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Soft X-ray induced excited spin state trapping and soft X-ray photochemistry at the iron $L_{2,3}$ edge in $[Fe(phen)_2(NCS)_2]$ and $[Fe(phen)_2(NCSe)_2]$ (phen = 1,10-phenanthroline)‡

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The first observation of soft X-ray induced excited spin state trapping has been made for $[Fe(phen)_2(NCS)_2]$ and $[Fe(phen)_2(NCSe)_2]$ (phen = 1,10-phenanthroline) at *ca.* 45 K, analogous to light induced excited spin state trapping but at much higher energy. Soft X-ray photochemistry has also been observed in the high- and low-spin states of $[Fe(phen)_2(NCS)_2]$ and $[Fe(phen)_2(NCSe)_2]$, resulting in the formation of a thermally irreversible low-spin state. The rate of formation of this low-spin state is greater from low than from high spin, and is also greater in $[Fe(phen)_2(NCSe)_2]$ than in $[Fe(phen)_2(NCS)_2]$.

Among the transition-metal complexes which undergo the phenomenon of spin crossover, those involving Fe^{II} and N-donor ligands are probably the most studied.[1] Complexes of bidentate N-donor ligands such as 1,10-phenanthroline (phen) are often regarded as prototypical. For $[Fe(phen)_2(NCS)_2]$ the abrupt spin crossover ($^5T_2$ high spin to $^1A_1$ low spin)§ near 175 K has been investigated by a variety of means, including magnetic susceptibility[2–9] and calorimetric[7,10,11] measurements, ^{57}Fe Mössbauer,[3,4,6,7,12,13] IR,[4,10,13–16] UV/VIS,[4,9] NMR,[12,17] ESR,[18] X-ray photoelectron (XPS)[19,20] and muon[21] spectroscopic techniques. In addition to X-ray powder diffraction,[2–5,7] single-crystal X-ray diffraction has been used to study the structural changes associated with temperature-[22] or pressure-[23] induced spin transitions. Iron K-edge X-ray absorption fine structure spectroscopy (XAFS) has been used to monitor the structural modifications both on cooling[24–27] and on increasing pressure.[28] Iron $L_{2,3}$-edge XAFS has been utilised to observe the changes in the electronic structure of the iron above and below the transition temperature.[26,29,30] Whilst $[Fe(phen)_2(NCSe)_2]$ has received less attention than $[Fe(phen)_2(NCS)_2]$, the spin transition at *ca.* 235 K has been studied by magnetic susceptibility[2,3] and calorimetric[10] measurements, as well as ^{57}Fe Mössbauer,[3,4] IR,[3,4,10,15] UV/VIS[3,4] and NMR[31] spectroscopies. Although there have been several powder X-ray diffraction reports[2–4] there appear to be no single-crystal X-ray or XAFS structural determinations in the literature.

At temperatures well below the transition temperature, a further aspect of spin-crossover behaviour is apparent. This concerns the possibility of conversion of the low-spin state, LS, into a metastable high-spin state, HS*, by irradiation of the electronic absorption bands with visible or ultraviolet light. This process is usually known as *light induced excited spin state trapping* (LIESST),[32] although we have also previously used the term *susceptibility of transient electron paramagnetic states* (STEPS) to describe this effect.[33] The population of metastable high-spin states during Mössbauer emission spectroscopy has also been reported at low temperature and is known as *nuclear decay induced excited spin state trapping* (NIESST).[34] In the case of $[Fe(phen)_2(NCS)_2]$, UV/VIS radiation has been shown by ^{57}Fe Mössbauer[35] and IR[36,37] spectroscopy to induce LIESST, and IR spectroscopy has been used to demonstrate the LIESST effect in $[Fe(phen)_2(NCSe)_2]$.[38] Some FeN_6 (where N_6 represents a compound with six N-donor atoms) spin-crossover complexes have been suggested as potential data-storage and display devices[39] or as temperature sensors and thermal switches,[40] therefore it is important to know the nature of all stimuli that can produce spin-state transitions. We present here an entirely new way to change spin states using soft X-ray irradiation at the iron $L_{2,3}$ edge *via soft X-ray induced excited spin state trapping* (SOXIESST).

The $L_{2,3}$-edge X-ray absorption spectra result from the excitation of 2p electrons, and in the case of 3d transition metals the spectra are dominated by intense, dipole-allowed $2p^63d^n \longrightarrow 2p^53d^{n+1}$ transitions[41] which have about a quarter of the natural linewidths of the corresponding K-edge spectra;[42] whilst $2p \longrightarrow 4s$ transitions are allowed, the transition probabilities are much smaller. The L_3 ($2p_{3/2}$) and L_2 ($2p_{1/2}$) components are split (*ca.* 12 eV) by spin–orbit coupling of the core hole, and as there is a strong interaction between the 2p core hole and the valence 3d orbitals the structure on the $L_{2,3}$ absorptions is very sensitive to oxidation state, spin state, ligand field and local environment, as well as being element specific.[41] In general the structure on the L_2 feature is broadened due to interaction with the L_3 continuum states.[41] The technique has found use in the study of minerals,[43] metalloproteins and their models,[44] and co-ordination compounds.[45,46] The application to solid-state physics and chemistry has recently been reviewed.[47]

