

COMPARISON OF LOW TEMPERATURE AND HIGH PRESSURE EFFECTS ON THE STRUCTURAL BEHAVIOUR OF TWO IRON (II) SPIN TRANSITION COMPLEXES: $\text{Fe}(\text{PHEN})_2(\text{NCS})_2$ AND $\text{Fe}(\text{BTZ})_2(\text{NCS})_2$

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Spin transition phenomenon was first evidenced in 1931 by L. Cambi and A. Cagnasso, on tris (N,N-dialkyldithiocarbamate) iron (III) complexes and has been observed, since then, on numerous first row transition metal complexes with d^4 to d^7 electronic configurations. Such compounds have been attracting a lot of attention for the last 15 years, both from theoretical and experimental sides, while potentially interesting applications are expected in molecular electronics (J. Zarembowitch and O. Kahn, 1991).

Although its investigation has called for various techniques, several aspects of spin transition mechanism still remain unclear. More particularly, if it is admitted that physical and structural properties are strongly correlated in these materials, the part that some structural parameters play in the characteristics of the spin transition is still to be defined. One of the reasons of this lack of comprehension comes certainly from the fact that most of the complexes that have been studied are polycrystalline samples, which prevents from systematic full structure investigations.

We present in the following a comparative structural X-ray diffraction study conducted as a function of temperature or pressure, on single crystals of two iron (II) octahedral complexes: $\text{FeL}_2(\text{NCS})_2$ where L is a bidentate ligand [1,10-phenanthroline, (Phen) or 2,2'-bi-4,5 dihydrothiazine, (Btz)].

After having set out in the next section the motivations of this investigation, we discuss the most important results of the full structure determi-

nations performed at room temperature, low temperature ($T \cong 135\text{K}$), high pressure ($P \cong 1.0\text{GPa}$, $T = 300\text{K}$), as well as thermal dilatation and compressibility data, and we shall relate these data with the physical properties these compounds exhibit under the same conditions.

I. IRON (II) SPIN TRANSITION COMPLEXES: CORRELATIONS BETWEEN PHYSICAL AND STRUCTURAL PROPERTIES:

Iron (II) (d^6 configuration) octahedral complexes are known to exhibit under constraint the most versatile spin crossover behaviors: these compounds may present two different isomeric spin states, the stabilization of which depends on the magnitude difference between the ligand field energy Δ which induces a degeneracy lifting of d orbitals, and π , the mean electron spin pairing energy (see figure 1): the High Spin (HS) state ($S=2$) is established when $\Delta < \pi$ (t_{2g} and e_g orbital occupancy obeys the Hund rule); when $\Delta > \pi$, the complex is in its Low-Spin (LS) state ($S=0$). If Δ and π have comparable magnitudes, then the compound may be capable of switching from one state to the other under an external applied constraint (temperature, pressure): the spin transition occurs (figure 2).

A similar behaviour may be induced by Light-Induced Excited Spin State Trapping (LIESST) (S. Decurtins, P. Gülich, C.P. Köhler, H. Spiering, 1984; S. Decurtins, P. Gutlich, C.P., Köhler, H. Spiering and A. Hauser, 1985; P. Gülich and A. Hauser, *Pure and Appl. Chem.*, 61, 849, 1989; P. Gülich and A. Hauser, *Coord. Chem. Rev.*, 97, 1, 1990) where molecules (see figure 2-b), in the LS state well below the HS to LS transition temperature, are excited by light radiation into the HS state, remain trapped in this state, and then may recover their LS state by relaxation at higher temperature.

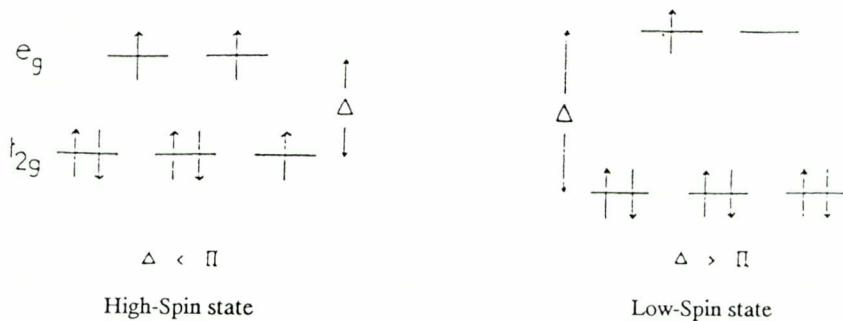


Fig. 1. High-Spin and Low-Spin d^6 electronic configurations of an iron (II) complex

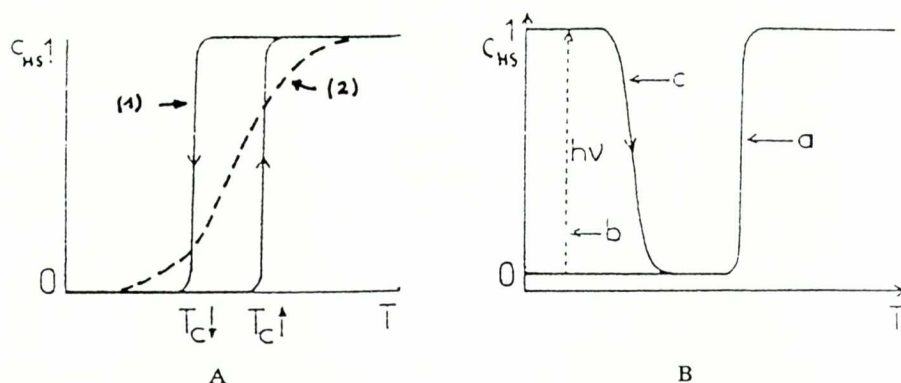


Fig. 2. A: Variation of the HS fraction. (C_{HS}) as a function of temperature; (1) sharp transition with hysteresis effect; (2) gradual transition. B: a - sharp transition; b - LS to HS state transition induced by light radiation; c - HS to LS relaxation.

Moreover, experimental data show that the characteristics of spin transitions such as the more or less gradual shape of the spin conversion, an eventual hysteresis effect (see figure 2-a), the residual paramagnetism at low temperature, may differ strongly from one compound to another and are influenced by various factors such as intraligand substitution, ligand replacement, metal dilution effect, sample preparation and treatment (for a review see Gülich (1981), König, Ritter and Kulshreshtha (1985) and Rao (1985)). Crucial questions to better understand the mechanisms which drive spin transitions concern the changes of molecular and crystal structures which are known to be associated with the spin crossover.

