the competition between the dependence of the ligand-field strength on the metal–ligand bond length and the spin pairing energy, external perturbations such as pressure may effectively influence the spin crossover properties. Moreover, the application of pressure to compounds with thermal SCO is a powerful tool in investigations of thermodynamic characteristics and microscopic aspects of the mechanism for the spin transition in molecule-based compounds. Systematic and detailed studies of the concerted action of temperature and pressure variation on SCO compounds have only recently become possible with the development of special hydrostatic pressure cells in connection with various

* To whom correspondence should be addressed.

[†] Johannes Gutenberg Universität.

[‡] National Academy of Science of Ukraine.

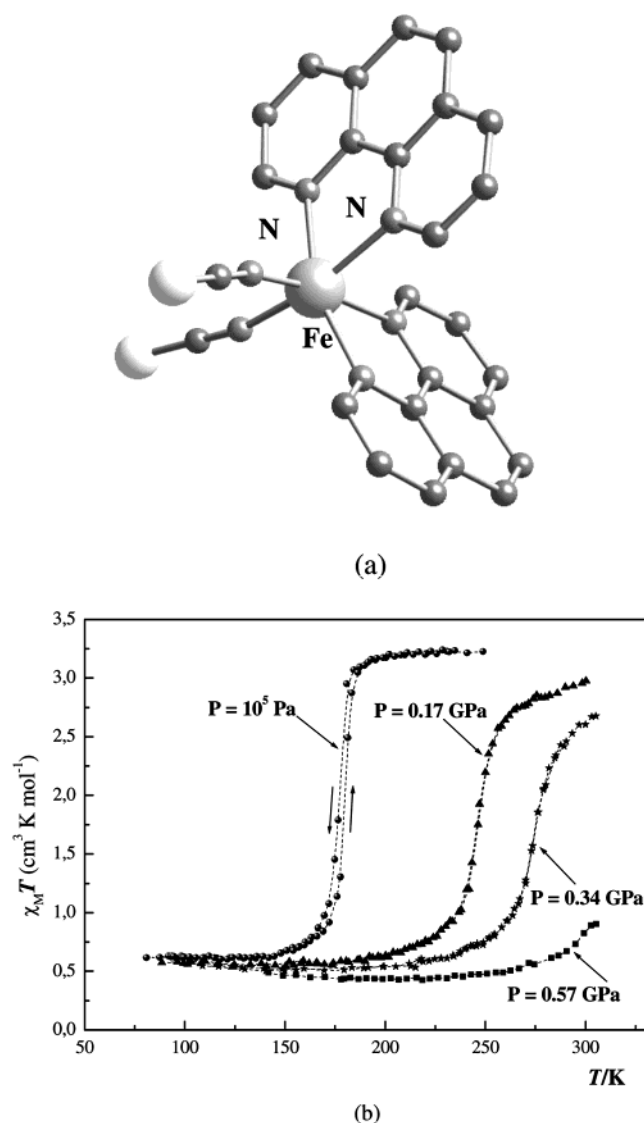


Figure 2. Molecular structure (a) and $\chi_M T$ versus T curves at different pressures for $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ polymorph II, dashed lines are guides for the eyes (b). The magnetic properties of the sample were found identical after release of pressure which indicates that the sample has not been modified in an irreversible manner.

physical techniques such as magnetic susceptibility, optical and Mössbauer measurements, EXAFS, and vibrational spectroscopy. The earlier, significant publications⁸ cited in the review article^{3a} published in 1994 refer to results obtained using mainly a Mössbauer high-pressure cell. Much progress has been made since then also regarding the pressure studies in liquid state.⁹