Experimental

Compound preparation

The sharpness and reversibility of the spin transitions in $[Fe(phen)_2(NCS)_2]$ and $[Fe(phen)_2(NCSe)_2]$ are closely related to the methods of preparation and purification.[1] As previous workers[7,29] have recommended the removal of one phen ligand from $[Fe(phen)_3][NCS]_2$ or $[Fe(phen)_3][NCSe]_2$ using Soxhlet extraction, this method was employed in these studies. The complexes $[Fe(phen)_3][NCS]_2$ and $[Fe(phen)_3][NCSe]_2$ were prepared from the addition of a saturated aqueous solution of KSCN or KSeCN to an aqueous solution of $(NH_4)_2$-

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‡ *Non-SI units employed*: eV ≈ 1.60×10^{-19} J, bar = 10^5 Pa.

§ In keeping with previous studies the O_h nomenclature is used.

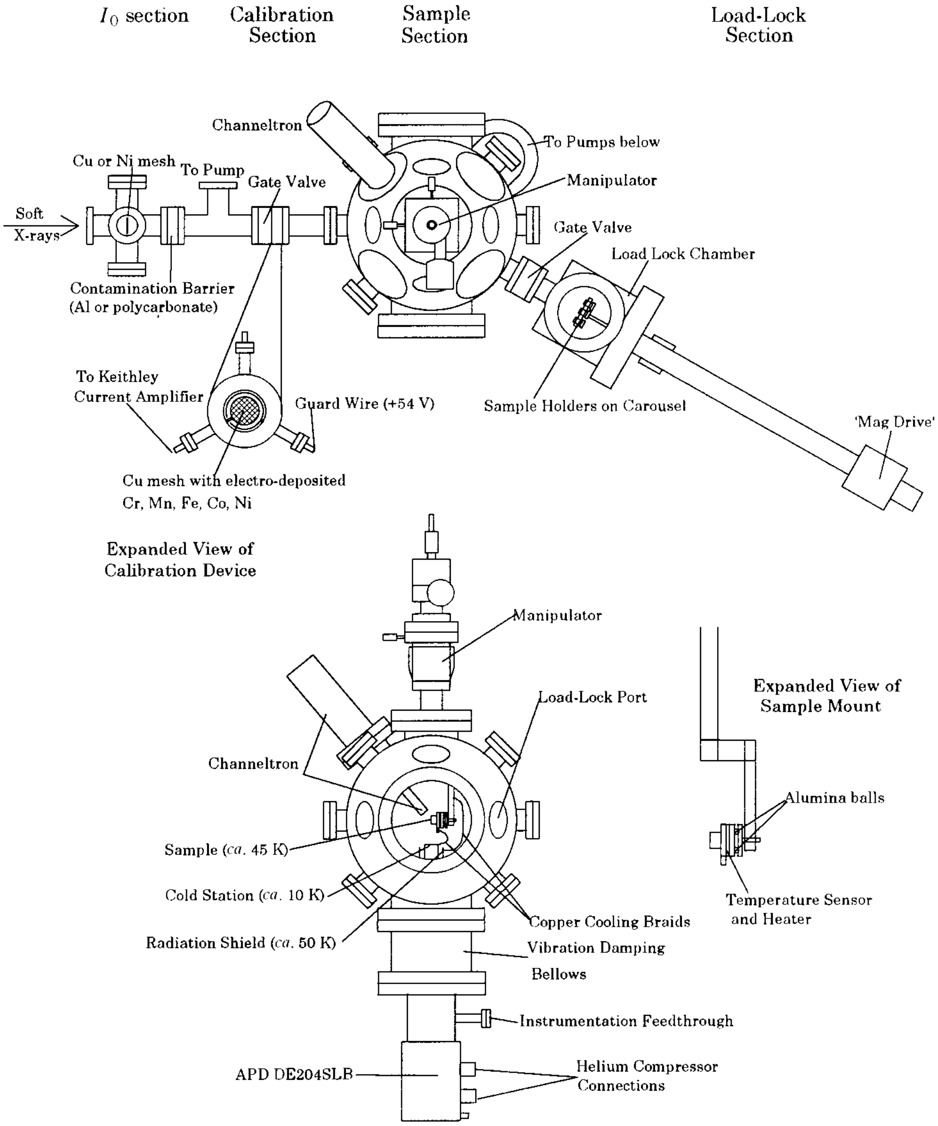

Fig. 1 Apparatus used for variable-temperature 3d $L_{2,3}$-edge XAFS experiments

$Fe(SO_4)_2{\cdot}6H_2O$ and 1,10-phenanthroline in stoichiometric amounts. The blood red precipitates were recrystallised from hot water and the chemical purity checked by elemental analysis (C, H, N) before loading into the Soxhlet thimbles. Purple powders were obtained from the Soxhlet thimble after 3 weeks extraction with acetone under argon, whereas when pyridine was used as the extraction solvent black-purple crystals were recovered slowly from the receiver over a period of 2–3 d; all samples were checked for chemical purity by elemental analysis (C, H, N). The completeness and reversibility of the spin transitions in $[Fe(phen)_2(NCS)_2]$ and $[Fe(phen)_2(NCSe)_2]$, as well as evidence of an optical LIESST effect, were checked by variable temperature (VT) IR (300–9 K) measurements.[36–38] As has been observed previously,[36] the He–Ne laser in the FTIR spectrometer (Bruker IFS66) was found to be capable of inducing LIESST, but this could be prevented by use of a black Polythene film. In our hands the highest-quality samples (in terms of spin-crossover behaviour) were obtained for acetone-extracted $[Fe(phen)_2(NCS)_2]$ and pyridine-extracted $[Fe(phen)_2(NCSe)_2]$, therefore these were used for the XAFS experiments.