Several full structure determinations on single crystals (for a review, see for example König, 1987) as well as EXAFS experiments performed on powder samples (C. Cartier, P. Thuery, M. Verdagner, J. Zarembowitch, A. Michalowitz, 1986, P. Thuery, J. Zarembowitch, A. Michalowitz, and O. Kahn, 1987) have clearly shown that the change of spin state is associated with intramolecular modifications of the metal-ligand bond lengths, which shorten when the molecule goes from a HS to a LS state; this is due to the population reduction, in the LS phase, of the antibonding e_g orbitals, which point towards the ligands.

These structural investigations have led to put forward several assumptions in order to find an optimal congruence between available structural data and the experimentally determined spin transition characteristics. For instance:

- the volume difference ΔV between HS and LS isomers, which depends on the metal-ligand bond length changes, is expected to play a prominent part in the spin crossover mechanism: the larger ΔV , the more abrupt the transi-

tion and the wider the hysteresis loop should be (E. König, G. Ritter and S.K. Kulshreshtha, 1985; E. König, G. Ritter, W. Irler and H.A. Goodwin, 1980).

– continuous transitions are expected to only involve a single crystallographic phase whereas two crystallographically different phases characterize discontinuous transitions (E. König, G. Ritter and S.K. Kulshreshtha, 1985).

– lattice rigidity may influence the nature of the spin transition: the greater the bulk modulus, the sharper the transition should be (P. Adler, L. Wiehl, E. Meissner, C.P. Köhler, H. Spiering and P. Gülich, 1987).

In the following, the comparative study we have performed on the two title compounds brings out interesting information with regard to these assumptions and to the relationship between the physical and structural behavior of such compounds.

II. $\text{Fe}(\text{PHEN})_2(\text{NCS})_2$ AND $\text{Fe}(\text{BTZ})_2(\text{NCS})_2$: AN EXAMPLE OF TWO IRON (II) OCTAHEDRAL COMPLEXES WHICH BEHAVE VERY DIFFERENTLY REGARDING THEIR MAGNETIC PROPERTIES:

Of these two compounds, $\text{Fe}(\text{Phen})_2(\text{NCS})_2$ has been most investigated and can be considered as a model compound among the iron (II) spin transition complexes. It undergoes an abrupt HS to LS transition at a temperature $T_c \cong 176\text{K}$ (W.A. Baker, H.M. Bobonich, 1964, E. König, K. Madeja, 1966). Various techniques were used to study its transition such as magnetic susceptibility (W.A. Baker, H.M. Bobonich, 1964, E. König, K. Madeja, 1966, E. König, K. Madeja, 1967, A.T. Casey, F. Issac, 1967, P. Ganguli, P. Gülich, 1980, P. Ganguli, P. Gülich, E.W. Müller, W. Irler, 1981), Mössbauer spectroscopy (E. König, K. Madeja, 1966, E. König, K. Madeja, 1967, P. Ganguli, P. Gülich, 1980, P. Ganguli, P. Gülich, E.W. Müller, W. Irler, 1981, I. Dezsi, B. Molnar, T. Tarnoczi, K. Tompa, 1967, S. Savage, Z. Jia-Long, A.G. Maddock, 1985), I.R. spectrometry (W.A. Baker, G.J. Long, 1965, E. König, K. Madeja, 1967, P. Ganguli, P. Gülich, 1980, P. Ganguli, P. Gülich, E. Müller, W. Irler, 1981, I. Dezsi, B. Molnar, T. Tarnoczi, K. Tompa, 1967, S. Savage, Z. Jia-Long, A.G. Maddock, 1985), U.V.-visible spectrometry (E. König, K. Madeja, 1967), X-ray powder diffraction (W.A. Baker, H.M. Bobonich, 1964, E. König, K. Madeja, 1966, E. König, K. Madeja, 1967, P. Ganguli, P., Gülich, E. Müller, W. Irler, 1981), calorimetric measurements (P. Ganguli, P., Gülich, E. Müller, W. Irler, 1981, M. Sorai, S. Seki, 1972).

Moreover, I.R. (J.R. Ferraro, J. Takemoto, 1974) and U.V.-visible (D.C. Fisher, H.G. Drickhamer, 1971) spectrometries, Mössbauer (J. Pe-

bler, 1982, D.C. Fisher, H.G. Drickhamer, 1971) and EXAFS (C. Roux, J. Zarembowitch, R. Claude, J.P. Itié, A. Polian, E. Dartyge, A. Fontaine, H. Tolentino, M. Verdaguer, 1990) experiments were also conducted as a function of pressure, while magnetic susceptibility experiments have been performed both as a function of temperature and pressure (S. Usha, R. Srinivasan, C.N.R. Rao, 1985): all the results agree with the occurrence of a spin state conversion under pressure, the critical pressure P_c of which is not well defined, and authors still disagree on its value at room temperature: $P_c \cong 0.6$ GPa (S. Usha et al. 1985), 0.8 GPa (D.M. Adams et al., 1982), 1.35 GPa (J. Pebler, 1982), 0.6 GPa (D.C. Fisher, H.G. Drickhamer, 1971) and 0.6-0.7 GPa (C. Roux, J. Zarembowitch, R. Claude, J.P., Itié, A. Polian, E. Dartyge, A. Fontaine, H. Tolentino, M. Verdaguer, 1990). Finally let us mention that LIESST effect has been recently observed at low temperature ($T_c \cong 6$ K) on this compound (S. Decurtins, P. Gülich, C.P., Köhler, H. Spiering, 1985).

Less attention, on the other hand, has been devoted to $\text{Fe}(\text{Btz})_2(\text{NCS})_2$. To our knowledge, this compound has been studied so far only as a function of temperature: it undergoes a HS-LS conversion over a much wider temperature range centered at about $T_c \cong 215$ K (G. Bradley, V. Mc Kee, S.M. Nelson, J. Nelson, 1978), temperature at which HS and LS isomers are in nearly equivalent ratio.