$[\text{Fe}(\text{phen})_2(\text{NCX})_2]$ ($X = \text{S}, \text{Se}$) systems are the first and still among the most thoroughly studied SCO systems of iron(II)¹⁰ (Figure 2a). Fisher and Drickamer¹³ investigated the effect of pressure on the spin transition behavior of this system using the Mössbauer effect. Their results demonstrated not only the expected increase of HS \rightarrow LS conversion with increasing pressure at a given temperature but even a partial reverse LS \rightarrow HS transformation above a certain threshold of pressure. Subsequent studies of Adams et al.^{8b} and Pebler^{8c} did not confirm the reverse LS \rightarrow HS process, raising the question about the presence of hydrostatic conditions in the experiments carried out by Fisher and Drickamer. The first magnetic susceptibility measurements under pressure on the title compound have been carried out by Usha et al.^{8e} All of the results obtained in these studies provided the evidence for HS \rightarrow LS conversion under

pressure, the reported values of the critical pressure $P_{1/2}$ for 50% spin state conversion at room-temperature ranging between 0.6 and 1.2 GPa. König et al. have demonstrated the existence of two crystallographic modifications of $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$.^{10a} Polymorph I undergoes an almost complete thermal spin transition, whereas in polymorph II, a fraction of HS molecules of ca. 17% is retained at low temperatures. A possible reason for the range of $P_{1/2}$ values indicated above is that the studies were carried out with different polymorphs. Whereas in ref 8b the actual polymorph that was investigated is not specified, in refs 8c and 13, the experiments were carried out on polymorph II. The non-hydrostatic nature of the pressure in the experiments using diamond anvil cells could also contribute to the discrepancy in $P_{1/2}$ values. X-ray diffraction on a single crystal of polymorph II did not reveal a change of the space group, neither during the thermal spin crossover nor under pressure up to 1.3 GPa.^{10b} Despite the existence of detailed structural knowledge, several important thermodynamical features of the spin transition in $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ polymorph II under pressure have not been explored up to now.

In the following, we report on the results of detailed investigations of the effects of pressure on $[\text{Fe}(\text{phen})_2(\text{NCX})_2]$ and $[\text{CrI}_2(\text{depe})_2]$. Both are mononuclear spin crossover systems (SCO) and show similar (abrupt) spin transition properties at atmospheric pressure despite the differences in the chemical coordination sphere.

Experimental Section

Materials. The compounds have been synthesized and characterized according to procedures described elsewhere.^{10–11}

Magnetic Susceptibility Measurements under Hydrostatic Pressure. The variable-temperature magnetic susceptibility measurements were performed using the PAR 151 Foner-type magnetometer, equipped with a cryostat operating in the temperature range 2–300 K. The hydrostatic pressure cell made of hardened beryllium bronze with silicon oil as the pressure transmitting medium operates in the pressure range $10^5 \text{ Pa} < P < 1.3 \text{ GPa}$ and has been described elsewhere.¹² Hydrostaticity was established in our previous studies of spin crossover compounds.⁹ Cylindrically shaped powder sample holders with dimensions of 1 mm in diameter and 5–7 mm in length were used. The pressure was measured using the pressure dependence of the superconducting transition temperature of a built-in pressure sensor made of high purity tin. Experimental data were corrected for diamagnetism using Pascal's constants.

Results and Discussion

Effect of Pressure on $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ Polymorph II.

The $\chi_M T$ versus T curves measured at different pressures for $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ polymorph II are shown in Figure 2b. At ambient pressure, the transition curve is extremely steep with $T_{1/2} = 177 \text{ K}$. The presence of a narrow temperature hysteresis and the value of residual HS fraction ($\approx 17\%$) are in agreement with published data.^{10c} As the pressure is increased, the transition curve is displaced to higher temperatures with an average dependency of 220 K/GPa. With the application of pressure, the narrow hysteresis loop disappears and the transition curves become gradual. At pressures around 0.6 GPa, the sample is mostly in the LS state up to room temperature; however, the residual HS fraction below the transition remains essentially unaltered. This observation is in line with results found in ref 10b, viz. conservation of the space group during the spin crossover transition under pressure up to 1.3 GPa and the structure being a decisive factor for the completeness of the spin transition