Soft X-ray absorption measurements

The samples for iron $L_{2,3}$-edge XAFS experiments were prepared on nickel stubs or Al-covered nickel stubs either as powders on carbon tape (Agar Products, Cambridge, UK) or as acetone–graphite (Goodfellows, Cambridge, UK) slurries allowed to evaporate to dryness. No sample-preparation dependence was observed. Soft X-ray absorption spectra were measured on station 5U.1[48] of the undulator beamline at the Daresbury Laboratory Synchrotron Radiation Source (SRS) operating at 2 GeV with circulating currents in the range 150–260 mA and lifetimes of 18–24 h. The undulator (1 m long, ten-period, variable-gap, $SmCo_5$ magnet with a remnant magnetic field of 0.9 T) was operated at minimum gap (42 mm), giving a deflection parameter $K = 3.2$, with the fundamental at 62 eV, and a quasi-continuous output of harmonic radiation up to 2 keV. The beamline optical components consist of an entrance slitless SX700 monochromator (Pt-coated plane pre-mirror, Pt-coated 1200 lines mm^{-1} diffraction grating, Pt-coated spherical focusing mirror), a series of zero-order baffles, a vertically defining exit slit and a Pt-coated ellipsoidal post-focusing mirror. The 50 μm exit slit gave an estimated total resolution of 0.35 eV at 700 eV, and the focusing mirrors gave a beam size of *ca.* 1.5 × 0.5 mm (vertical × horizontal) at the sample. The photon flux at the sample is estimated to be *ca.* 10^{11} photons s^{-1}.

The apparatus used for the variable-temperature $L_{2,3}$-edge XAFS experiments is shown in Fig. 1 and was connected to the main beamline at the I_0 (high transmission copper or nickel mesh) section. The main ultra-high vacuum (UHV) sample chamber, which is based on a 320 mm sphere, with ports for the manipulator (equipped with x, y, z travel and φ and θ rotation), cryostat, load-lock, gauges and a residual gas analyser (RGA), is pumped by a turbo-drag pump, backed by a diaphragm pump. The load-lock consists of a small chamber isolated from the main chamber by a gate valve and pumped by a turbo-drag pump, backed by a diaphragm pump. The samples on nickel stubs or Al-covered nickel stubs are mounted on a carousel accessed by a Viton-sealed door (if necessary a glove-bag is used on the load-lock port for the transfer of air-sensitive materials) and the transfer to the manipulator sample stage was accomplished with a Surface Interface magnetically coupled sample transporter ('mag drive'). The cooling was provided by an APD Cryogenics DE204SLB (UHV) closed-cycle cryostat cold stage connected by OFHC copper braids to the sample stage, with the cryostat radiation shield linked to the manipulator arm to reduce thermal losses. Temperature measurement and control was carried out by a Scientific Instruments 9650 controller with a diode temperature sensor and Carel Components Kapton encapsulated heating element. The base temperature at the sample was *ca.* 45 K, and we are currently developing a design incorporating better radiation shielding to improve the base temperature performance. Total electron yield (TEY) detection was used both in the drain current and channeltron mode, giving an estimated sampling depth of 30–50 Å. The only significant difference between the two detection methods was that the drain current gave significantly higher quality data in terms of counting statistics, but use of the channeltron was preferred so that the diode temperature sensor could be directly attached to the sample stage. All viewports were carefully covered by several layers of aluminium foil to exclude external light, and the pressure (*ca.* 2×10^{-8} mbar) was measured by a cold-cathode (Penning) gauge. To prevent contamination of the beamline, and to exclude any scattered visible light from the SRS reaching the sample, a thin aluminium window (1500 Å) was placed between the UHV chamber and the beamline. On occasions when a Lexan window (1000 Å polycarbonate with 300 Å carbon overcoat) had to be used no difference in behaviour was observed. The spectra were normalised with respect to beam decay using I/I_0 and the background was subtracted using a multiline fit. Calibration was achieved by the simultaneous collection of a spectrum of electrodeposited Fe on a high-transmission copper mesh mounted in a CF70 flange as indicated in Fig. 1. This mesh has also been treated with Cr, Mn, Co and Ni to provide a very versatile *in-situ* calibration device. No evidence of cross-talk or spectral interference between the calibration and signal channels were observed. The calibration mesh was referenced using the Fe_2O_3 L_3 maximum at 708.5 eV.[29] We note that other workers have used the Fe_2O_3 L_3 maxima at 709.1 eV as a calibrant;[44h] the value of 708.5 eV for Fe_2O_3 was used to maintain consistency with the earlier work on $[Fe(phen)_2(NCS)_2]$.[29] The compound $K_4[Fe(CN)_6]$ has also been used as a calibrant.[44f]