Although much information could be obtained concerning the physical behavior of these two compounds, it is only recently that a different method of preparation yielding single crystals of suitable size allowed us to undertake full X-ray diffraction investigations (B. Gallois, J.A. Real, C. Hauw, J. Zarembowitch, 1990, B. Gallois, T. Granier, F. Suez-Panama, J.A. Real, J. Zarembowitch, 1991, J. Gaultier, T. Granier, B. Gallois, J.A. Real, J. Zarembowitch, 1991). The opportunity of such a comparative investigation appeared at the first stages of their structure determination: $\text{Fe}(\text{Phen})_2(\text{NCS})_2$ and $\text{Fe}(\text{Btz})_2(\text{NCS})_2$ are isostructural; they crystallize in the same space group with similar lattice parameters and exhibit the same molecular packing.

III. EXPERIMENTAL

Room and low temperature experiments were conducted on an Enraf-Nonius CAD-4 diffractometer. Crystal cooling was achieved by a cold nitrogen gas flow.

High pressure diffraction experiments were performed with a gasketed diamond-anvil cell designed by A. Ahsbahr, (1984) and mounted on a single crystal X-ray diffractometer (for details see H. Loumhrari, 1983, B. Ga-

lois, J. Gaultier, C. Hauw, T. Lamcharfi, A. Filhol, 1986). The pressure-transmitting medium was Flourinert FC75 (C_8F_{18}) (Flourinert is a trade mark of the 3M Company). Pressure in the cell was measured from the shift ($d\lambda/dP=42.6 \cdot 10^2 \text{ \AA MPa}^{-1}$) of the optical absorption maximum ($\lambda_0 = 5270 \text{ \AA}$ at $P = 0.1 \text{ MPa}$) of Nickel(dimethylglyoxime) $_2$ with an estimated accuracy of 0.05 GPa (H.W. Davies, 1963).

Crystal data collection and reduction have been detailed elsewhere (B. Gallois, J.A. Real, T. Granier, C. Hauw, J. Zarembowitch, 1990, B. Gallois, J.A. Real, T. Granier, F. Suez-Panama, J. Zarembowitch, (to be submitted), T. Granier, B. Gallois, J. Gaultier, J.A. Real, J. Zarembowitch, (to be submitted)). Table I shows that both low temperature and high pressure experiments yield good quality results, even though, in the case of high pressure, the number of observed reflections is only about 60% of the one obtained at low temperature, which is mainly due to the smaller crystal size and the increase of diffuse background scattered by the beryllium gasket and the diamond anvils.

Table 1. X-ray data collection characteristics

	Fe(Phen) $_2$ (NCS) $_2$			Fe(Btz) $_2$ (NCS) $_2$		
	T=293K	T=130K	P=1.0GPa	T=293K	T=130K	P=1.0GPa
a (Å)	13.161(2)	12.770(2)	12.656(3)	13.288(1)	13.055(2)	12.839(4)
b (Å)	10.163(1)	10.090(2)	9.848(2)	10.861(1)	10.650(2)	10.454(3)
c (Å)	17.480(2)	17.222(3)	16.597(4)	16.920(2)	16.672(4)	16.362(4)
V (Å 3)	2338	2219	2068.5	2441.9	2318.1	2196.7
nb measd refl	1736	1814	1629	1789	1697	1723
nb obs refl (Fo>4σ(Fo))	1050	1115	631	1102	1095	662
refined parameters	159	159	159	154	154	154
refinement SHELX76						
minimized function						
w[Fo - Fc] 2						
weighting scheme						
w=[σ 2 (Fo)+gFo 2] $^{-1}$						
g	0.0001	0.0006	0.000	0.0007	0.0002	0.001
R	0.034	0.041	0.055	0.059	0.062	0.058
Rw	0.032	0.039	0.043	0.057	0.063	0.056
max. peak in final: Δρ(eÅ $^{-3}$)	0.6	0.5	0.7	0.7	0.8	0.4
	(a)	(a)	(c)	(b)	(b)	(d)

(a) B. Gallois et al. (1990)
(c) J. Gaultier et al. (1991)

(b) B. Gallois et al. (1991)
(d) T. Granier et al. (submitted)

IV. STRUCTURAL MODIFICATIONS UNDER CONSTRAINT

For both compounds, no change of symmetry was evidenced over the temperature range 300-130K or the pressure range 0-1.3GPa; the space group remains orthorhombic $Pbcn$ and molecular packings are very similar whatever the temperature or pressure may be. Figures 3a and 3b give the molecular units of $\text{Fe}(\text{Phen})_2(\text{NCS})_2$ and $\text{Fe}(\text{Btz})_2(\text{NCS})_2$ and the projections of crystal structures along their a axis: in both cases, the iron atom is located on a 2-fold axis and, as a consequence, two ligands of same nature belonging to the same molecular unit deduce from one another by this axis. Molecular packing is made of sheets of complex molecules parallel to the (a, b) planes, which stack along the c axis.