in $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$. It should be noted that usually a complete spin transition is accomplished under hydrostatic pressure. A progressive diminution of the pressure influence on the transition temperature ($\partial T_{1/2}/\partial P = 410 \text{ K/GPa}$ at 0.17 GPa, 180 K/GPa at 0.34 GPa, and 150 K/GPa at 0.57 GPa) points at the presence of a steric barrier, which can be a possible factor preventing a complete $\text{HS} \rightarrow \text{LS}$ transformation in polymorph II of $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$. In fact, π interactions between $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ units are found within the (*a*, *b*) layers, and more precisely, these interactions are oriented in the *b* direction.¹⁴ The pressure dependence of the lattice parameters *a*, *b*, and *c* reveals a significant discontinuity for *a* but quasi-linear behavior for *b* and *c*. The discontinuity along *a* seems to be related to the spin state change, as a similar effect has been observed in the dilatation experiments.¹⁴ Finally, a comparison between the evolution of the unit cell volume and the $\chi_M T$ product under pressure clearly shows the correlation between the magnetic and structural properties for this compound.

The influence of pressure on the thermodynamic parameters of the $\text{HS} \leftrightarrow \text{LS}$ transition in $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ can be interpreted in the frame of a phenomenological mean-field description.¹⁵ This compound appears to be ideal for this purpose, because of the proven absence of a structural phase transition in both temperature and pressure variation. The pressure effect on the spin crossover behavior is determined by the magnitude of the volume change of the unit cell per spin crossover complex, ΔV , and by the intermolecular interaction free energy $F_{\text{int}}(\gamma, T)$. The change of the Gibbs free energy at an external pressure *P* is given by

$$\Delta G = \gamma \Delta F_{\text{HL}} + F_{\text{int}}(\gamma, T) - TS_{\text{mix}}(\gamma) + \gamma P \Delta V \quad (1)$$

γ is the fraction of HS molecules and ΔF_{HL} the change of the free energy due to the spin transition. The mixing entropy is given by the expression

$$S_{\text{mix}}(\gamma) = -k_B[\gamma \ln \gamma + (1 - \gamma) \ln(1 - \gamma)] \quad (2)$$

Following ref 15, the energy shift Δ_s and the interaction constant Γ in the serial expansion of the interaction energy yield

$$F_{\text{int}}(\gamma, T) = \Delta_s \gamma - \Gamma \gamma^2 \quad (3)$$

The change of the free energy may be expressed as

$$\Delta F_{\text{HL}}(T) = \Delta H(T_{1/2}) - \Delta S_{\text{HL}} T \quad (4)$$

Here, $\Delta H(T_{1/2})$ and ΔS_{HL} are the changes of the enthalpy and the entropy at ambient pressure. Under the condition that the lattice is in thermal equilibrium

$$(\partial \Delta G / \partial \gamma)_{T,P} = 0 \quad (5)$$

Finally, the pressure influence on the spin crossover is described by the equation of state

$$T = (\Delta H(T_{1/2}) + \Delta_s + P \Delta V - 2\gamma \Gamma) / \left(k_B \ln \frac{1-\gamma}{\gamma} + \Delta S_{\text{HL}} \right) \quad (6)$$

Figure 3 shows the HS fraction vs temperature calculated from the magnetic susceptibility measurements under pressure for $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$. Applying eq 6 to the $\gamma(T)$ data, several important thermodynamical features have been drawn (Table 1). Assuming, according to refs 16 and 17, Δ_s being independent of temperature, one can extract the volume changes ΔV per spin

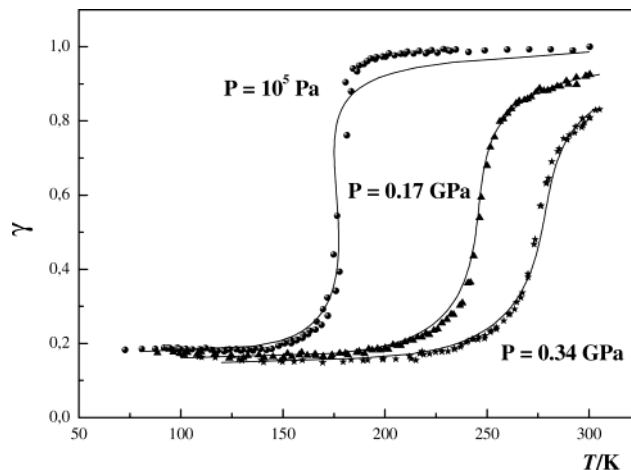


Figure 3. HS fraction γ versus temperature T at different pressures for $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ polymorph II. Solid lines represent the simulation of transition curves using the eq 6.