Results

$[Fe(phen)_2(NCS)_2]$

Previous iron $L_{2,3}$-edge measurements[26,29,30] at 300 and 77 K have established the spectroscopic fingerprints of the high-spin, HS, and low-spin, LS, states in $[Fe(phen)_2(NCS)_2]$. Under our experimental conditions the spectra obtained at 300 [Fig. 2(*a*)] and 80 K [Fig. 2(*b*)] were essentially identical to those observed previously[26,29,30] and therefore can be considered to be characteristic HS and LS spectra, respectively. The shift in energy, change in structure of the principal spectral features and the different branching ratio between the HS and LS states have previously been simulated using multiplet theory.[26] On reducing the temperature further to *ca.* 51 K [Fig. 2(*c*)], there was clear evidence of the presence of a high-spin spectrum, implying the formation of a high-spin state, with some low-spin fraction present. On warming the sample to 80 K again [Fig. 2(*d*)] a low-spin spectrum was obtained, implying complete conversion back into the LS state. When the sample was returned to room temperature [Fig. 2(*e*)] a high-spin spectrum was observed, with a high-energy shoulder on the L_3 feature, indicative of a proportion of low-spin remaining. All of these spectra were recorded with the soft X-ray beam in the same sample position. For a sample that had been thermally cycled and irradiated at the same sample position at 300, 80 and 300 K it was only possible to obtain a full high-spin spectrum back at room temperature if a fresh non-irradiated sample position was then used. This clearly implies that irradiation in the LS state results in the formation of a new, stable, thermally irreversible low-spin state, LS′, that cannot be converted back into the HS state. The previous work[26,29,30] had shown that the spin transition was reversible, but it is not clear whether the same sample or sample position had been used for all the measurements.

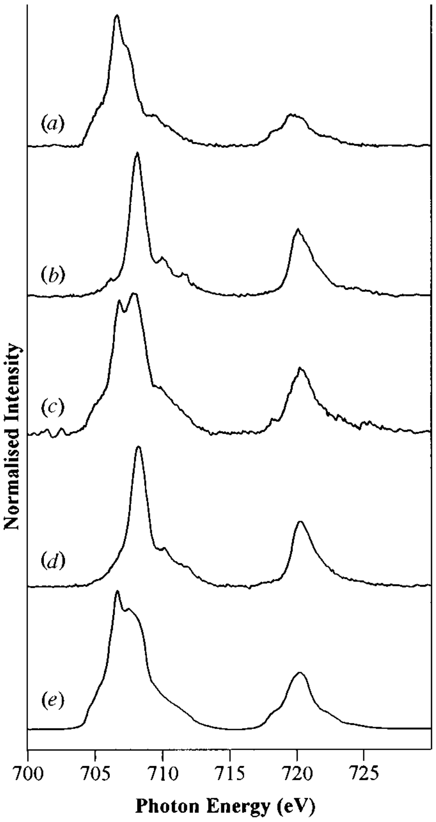

Fig. 2 Iron $L_{2,3}$-edge spectra of $[Fe(phen)_2(NCS)_2]$: (*a*) 300 K initial spectrum; (*b*) 80 K; (*c*) 51 K; (*d*) 80 K; (*e*) 300 K final spectrum. All spectra recorded in same sample position

Having identified that irradiation in the LS state results in *soft X-ray photochemistry* (SOXPC) causing some residual LS′ fraction to remain when the sample was returned to the room-temperature HS state, we investigated whether this had been the case on going from 80 to 51 K. A sample previously unexposed to soft X-rays was cooled to *ca.* 45 K,¶ and the resultant spectrum [Fig. 3(*a*)] was practically identical to that obtained from the initial 300 K HS state [Fig. 2(*a*)]. Therefore at 45 K, the sample was present in almost entirely high-spin form, having passed through the LS state on cooling. These observations clearly indicate that SOXIESST has occurred, with the formation of a metastable, high-spin state, HS*, on soft X-ray irradiation at low temperature. This is analogous to the optical LIESST effect,[35] where a temperature of less than 55 K was essential to stabilise the HS* state. Conversion into this soft X-ray-induced HS* state at low temperature was complete by the time the L_3 feature had been scanned (*ca.* 5 min). Raising the temperature above 60–70 K afforded very rapid relaxation back to the characteristic low-spin spectrum at 80 K [Fig. 3(*b*)],

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¶ A small improvement in the base temperature was achieved after a minor modification of the sample stage.