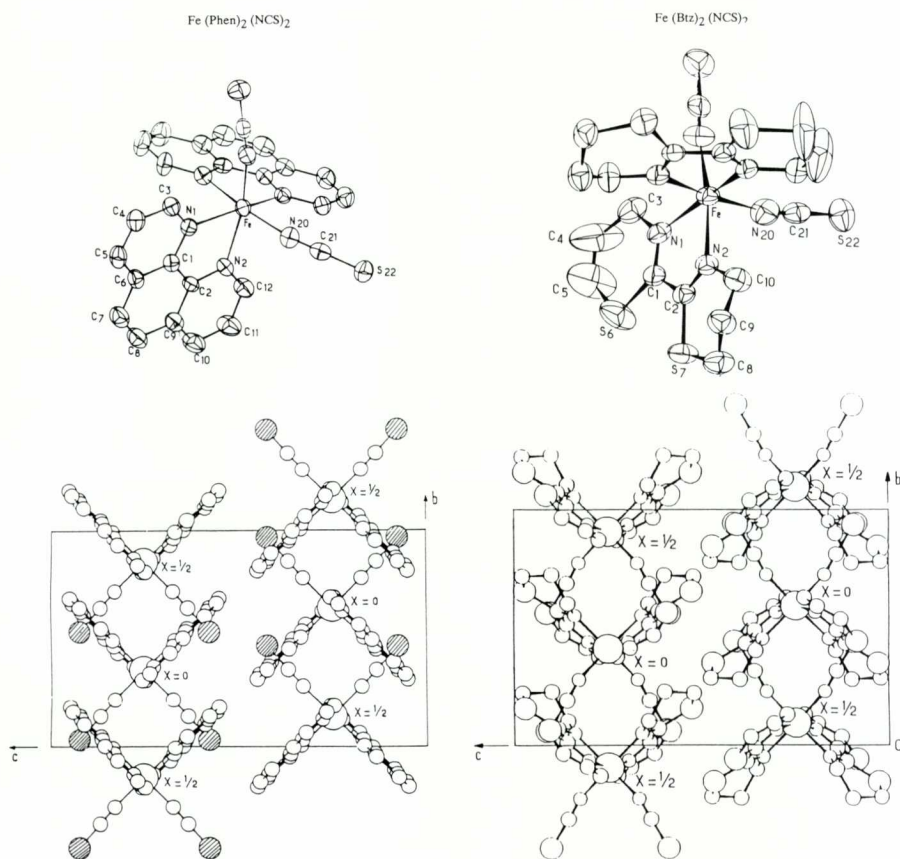


Fig. 3. Molecular conformation and crystal packing of $\text{Fe}(\text{Phen})_2(\text{NCS})_2$ and $\text{Fe}(\text{Btz})_2(\text{NCS})_2$: projections of the crystal lattice along the a axis.

A. Structural changes associated with the spin transition

As mentioned above, the change of spin state is expected to induce geometrical modifications of the iron octahedral environment. Table 2 gives the Fe-N(Ligand) bond lengths and N-Fe-N bond angles obtained for both compounds at room temperature, low temperature ($T \cong 130$ K), high pressure ($P \cong 1.0$ GPa). This table contains the most important modifications observed under constraint. In fact, one does not observe significant changes of ligand geometry under constraint: phenanthroline remains planar, Btz is still slightly distorted, NCS groups remain linear, whatever the applied constraint.

a) Room temperature (HS) configurations:

In the HS state (300K, ambient pressure), both complexes exhibit a strong distortion of the $[\text{Fe-N}_6]$ octahedron, with very large differences in the N-Fe-N angles and shorter Fe-N(CS) distances as compared with those of the Fe-N(Phen, Btz) bonds.

b) Low temperature (LS) molecular configurations:

The change of spin state induces noticeable shortenings of the Fe-N bonds: $\cong 0.20$ Å on the average for Fe-N(Phen) bonds and Fe-N(Btz) ones, $\cong 0.10$ Å for Fe-N(CS) bonds. One also observes important N-Fe-N bond

Table 2. $[\text{FeN}_6]$ octahedron geometry: modifications under constraint of Fe-N (Å) bond lengths and N-Fe-N bond angles ($^\circ$).

	$\text{Fe}(\text{Phen})_2(\text{NCS})_2$			$\text{Fe}(\text{Btz})_2(\text{NCS})_2$		
	293K (1 bar) (a)	135K (1 bar) (a)	1.0GPa (293K) (c)	1.0GPa (293K) (d)	135K (1 bar) (b)	293K (1 bar) (b)
Fe-N ₁ (Å)	2.199(3)	2.014(4)	2.003(7)	1.973(8)	1.982(7)	2.165(6)
Fe-N ₂	2.213(3)	2.005(4)	1.975(8)	1.968(9)	1.965(6)	2.176(6)
Fe-N ₂₀	2.057(4)	1.958(4)	1.954(7)	1.947(9)	1.948(8)	2.064(7)
N ₁ -Fe-N ₂ ($^\circ$)	76.1(1)	81.8(1)	82.6(3)	80.3(4)	80.3(3)	74.7(2)
N ₁ -Fe-N ₂₀	103.2(1)	95.3(1)	96.1(3)	91.9(4)	91.1(3)	97.4(2)
N ₂ -Fe-N ₂₀	89.6(1)	89.1(1)	90.6(3)	89.5(4)	89.7(3)	90.7(2)
N ₂₀ -Fe-N ₂₀ '	94.9(1)	90.6(1)	90.7(3)	89.3(4)	90.1(3)	95.0(2)
Spin state	Hs	LS	LS	LS	LS	HS

(numbers in brackets are last digit standard deviations)

(a) B. Gallois et al. (1990)

(b) B. Gallois et al. (1991)

(c) J. Gaultier et al. (1991)

(d) T. Granier et al. (to be submitted)

angle variations. These modifications lead to a much more regular shape of the $[\text{Fe-N}_6]$ octahedron of each compound. These first data show unambiguously that the sharpness of the spin transition cannot find an explanation taking only into account the difference of the intramolecular geometrical modifications between the two spin states.

c) High pressure (LS) molecular configurations:

Here again, as shown in table 2, the structure determinations performed at a pressure of 1.0 GPa yield very similar $[\text{Fe-N}_6]$ octahedron characteristics for both compounds, characteristics which are very close to the ones observed at low temperature. These results lead to the following conclusions:

- at $P = 1.0\text{GPa}$ both compounds have reached a LS state.
- the LS molecular configuration does not depend on the applied constraint, temperature or pressure.

The critical pressure P_c , for $\text{Fe}(\text{Phen})_2(\text{NCS})_2$ is lower than $P = 1.0\text{GPa}$, in contradiction with some results (see above) obtained earlier.

d) Intermolecular interactions:

Lowering temperature or increasing pressure does not induce drastic changes in the molecular packing. Molecular units do not change their orientations with respect to unit cell axes. The shortening of Fe-N bonds is expected to modify intermolecular contacts. These latter happen to increase at low temperature or high pressure. Table 3 lists the contacts which are shorter than the Van der Waals distances. They are classified into two kinds: those that occur within (**a,b**) sheets (intrasheet contacts), and those that concern molecular units which belong to different (**a,b**) sheets (intersheet contacts). This classification allows one to point out that $\text{Fe}(\text{Phen})_2(\text{NCS})_2$ has predominant contacts inside the (**a, b**) sheets, while $\text{Fe}(\text{Btz})_2(\text{NCS})_2$ exhibits many more intersheet contacts. This difference is reinforced at low temperature or high pressure.

B. Lattice behavior

It is clear that the bond lengths shortenings and the bond angle variations observed upon the change of spin state of the complex molecules induce lattice parameter variations and that, in turn, the lattice parameter evolution may reflect the change of spin state in the molecular solid.

a) Thermal dilatation data:

Figure 4 gives the evolution of the lattice parameters of both com-

pounds as a function of temperature. $\text{Fe(Phen)}_2(\text{NCS})_2$ and $\text{Fe(Btz)}_2(\text{NCS})_2$ behave very differently:

– $\text{Fe(Phen)}_2(\text{NCS})_2$ exhibits an abrupt variation of the lattice parameter **a** around $T_c \cong 176\text{K}$, along with a small dilatation of parameter **b**, and no accident on parameter **c**.