TABLE 1: Thermodynamic Parameters Obtained from Magnetic Susceptibility Measurements under Pressure for $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ Polymorph II

<i>P</i> , GPa	$\Delta H(T_{1/2}) + \Delta_s + P \Delta V$, kJ/mol	Γ , kJ/mol
10^{-4}	11.7	3.3
0.17	15.7	3.7
0.34	17.5	4.0

crossover complex molecule to be 39 and 28 Å³ at 0.17 and 0.34 GPa, respectively. The average change of the unit cell volume of 134 Å³ is comparable with the value of 119 Å³ found in the structural study of the $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ polymorph II under pressure.¹⁴ The slight difference may be attributed to a possible pressure influence on the energy shift Δ_s . One notices that, despite the interaction constant Γ increasing under pressure, the transition curves become more gradual. It can be understood, considering the so-called reduced pressure introduced by Köhler et al.^{8j}

$$\Pi^* = \frac{\Delta F_{\text{HL}}(T) + \Delta_s + P \Delta V}{\Gamma} \quad (7)$$

which characterizes the type of the spin crossover transition.^{8j} A first-order transition with hysteresis is expected to occur at critical temperatures

$$T_{1/2} < T_c = \frac{\Gamma}{2k_B} \quad (8)$$

if $\Pi^*(T_c) < 1$; the spin transition is of continuous type if $\Pi^*(T_c) > 1$. At ambient pressure with $\Gamma = 3.3 \text{ kJ/mol}$, the critical temperature is $T_c = 198 \text{ K}$ and the reduced pressure $\Pi^* = 0.62$. As a consequence, a first-order transition with a very steep transition curve is observed. One can estimate that at an external pressure $P \geq 0.05 \text{ GPa}$ the parameter Π^* exceeds 1, giving rise to gradual transitions. The observation of smooth transition curves at $P \geq 0.17 \text{ GPa}$ confirms this conclusion. From the fact that Γ increases under pressure, one might expect that the intermolecular interactions, responsible for cooperative effects and thus for the abruptness of the transition, should be stronger at higher pressure. However, the stabilization of the LS state with increasing pressure due to the $P \Delta V$ term dominates over the increase of the interaction constant Γ under pressure. At a given temperature, the HS fraction is reduced, and this dilution effect in turn reduces the cooperativity of the transition.