indicating the reversibility of the SOXIESST process. When the sample was recooled to *ca.* 45 K, incomplete conversion into the HS* state was observed [Fig. 3(*c*)], confirming the reversibility of the LS to HS* transition, and that irradiation in the LS state did indeed result in the formation of a residual low-spin fraction, LS′. Fig. 3(*d*) shows the result of summing the spectra in Fig. 3(*a*) and 3(*b*) in a 0.77 : 0.23 ratio, confirming that Fig. 3(*c*) was a mixture of HS* and LS′ components. The proportion of LS′ remaining at 45 K (and 300 K) after irradiation in the LS state increased with the number of cycles performed at the same sample position, and the SOXIESST process could be repeated until the supply of 'fresh' LS form was exhausted. Having identified that irradiation in the LS state resulted in photochemistry, the sensitivity of the 300 K HS state to soft X-ray exposure was examined, as little change had been noted during the two scans initially recorded. Over a period of 150 min (5 × 30 min spectra) there was a small but significant change in the spectra [Fig. 4(*a*)] which manifested itself as a broadening of the L_3 absorption band on the high-energy side, indicating the formation of a LS′ state. The changes at the L_2 feature were less marked, but were consistent with a small but gradual change to LS′. Deconvolution of the final spectrum implied a conversion of *ca.* 10% over a period of 150 min, compared to *ca.* 25% conversion after irradiation in the LS state at 80 K for 60 min. Successive spectra recorded in the LS or LS′ state showed no significant change with time.

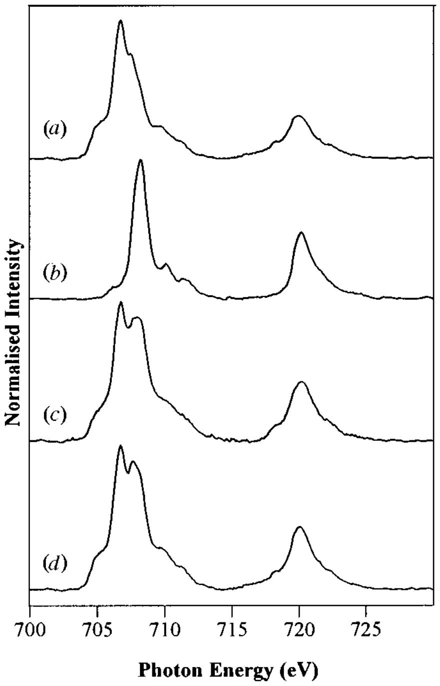


Fig. 3 Iron $L_{2,3}$-edge spectra of $[Fe(phen)_2(NCS)_2]$: (*a*) 45 K, previously non-irradiated sample; (*b*) 80 K; (*c*) recooled to 45 K; (*d*) sum of (*a*) and (*b*) in 0.77 : 0.23 ratio. All spectra recorded in same sample position

$[Fe(phen)_2(NCSe)_2]$

In the case of $[Fe(phen)_2(NCSe)_2]$ irradiation of the iron $L_{2,3}$ edge at 300 K resulted in a change from a high-spin spectrum to a spectrum containing a significant low-spin proportion over a period of 120 min (4 × 30 min spectra) [Fig. 4(*b*)], implying formation of an LS′ state. Deconvolution of the final spectrum implied a conversion of *ca.* 50% in 120 min compared to *ca.* 10% after 150 min for $[Fe(phen)_2(NCS)_2]$ at 300 K. On cooling the sample to 80 K there was no evidence of a change from LS′ to HS before the transition temperature at *ca.* 235 K, after which a characteristic low-spin spectrum was obtained, implying conversion of the remaining HS fraction into a LS state. On further cooling to 45 K a small proportion of high spin was observed, indicating that a SOXIESST process was occurring resulting in the formation of a metastable HS* state. When a previously non-irradiated sample was cooled to 45 K the spectrum showed an appreciable quantity of high-spin character, confirming that soft X-ray irradiation of $[Fe(phen)_2(NCSe)_2]$ at low temperature results in SOXIESST leading to a HS* state. The high-spin spectrum at 45 K then changed to one containing increasing amounts of LS′ over successive spectra, mirroring the behaviour of the HS state at 300 K, and again confirming the formation of an LS′ state. On warming to 80 K a characteristic low-spin spectrum was obtained, indicating the reversibility of the SOXIESST effect. On cooling the sample to 45 K again the resultant spectrum contained an increased proportion of the LS′ state. The SOXIESST behaviour is very similar to that observed for $[Fe(phen)_2(NCS)_2]$, but the rate of change to the irreversible LS′ state caused by SOXPC is much higher for $[Fe(phen)_2(NCSe)_2]$ than for $[Fe(phen)_2(NCS)_2]$ in the HS, HS* and LS states.

Discussion

It is clear from the above results that during soft X-ray irradiation at the iron $L_{2,3}$ edge of $[Fe(phen)_2(NCS)_2]$ and $[Fe(phen)_2(NCSe)_2]$ there is a competition between at least two photochemical processes, SOXIESST and SOXPC (see Scheme 1). For both of these, soft X-ray irradiation results in well defined (if not readily identifiable) species, rather than just a broad distribution of decomposition products, and SOXIESST is a much faster process than SOXPC.