– $\text{Fe(Btz)}_2(\text{NCS})_2$, on the other hand, presents a gradual evolution of all the three parameters, with a change of derivative at $T' \cong T_c = 215\text{K}$.

Finally, in figure 5-a and 5-b, one clearly notices the strong correlation obtained for both compounds between magnetic susceptibility and unit cell volume evolution as a function of temperature, with a good agreement of the critical temperatures for both compounds. So the unit cell volume, which depends on the volume of molecular units, therefore on their spin state, reflects in its variation, the cooperativity of the spin conversion.

Table 3. Intermolecular contacts shorter than Van der Waals distances for $\text{Fe(Phen)}_2(\text{NCS})_2$ and $\text{Fe(Btz)}_2(\text{NCS})_2$ at 300K, 135K, 1.0GPa.

	$\text{Fe(Phen)}_2(\text{NCS})_2$				$\text{Fe(Btz)}_2(\text{NCS})_2$		
	300K	135K	1.0GPa		300K	135K	1.0GPa
intrasheet contacts:							
(2) $\text{C}_5\text{-C}_{21}$	–	3.50	3.41	$\text{C}_5\text{-S}_{22}$	–	–	3.55
$\text{C}_7\text{-C}_3$	3.53	3.54	3.36				
$\text{C}_8\text{-C}_4$	–	3.55	3.42				
$\text{C}_8\text{-C}_5$	–	3.53	3.40				
$\text{C}_9\text{-C}_4$	3.58	3.51	3.39				
$\text{C}_9\text{-C}_5$	–	3.60	3.48				
$\text{C}_2\text{-C}_4$	–	–	3.58				
$\text{C}_6\text{-C}_3$	–	–	3.46				
(4) $\text{S}_{18}\text{-C}_{16}$	–	–	3.58	$\text{C}_{10}\text{-S}_{22}$	3.61	3.61	3.48
(5)				$\text{S}_{22}\text{-C}_9$	–	–	3.52
(6)				$\text{C}_3\text{-C}_9$	–	–	3.56
intersheet contacts:							
(1) $\text{S}_{22}\text{-C}_7$	3.36	3.37	3.16	$\text{S}_{22}\text{-S}_6$	–	–	3.59
$\text{S}_{22}\text{-C}_8$	–	–	3.55				
(3) $\text{C}_{14}\text{-C}_{17}$	–	–	3.59	$\text{C}_{21}\text{-S}_7$	3.35	3.27	3.18
				$\text{S}_7\text{-S}_{22}$	–	–	3.63
				$\text{C}_8\text{-C}_{21}$	3.52	3.45	3.37
				$\text{C}_2\text{-S}_7$	–	–	3.57
				$\text{S}_7\text{-S}_7$	–	–	3.62
				$\text{S}_7\text{-N}_{20}$	–	–	3.35

(2): $1/2\text{-x}; 1/2\text{+y}; z; \bar{1} 0 0$

(5): $x; y; z; 0 1 0$

(1): $1/2\text{+x}; 1/2\text{-y}; \text{-z}; \bar{1} 1 1$

(4): $1/2\text{-x}; 1/2\text{+y}; z$

(6): $1/2\text{+x}; 1/2\text{+y}; 1/2\text{-z}; \bar{1} 0 0$

(3): $\text{-x}; \text{-y}; \text{-z}; \bar{1} 0 0$

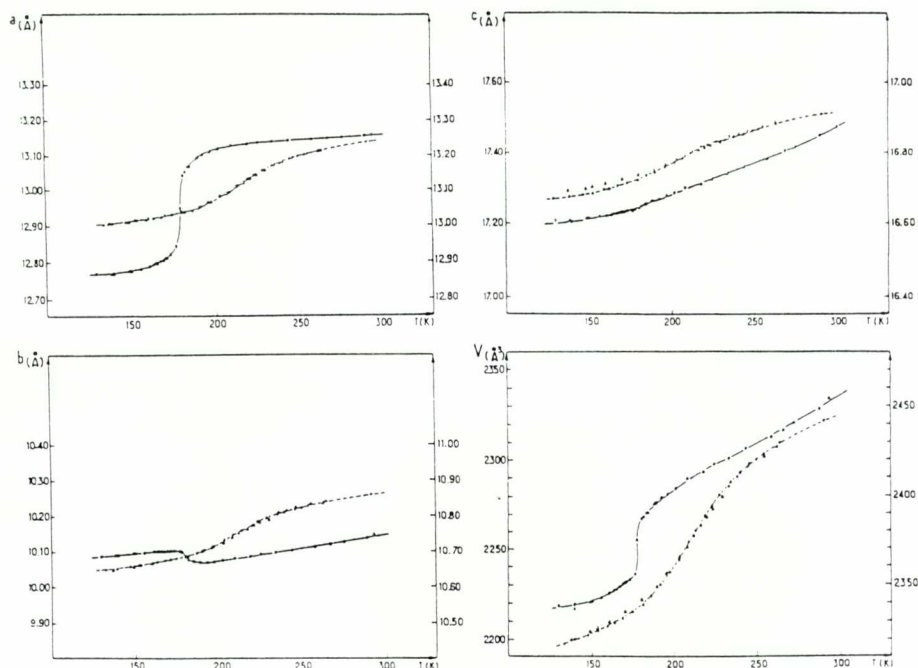


Fig. 4. Temperature dependence of the lattice parameters of $\text{Fe}(\text{Phen})_2(\text{NCS})_2$ (full line) and $\text{Fe}(\text{Btz})_2(\text{NCS})_2$ (dashed line). Related scales to $\text{Fe}(\text{Phen})_2(\text{NCS})_2$ and $\text{Fe}(\text{Btz})_2(\text{NCS})_2$ data are reported on the left and on the right side respectively (opened characters: cooling; dark characters: heating).

b) Isothermal compressibility data:

In figure 6, we have reported the relative variations of lattice parameters as a function of pressure. Here again, one may notice a strong difference of behavior between $\text{Fe}(\text{Phen})_2(\text{NCS})_2$ and $\text{Fe}(\text{Btz})_2(\text{NCS})_2$: the former exhibits an important change of derivative in the parameter **a**, while the latter presents a quasi-linear variation of **a** with pressure; moreover, the lattice parameter **c** decreases much faster in the case of $\text{Fe}(\text{Phen})_2(\text{NCS})_2$ than in the case of $\text{Fe}(\text{Btz})_2(\text{NCS})_2$.