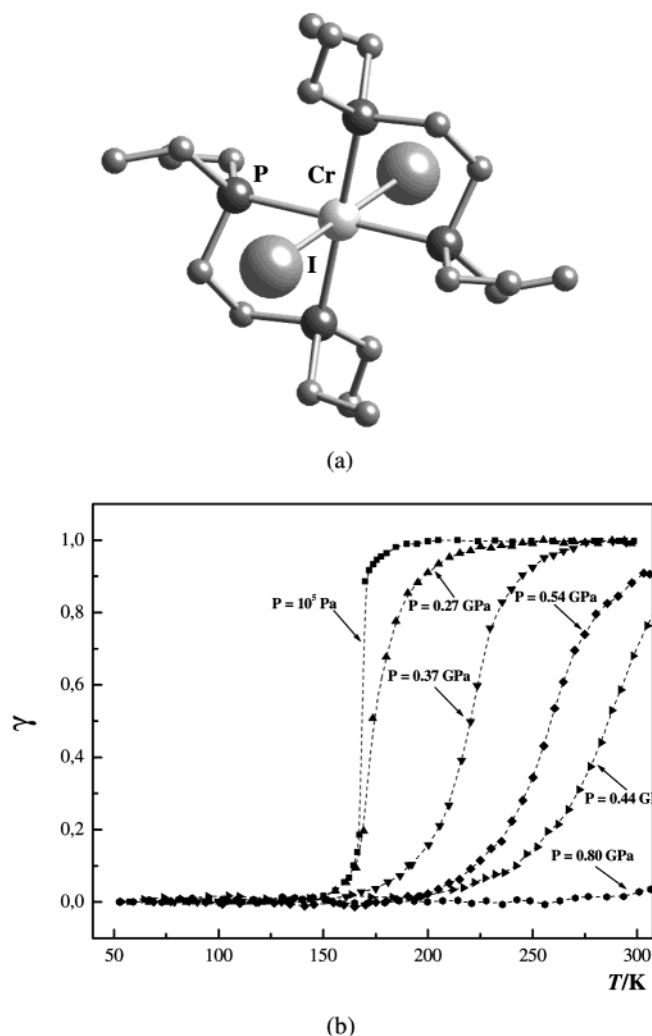


Figure 4. Molecular structure (a) and $\gamma(T)$ curves at different pressures for $[\text{CrI}_2(\text{depe})_2]$, dashed lines are guides for the eyes (b). The magnetic properties of the sample were found identical after release of pressure which indicates that the sample has not been modified in an irreversible manner.

A detailed thermodynamical treatment of the spin transition under the influence of external pressure was reported for $[\text{Fe}(\text{ptz})_6](\text{PF}_6)_2$ ($\text{ptz} = 1$ -*n*-propyltetrazole).^{9d} This compound shows a rather steep transition with strong cooperativity, but without hysteresis. The interaction constant $\Gamma = 101 \text{ cm}^{-1}$ was found to be very close to the critical value above which hysteresis solely due to the cooperative effects is expected. In contrast to the case of $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ polymorph II, the interaction constant was found to be pressure independent presumably because of the comparatively low-pressure applied in this study.

Spin Crossover under Pressure in $[\text{CrI}_2(\text{depe})_2]$. Thermal spin crossover in chromium(II) compounds was first reported by Halepoto et al. in 1989.¹¹ The compound *trans*-bis[1,2-bis-(diethylphosphino)ethane]di-iodochromium(II) ($[\text{CrI}_2(\text{depe})_2]$) (Figure 4a) exhibits a very sharp $^3\text{T}_{1g}$ ($S = 1$) \leftrightarrow $^5\text{E}_g$ ($S = 2$) spin transition with $T_{1/2} = 169 \text{ K}$ without noticeable thermal hysteresis at ambient pressure. A magnetic susceptibility study under pressure shows a progressive increase of $T_{1/2}$ and a decrease of the transition steepness with increasing pressure (Figure 4b). Application of pressure of ca. 0.8 GPa transforms the compound entirely to the low-spin state at ambient temperature. Qualitatively, one can interpret this pressure effect on the grounds of mean-field theory.¹⁵ In mean field approximation,

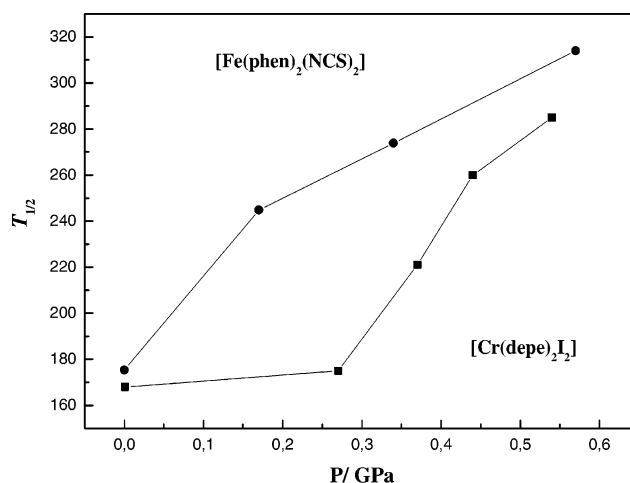


Figure 5. Plot of $T_{1/2}$ versus P for $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ polymorph II and $[\text{CrI}_2(\text{depe})_2]$.