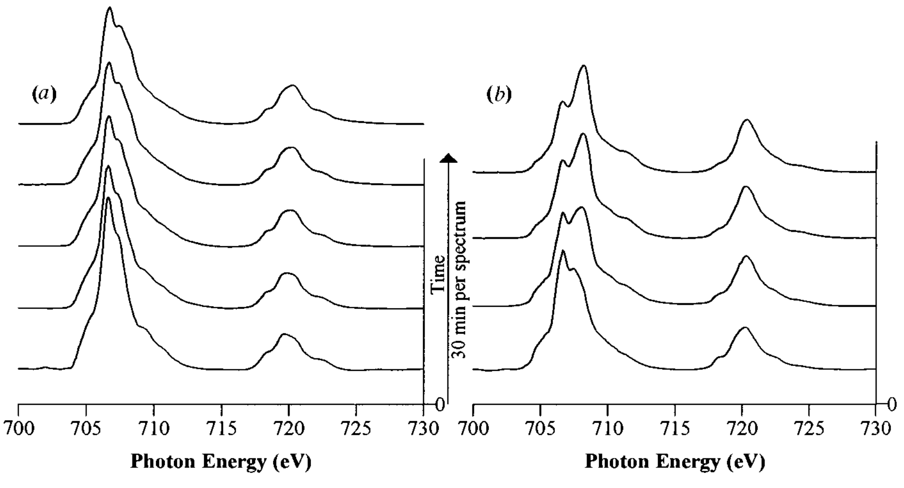
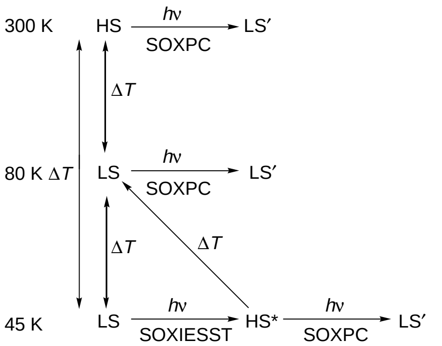


Fig. 4 Successive iron $L_{2,3}$-edge spectra at 300 K of (*a*) $[Fe(phen)_2(NCS)_2]$ and (*b*) $[Fe(phen)_2(NCSe)_2]$



Scheme 1 Summary of soft X-ray photochemical (*h*ν) and variable-temperature (Δ*T*) phenomena observed for [Fe(phen)$_2$(NCS)$_2$] and [Fe(phen)$_2$(NCSe)$_2$] at the iron $L_{2,3}$ edge. HS = High spin, LS = low spin, HS* = metastable high spin, LS′ = thermally irreversible stable low spin. Thermal spin transition temperatures are *ca.* 175 and *ca.* 235 K for [Fe(phen)$_2$(NCS)$_2$] and [Fe(phen)$_2$(NCSe)$_2$] respectively

The SOXIESST effect is analogous to the (optical) LIESST effect and behaves very similarly, but the significant energy difference (iron $L_{2,3}$ edge *ca.* 710 eV, UV/VIS, *ca.* 2–3 eV) between the two exciting sources should be noted. We can find no evidence from either the literature or our own IR studies for an optical effect analogous to the soft X-ray photochemistry (SOXPC). The reporting of soft X-ray-induced radiation damage during 3d $L_{2,3}$-edge experiments involving *molecular* compounds appears to be limited to the recent observation of photoreduction of Mn^{IV} in catalase, but not in any of the associated model compounds,[44g] and statements of the form 'To minimise radiation damage, the position of the X-ray beam on the sample was moved every few scans. No evidence was observed for changes over time in the beam'[44e] and that the experiments were carried out at low temperature, and 'no significant changes in absorption spectra . . . were observed in the temperature range 10–293 K'.[44f] Although there are reports in the literature describing radiation damage (usually photoreduction) observed during XPS experiments,[49] there was no reported evidence of any radiation damage in the previous XPS studies on [Fe(phen)$_2$(NCS)$_2$].[19,20] Whilst carrying out iron K-edge XAFS experiments on [Fe(phen)$_2$(NCS)$_2$] and [Fe(phen)$_2$(NCSe)$_2$] no change in the spectra was observed after irradiation for *ca.* 2.5 h at 300, 80 or 8 K, and in the case of [Fe(phen)$_2$(NCS)$_2$] no change at the sulfur K-edge was observed after 4 h of irradiation at 300 K. These observations clearly imply that SOXIESST and SOXPC arise from either the L-edge absorption process or exposure to soft X-rays, rather than general X-ray irradiation.

To date we have no direct evidence for a mechanism for either SOXIESST or SOXPC, but in both cases we postulate that the excited state(s) arising from the $2p^63d^6 \longrightarrow 2p^53d^7$ transitions decay(s) either with no chemical change *via* SOXIESST, or with some chemical change *via* SOXPC. We note that for the $2p^63d^6 \longrightarrow 2p^53d^7$ transitions in a low-spin configuration the promoted electron can only be accommodated within the e_g orbitals, whereas in a high-spin configuration the electron can go into either the t_{2g} or e_g orbitals. The different mechanisms by which these excited states decay may give rise to the difference in behaviour noted above. Mechanisms for LIESST involving intersystem crossing (ISC) have been proposed previously[32] and it is believed that they are the same in NIESST,[34] therefore similar processes may be at work in SOXIESST. Although the spectral features associated with the LS and LS′ states are very similar, implying that the electronic structure, and hence the local geometric structure at the iron centre, are very similar, the complex must have changed chemically during the SOXPC because the HS or HS* state cannot be accessed either thermally or photochemically from the LS′ state. The fact that [Fe(phen)$_2$(NCSe)$_2$] is more susceptible to SOXPC than is [Fe(phen)$_2$(NCS)$_2$] may imply that the potentially redox active sulfur and selenium sites are involved in the SOXPC process. Presumably the greater rate of change from LS to LS′, as compared to HS (or HS*) to LS′, is due to the significant difference in Fe–N (phen) (*ca.* 0.20 Å) and Fe–N (NCS) (*ca.* 0.1 Å) bond lengths[22] between the molecules in the two spin states.