Concerning $\text{Fe}(\text{Phen})_2(\text{NCS})_2$, the change of derivative in the parameter **a** recalls the anomaly observed on the same parameter as a function of temperature. It occurs at a pressure value of $\cong 0.60\text{GPa}$ and, despite the strong variation of the parameter **c** as a function of pressure, is still detectable on the volume variation. In figure 5-c, we have plotted the unit cell volume of $\text{Fe}(\text{Phen})_2(\text{NCS})_2$ along with the magnetic susceptibility observed at room temperature as a function of pressure, deduced from Usha et al. (1985) results: here again a strong correlation between unit cell volume and

magnetic susceptibility is clearly evidenced. Our critical pressure value $P_c \cong 0.6\text{GPa}$ (change of derivative on the unit cell volume) is very close to the one deduced from Usha et al. (1985) data, $P_c \cong 0.6\text{GPa}$, and agrees also quite well with recent EXAFS experiments (C. Roux, J. Zarembowitch, R. Itie,

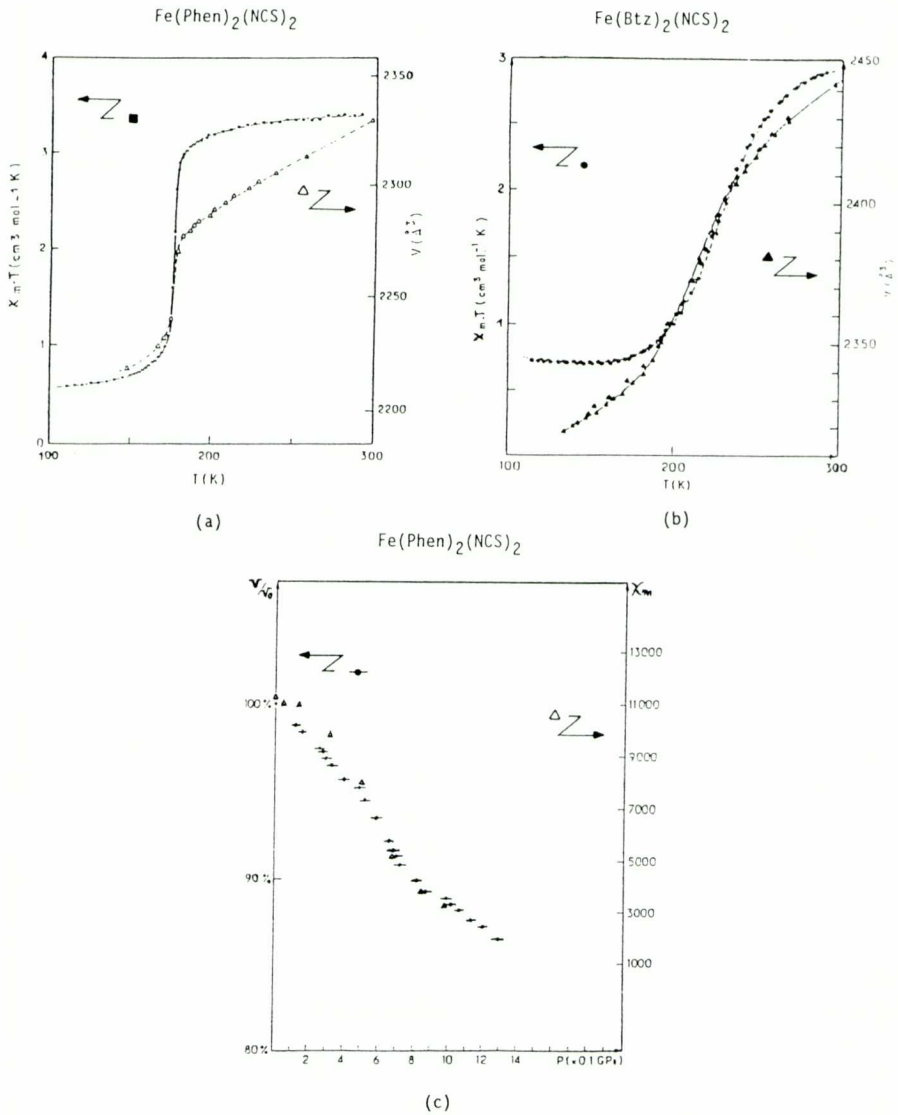


Fig. 5. Comparison of $X_m \cdot T$ and V variations as a function of temperature for a) $\text{Fe}(\text{Phen})_2(\text{NCS})_2$ and b) $\text{Fe}(\text{Btz})_2(\text{NCS})_2$, as a function of pressure for c) $\text{Fe}(\text{Phen})_2(\text{NCS})_2$.

A. Polian, E. Dartyge, A. Fontaine, H. Tolentino, M. Verdager (1990)) for which P_c is estimated at 0.6-0.7 GPa. These most recent coherent results question the data obtained earlier by J. Pebler (1982) and D.M. Adams, G.J. Long, A.D. Williams (1982). It is not clear to us whether the discre-