the pressure dependence of the spin transition temperature obeys the Clausius–Clapeyron relation

$$\frac{\partial T_{1/2}}{\partial P} = \frac{\Delta V}{\Delta S_{HL}} \quad (9)$$

This relation reflects the scaling of the transition temperature $T_{1/2}$ and the volume change ΔV . Figure 5 shows the plots of $T_{1/2}$ versus pressure for $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ polymorph II and $[\text{CrI}_2(\text{depe})_2]$. For the latter compound, strong nonlinearity contrasts the almost linear dependence for $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$. A detailed interpretation of this is not possible without the knowledge of the thermal and pressure dependences of the elementary cell volume of $[\text{CrI}_2(\text{depe})_2]$, as has been accomplished for $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$.¹⁴ However, it looks as though the elementary cell volume of $[\text{CrI}_2(\text{depe})_2]$ hardly changes across the spin transition in the pressure range up to $\approx 0.3 \text{ GPa}$, similar to the findings in X-ray studies on $[\text{Fe}(\text{mtz})_6](\text{BF}_4)_2$ after LIESST effect at ambient pressure.¹⁸ The reason may be found in the different compressibilities of the large iodide ions as compared to the smaller and harder phosphorus donor atoms in the CrP_4I_2 core. Application of low pressure seems to reduce mainly the volumes of the iodide ions leaving the Cr-P donor atom distances essentially unchanged. The influence of pressure on $T_{1/2}$ in the present case seems to start above a certain threshold when the Cr-P bond lengths are noticeably altered by pressure. A quantitative interpretation of the influence of pressure on the spin crossover behavior of $[\text{CrI}_2(\text{depe})_2]$, particularly the pressure dependence of the transition temperature $T_{1/2}$, is only possible with a detailed crystallographic study of the compound under variable pressure and at variable temperatures.

Conclusion

The application of pressure provides important information on thermodynamical properties and on the driving force of thermal spin transition in SCO compounds. By analyzing the evolution of the spin transition curve obtained under pressure, it is possible to extract, along with the changes of enthalpy and entropy, the change of the volume of the unit cell ΔV upon spin conversion as well as the behavior of the interaction constant Γ . It has also been shown that application of pressure is a powerful tool to investigate the role of the structure and the interplay between spin transition and structural phase transition. Changes of the molecular volumes play a significant

role in the cooperative interactions in solid compounds exhibiting dynamical electronic structures such as in spin crossover systems. Application of hydrostatic pressure is an elegant method of changing the ligand field strength and thereby modifying the spin transition behavior in a controlled manner. In fact, pressure studies on mononuclear SCO systems has yielded results which are, on one hand, quite expected like the stabilization of the LS state due to its smaller molecular volume as compared to that of the HS state. On the other hand, some unexpected features in the SCO behavior have been unravelled under pressure and await quantitative theoretical interpretation. There are, for instance, the two types of pressure influence: (i) the shape of the ST curve remains essentially unchanged but is shifted to higher temperatures under pressure; (ii) the relatively steep ST curve at ambient pressure becomes more and more gradual, stabilizing the LS state and shifting $T_{1/2}$ upward, as pressure increases, until the HS state entirely disappears. In both cases it is, of course, the molecular volume change ΔV_{HL} that tends to stabilize the LS state under pressure. However, there must be other factors, most probably arising from special lattice properties (hydrogen bonding, π – π stacking, packing effects), which are held responsible for the cooperative interactions between the spin state changing molecules and also contribute to the pressure-induced changes of the SCO behavior. By the same token, it is believed that the unexpected stabilization of the HS state and gradual diminishing of the hysteresis with increasing pressure have their origin in particular lattice properties. Clearly, theoretical progress in understanding such unexpected pressure effects will only be possible with data from crystal structure determination under applied pressure and, of course, variable temperature.

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