Conclusion

We have shown that soft X-ray irradiation at the iron $L_{2,3}$ edge of [Fe(phen)$_2$(NCS)$_2$] and [Fe(phen)$_2$(NCSe)$_2$] at *ca.* 45 K results in SOXIESST from an LS to a metastable HS* state, analogous to that observed using visible or ultraviolet light (LIESST). In addition, irradiation of [Fe(phen)$_2$(NCS)$_2$] and [Fe(phen)$_2$(NCSe)$_2$] in either of the HS, HS* or LS states results in the formation of a stable, thermally irreversible low-spin, LS′ state *via* SOXPC. Whilst the HS into LS′ conversion is apparent in the iron $L_{2,3}$-edge spectra, the LS to LS′ conversion is observed only because this new state is unable to undergo either thermally or photochemically induced spin transitions. The rate of formation of the LS′ state is greater from the LS state than from HS and HS* states, and is also greater in [Fe(phen)$_2$(NCSe)$_2$] than in [Fe(phen)$_2$(NCS)$_2$]. In both cases the photoproducts appear to be well defined species. These soft X-ray photochemical (*h*ν) and variable-temperature (Δ*T*) phenomena are summarised in Scheme 1.

We have also clearly shown that $L_{2,3}$-edge XAFS is a powerful fingerprint of electronic structure at 3d-transition-metal centres, and are continuing our studies of these and other systems to increase the understanding of soft X-ray photochemistry and photophysics. It is clear from these experiments that the phenomenon of soft X-ray induced photochemical change may be more prevalent than previously thought, and should be considered when interpreting and simulating 3d L-edge spectra. The ability to create diamagnetic domains within a paramagnetic structure may have useful applications, bearing in mind the recent report of an X-ray induced insulator–metal transition in a magnetoresistive manganite using 7 keV radiation.[50]

Acknowledgements

We gratefully acknowledge: the EPSRC/SERC for an Advanced Fellowship (to N. A. Y.), equipment and SRS beamtime (GR/J 34200), personnel (C. M. McG) (GR/K 64662) and a postgraduate studentship (to J. M. W. S.), The Royal Society for a University Research Fellowship (to D. C.); I. Owen and R. Davies of CVT Ltd. (Milton Keynes, UK) for help with the design and construction of the UHV chamber, The University of Hull and The University of Manchester for equipment and the Director of the Synchrotron Radiation Department at Daresbury Laboratory for access to synchrotron and computing facilities.

References

1 See, for example, E. König, *Coord. Chem. Rev.*, 1968, **3**, 471; H. A. Goodwin, *Coord. Chem. Rev.*, 1976, **18**, 293; P. Gütlich, *Struct. Bonding* (*Berlin*), 1981, **44**, 83; E. König, G. Ritter and S. K. Kulshreshtha, *Chem. Rev.*, 1985, **85**, 219; M. Bacci, *Coord. Chem. Rev.*, 1988, **86**, 245; E. König, *Prog. Inorg. Chem.*, 1987, **35**, 527; H. Toftlund, *Coord. Chem. Rev.*, 1989, **94**, 67; E. König, *Struct. Bonding* (*Berlin*), 1991, **76**, 51.
2 W. A. Baker and H. M. Bobonich, *Inorg. Chem.*, 1964, **3**, 1184.
3 E. König and K. Madeja, *Chem. Commun.*, 1966, 61.
4 E. König and K. Madeja, *Inorg. Chem.*, 1967, **6**, 48.
5 A. T. Casey and F. Isaac, *Aust. J. Chem.*, 1967, **20**, 2765.
6 P. Ganguli and P. Gütlich, *J. Phys.*, *Colloq.*, 1980, **41**, C1, 313.
7 P. Ganguli, P. Gütlich, E. W. Müller and W. Irler, *J. Chem. Soc.*, *Dalton Trans.*, 1981, 441.
8 E. W. Müller, H. Spiering and P. Gütlich, *Chem. Phys. Lett.*, 1982, **93**, 567.
9 K. Madeja and E. König, *J. Inorg. Nucl. Chem.*, 1963, **25**, 377.