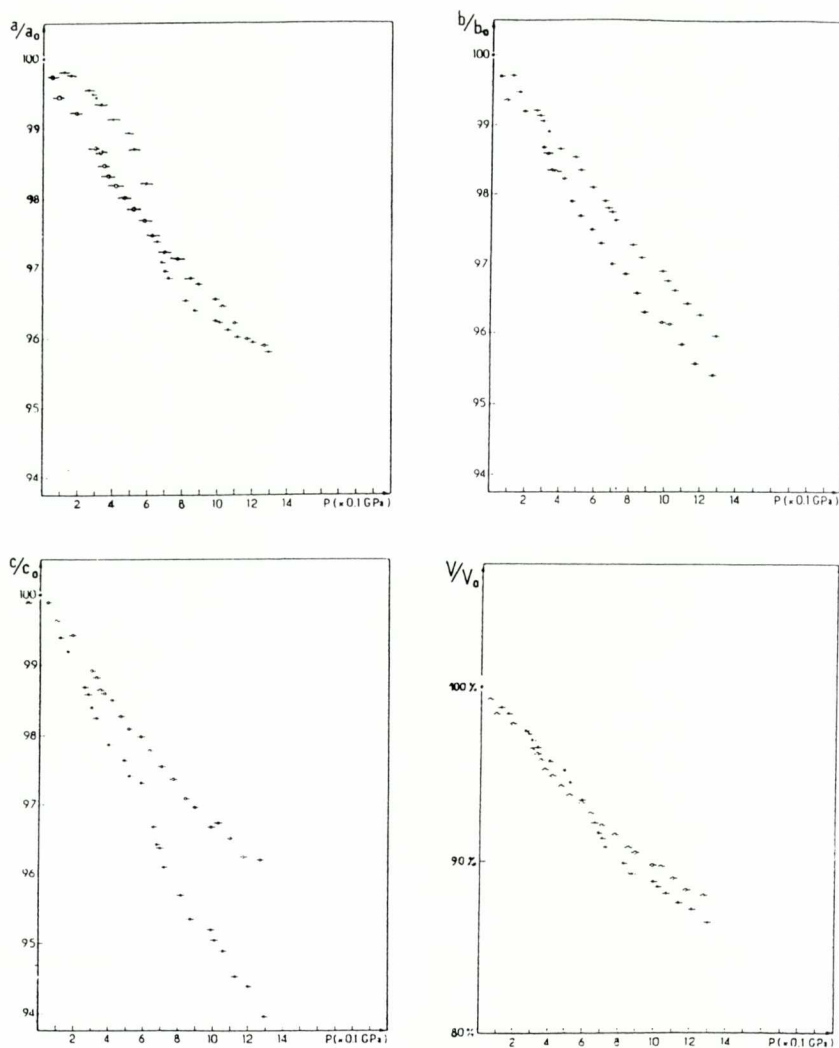


Fig. 6., Unit cell parameters evolution versus pressure of $\text{Fe(Phen)}_2(\text{NCS})_2$ and $\text{Fe(Btz)}_2(\text{NCS})_2$.

- $\text{Fe(Phen)}_2(\text{NCS})_2$
- $\text{Fe(Btz)}_2(\text{NCS})_2$

pancies observed are related to the sample preparation method or to the high pressure experimental conditions used by the authors.

Concerning $\text{Fe}(\text{Btz})_2(\text{NCS})_2$, the lack of physical data as a function of pressure does not allow us to be as much certain about its critical pressure. Nonetheless, one may notice a change of slope in the linear variations of lattice parameters, which occurs at a pressure $\cong 0.4\text{GPa}$. One is tempted to assert that the spin conversion, which is more gradual than in the case of $\text{Fe}(\text{Phen})_2(\text{NCS})_2$, begins at low pressure ($P = 0.0\text{GPa}$) and is complete at a pressure of 0.4GPa .

c) Volume variation at the spin transition:

These data allow us to discuss the unit cell volume variation at the spin transition temperature for each compound. The structures determined at 130K (1.0GPa) correspond to a volume contraction of 119\AA^3 (269\AA^3) and 124\AA^3 (251\AA^3) for $\text{Fe}(\text{Phen})_2(\text{NCS})_2$ and $\text{Fe}(\text{Btz})_2(\text{NCS})_2$, respectively. The volume variation due to the sole contraction of the molecular complex at the spin transition temperature, can be deduced by subtracting the contributions of the pure LS (LT) and HS (HT) thermal expansions. One finds:

$$\Delta V(T_c) \cong 44 \text{\AA}^3 \text{ for } \text{Fe}(\text{Phen})_2(\text{NCS})_2 \text{ and}$$

$\Delta V(T_c) \cong 47 \text{\AA}^3 \text{ for } \text{Fe}(\text{Btz})_2(\text{NCS})_2$ for 4 molecules of complex per unit cell.

Similar calculations as a function of pressure yield the following values:

$$\Delta V(P_c \cong 0.6\text{GPa}) \cong 56 \text{\AA}^3 \text{ for } \text{Fe}(\text{Phen})_2(\text{NCS})_2 \text{ and}$$

$$\Delta V(P_c \cong 0.0\text{GPa}) \cong 52 \text{\AA}^3 \text{ for } \text{Fe}(\text{Btz})_2(\text{NCS})_2$$

Whatever the applied constraint, the ΔV values agree very well with the Fe-N (ligand) bond lengths shortenings: similar metal-ligand bonds shortenings lead to similar unit-cell volume contractions at the spin transition. It is clear that ΔV cannot be a relevant parameter for differentiating a sharp transition compound from a gradual-transition one.

d) Volume expansion, Bulk modulus and lattice anisotropy:

From lattice parameter variations, one may deduce the values of linear and volume thermal expansion and compressibility coefficients; these are given in table 4 and 5 for high- and low-temperature regions, high- and low pressure regions.

α – Thermal expansion coefficients: (table 4)

Both compounds have very close volume coefficients, which decrease slightly at low temperature. At high temperature, however, $\text{Fe}(\text{Phen})_2(\text{NCS})_2$ exhibits very anisotropic linear coefficients: α_a is 4 times

smaller than α_b and 6 times smaller than α_c . In the LS phase, this anisotropy is much lower.

As for $\text{Fe}(\text{Btz})_2(\text{NCS})_2$, linear coefficients do not reveal a noticeable anisotropy, since they are found to have close values.

Table 4. Linear and volume thermal expansion coefficients

	Phen	Btz
T=300K	(10^{-4}K^{-1})	(10^{-4}K^{-1})
α_a	0.20	0.80
α_b	0.76	0.74
α_c	1.12	0.72
α_v	2.19	2.26
T=140K		
α_a	0.720	0.47
α_b	0.45	0.65
α_c	0.70	0.58
α_v	1.86	1.70

β – Compressibility coefficients: (table 5)

At low pressure, one finds again a large anisotropy in the linear coefficients of $\text{Fe}(\text{Phen})_2(\text{NCS})_2$. Concerning $\text{Fe}(\text{Btz})_2(\text{NCS})_2$, one does not notice any anisotropy both at low and high pressure. It is important to note that in the low-pressure range in which compressibility coefficients are evaluated ($0.0 < P < 0.3\text{GPa}$), the contribution of HS to LS conversion to the unit cell contraction is expected to be much greater in the case of

Table 5. Linear and volume compressibility coefficients for $\text{Fe}(\text{Phen})_2(\text{NCS})_2$ and $\text{Fe}(\text{Btz})_2(\text{NCS})_2$ at two different pressures: 0.0GPa and 1.0GPa.

	Phen	Btz
P=0.0GPa	(10^{-1}GPa^{-1})	(10^{-1}GPa^{-1})
k_a	-0.21	-0.41
k_b	-0.33	-0.43
k_c	-0.53	-0.37
K_v	-1.07	-1.21
P=1.0GPa		
k_a	-0.16	-0.28
k_b	-0.28	-0.33
k_c	-0.38	-0.28
K_v	-0.82	-0.89

$\text{Fe}(\text{Btz})_2(\text{NCS})_2$ than in the case of $\text{Fe}(\text{Phen})_2(\text{NCS})_2$. However the anisotropy of $\text{Fe}(\text{Phen})_2(\text{NCS})_2$ with respect to pressure, is still observed at high pressure where it has been clearly established that both compounds have reached their LS state.

Qualitatively, there is a certain correlation between such a lattice anisotropy and the spatial distribution of intermolecular contacts (table 3): in the case of $\text{Fe}(\text{Phen})_2(\text{NCS})_2$, the lowest values of linear compressibility, i.e. the stiffest lattice directions, concern **a** and **b** directions; these are intra-sheet directions in which one observes many intermolecular contacts (table 3); k_c , on the contrary, is greater than K_a and k_b , and corresponds to inter-sheet directions for which much less contacts are observed. In the case of $\text{Fe}(\text{Btz})_2(\text{NCS})_2$, the proportion of inter- and intra-sheet contacts is almost reversed, and one observes a quasi isotropic lattice with respect to temperature or pressure.

Spiering H., Meisner, E., Koppen H., Müller E.W., Gütlich P., (1982) have proposed a model based on elasticity theory: in such a model, the sharpness of the spin transition is related to the stiffness of the crystal lattice. P. Adler et al. (1987) have used this model for interpreting the experimental data obtained on two compounds: $[\text{Fe}(\text{2-pics})_3]\text{Cl}_2 \cdot \text{MeOH}$ (gradual-transition compound) and $[\text{Fe}(\text{2-pics})_3]\text{Cl}_2 \cdot \text{EtOH}$ (less gradual-transition compound). These authors suggest the ratio of their respective bulk moduli $K(\text{MeOH})/K(\text{EtOH})$ to be $\cong 1.3$ so as to fit with the model. Experimental values deduced from Lamb-Mössbauer factors lead to a ratio of $\cong 1.10$. P. Adler et al. (1987) conclude that a better agreement with the model should be obtained by taking into account the anisotropy of the lattice they have observed on linear thermal expansion coefficients. In our case the bulk moduli ratio is $K(\text{Btz})/K(\text{Phen}) = 1.10$. We suggest then that anisotropy of the lattice we have observed both as a function of temperature or pressure should also be taken into account.

V. CONCLUSION

We have carried out a comparative structural investigation on two iron (II) octahedral complexes which present different spin transition characteristics:

$\text{Fe}(\text{Phen})_2(\text{NCS})_2$ exhibits a sharp HS to LS conversion at $T_c = 176\text{K}$.

$\text{Fe}(\text{Btz})_2(\text{NCS})_2$ exhibits a gradual HS to LS conversion centered about $T_c = 225\text{K}$.

Both complexes crystallize in the same space group $Pbcn$ and present very similar crystal packing. Structure determinations at room temperature, low

temperature ($T = 130\text{K}$) or high pressure ($P = 1.0\text{GPa}$) have shown that both complexes:

- remain in the same space group $Pbcn$.
- exhibit very similar distortions of their $[\text{Fe-N}_6]$ octahedron in the HS phase, and similar Fe-N(ligand) bond length shortening and bond angle variation when going from the HS to the LS phase, no matter the applied constraint (T or P).

Thermal expansion and compressibility data have shown that:

- the crystal lattice is strongly correlated to the HS to LS conversion regime as a function of the applied constraint:

- there is a sharp drop of the unit cell volume at $T_c = 176\text{K}$ for $\text{Fe(Phen)}_2(\text{NCS})_2$

- a gradual variation with a change of slope at $T_c = 215\text{K}$ is observed for $\text{Fe(Btz)}_2(\text{NCS})_2$

- the compressibility data allow one to define a transition pressure $P_c \cong 0.6\text{GPa}$ for $\text{Fe(Phen)}_2(\text{NCS})_2$, in agreement with some of the previous results, and suggest that spin conversion is much more gradual in the case of $\text{Fe(Btz)}_2(\text{NCS})_2$ and takes place between 0.0 and 0.4GPa.

- the volume variation ΔV at the spin transition is shown to depend neither on the applied constraint nor on the compound considered.

- in their pure HS or LS phases, both complexes have similar volume thermal expansion coefficients and bulk moduli, but $\text{Fe(Phen)}_2(\text{NCS})_2$ exhibits a marked anisotropy which is not observed in the case of $\text{Fe(Btz)}_2(\text{NCS})_2$.

It is then clear that, contrary to what has been suggested so far,

- sharp transitions do not necessarily imply a change of space group symmetry.

- the volume variation ΔV of the molecular units between their HS and LS configuration cannot explain the sharpness of the spin transition.

Our compressibility data do not contradict the model proposed by Spiering et al. (1982), and support the conclusions given by Adler et al. (1987) when they suggest that lattice anisotropy has to be taken into account.

SUMMARY

$\text{Fe(Phen)}_2(\text{NCS})_2$ is known to exhibit a sharp High Spin to Low Spin transition at a temperature $T_c \sim 176\text{K}$ while $\text{Fe(Btz)}_2(\text{NCS})_2$ presents the same spin conversion on a wide temperature range centered about $T_c \sim 215\text{K}$. Room temperature and ambient pressure, low temperature ($\sim 130\text{K}$) or high pressure ($\sim 1.0\text{GPa}$) X-ray structures as well as lattice parameters evolution allow to discuss several structural parameters such as change of space group symmetry, intramolecular modifications, volume variation at the transition, lattice anisotropy which have been suggested before to play a relevant part in the difference of magnetic behavior of such compounds. Finally, our high pres-

sure data allow to define the transition pressure $P_c \cong 0.6$ GPa for $\text{Fe}(\text{Phen})_2(\text{NCS})_2$ in agreement with some previous results, and show that spin convention occurs gradually between ambient pressure and 0.4 GPa in the case of $\text{Fe}(\text{Btz})_2(\text{NCS})_2$.

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