10 M. Sorai and S. Seki, *J. Phys. Chem. Solids*, 1974, **35**, 555.

11 M. Sorai and S. Seki, *J. Phys. Soc. Jpn.*, 1972, **33**, 575.

12 I. Dezsi, B. Molnar, T. Tarnoczi and K. Tompa, *J. Inorg. Nucl. Chem.*, 1967, **29**, 2486.

13 S. Savage, Z. Jia-Long and A. G. Maddock, *J. Chem. Soc., Dalton Trans.*, 1985, 991.

14 W. A. Baker and G. J. Long, *Chem. Commun.*, 1965, 368.

15 E. König and K. Madeja, *Spectrochim. Acta, Part A*, 1967, **23**, 45.

16 J. H. Takemoto and B. Hutchison, *Inorg. Nucl. Chem. Lett.*, 1972, **8**, 769; *Inorg. Chem.*, 1973, **12**, 705.

17 P. S. Rao, P. Ganguli and B. R. McGarvey, *Inorg. Chem.*, 1981, **20**, 3682.

18 P. S. Rao, A. Reuveni, B. R. McGarvey, P. Ganguli and P. Gütlich, *Inorg. Chem.*, 1981, **20**, 204.

19 S. Vasudevan, H. N. Vasan and C. N. R. Rao, *Chem. Phys. Lett.*, 1979, **65**, 444.

20 K. Burger, C. Furlani and G. Mattogno, *J. Electron Spectrosc. Relat. Phenom.*, 1980, **21**, 249.

21 N. Shioyasu, K. Kagetsu, K. Mishima, M. K. Kubo, T. Tominaga, K. Nishiyami and K. Nagamine, *Hyperfine Interact.*, 1994, **84**, 477.

22 B. Gallois, J.-A. Real, C. Hauw and J. Zarembowitch, *Inorg. Chem.*, 1990, **29**, 1152.

23 T. Granier, B. Gallois, J. Gaultier, J.-A. Real and J. Zarembowitch, *Inorg. Chem.*, 1993, **32**, 5305.

24 Ch. Cartier, P. Thuéry, M. Verdaguer, J. Zarembowitch and A. Michalowicz, *J. Phys. (Paris)*, 1986, **47-C8**, 563.

25 Ch. Cartier dit Moulin, Ph. Sainctavit and V. Briois, *Jpn. J. Appl. Phys.*, 1993, **32** (**Suppl. 32-2**), 38.

26 V. Briois, Ch. Cartier dit Moulin, Ph. Sainctavit, Ch. Brouder and A.-M. Flank, *J. Am. Chem. Soc.*, 1995, **117**, 1019.

27 G. Sankar, J. M. Thomas, V. Varma, G. U. Kulkarni and C. N. R. Rao, *Chem. Phys. Lett.*, 1996, **251**, 79.

28 C. Roux, J. Zarembowitch, J. P. Itie, A. Polian and M. Verdaguer, *Inorg. Chem.*, 1996, **35**, 574.

29 Ch. Cartier dit Moulin, P. Rudolf, A.-M. Flank and C.-T. Chen, *J. Phys. Chem.*, 1992, **96**, 6196.

30 Ch. Cartier dit Moulin, A.-M. Flank, P. Rudolf and C.-T. Chen, *Jpn. J. Appl. Phys.*, 1993, **32** (**Suppl. 32-2**), 308.

31 B. Maiti, B. R. McGarvey, P. S. Rao and L. C. Stubbs, *J. Magn. Reson.*, 1983, **54**, 99.

32 See, for example, P. Gütlich and A. Hauser, *Coord. Chem. Rev.*, 1990, **97**, 1; P. Gütlich, A. Hauser and H. Spiering, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2024.

33 C. J. O'Connor, E. Sinn, T. J. Bucelot and B. S. Deaver, *Chem. Phys. Lett.*, 1980, **74**, 27; A. W. Addison, S. Burman, C. G. Wahlgren, O. A. Rajan, T. M. Rowe and E. Sinn, *J. Chem. Soc., Dalton Trans.*, 1987, 2621.

34 P. Gütlich, J. Ensling and F. Tuczek, *Hyperfine Interact.*, 1994, **84**, 447; P. Gütlich and J. Jung, *Nuovo Cimento Soc. Ital. Fis. D*, 1996, **18**, 107.

35 S. Decurtins, P. Gütlich, C. P. Köhler and H. Spiering, *J. Chem. Soc., Chem. Commun.*, 1985, 430.

36 R. Herber and L. M. Casson, *Inorg. Chem.*, 1986, **25**, 847.

37 K.-U. Baldenius, A. K. Campen, H.-D. Höhnk and A. J. Rest, *J. Mol. Struct.*, 1987, **157**, 295.

38 R. H. Herber, *Inorg. Chem.*, 1987, **26**, 173.

39 P. Gütlich and A. Hauser, *Pure Appl. Chem.*, 1989, **61**, 849; J. Zarembowitch and O. Kahn, *Nouv. J. Chim.*, 1991, **15**, 181; O. Kahn, J. Krober and C. Jay, *Adv. Mater.*, 1992, **4**, 718; C. Jay, F. Groliere, O. Kahn and J. Krober, *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A*, 1993, **234**, 255; E. Codjovi, L. Sommier, O. Kahn and C. Jay, *Nouv. J. Chim.*, 1996, **20**, 503; O. Kahn, *Curr. Opin. Solid State Mater. Sci.*, 1996, **4**, 547.

40 P. Gütlich, *Nucl. Instrum. Methods Phys. Res., Sect. B*, 1993, **76**, 387.

41 G. van der Laan and I. W. Kirkman, *J. Phys.: Condens. Matter*, 1992, **4**, 4189.

42 M. O. Krause, *J. Phys. Chem. Ref. Data*, 1979, **8**, 307.

43 G. van der Laan, R. A. D. Pattrick, C. M. B. Henderson and D. J. Vaughan, *J. Phys. Chem. Solids*, 1992, **53**, 1185; F. M. F. de Groot, M. O. Figueiredo, M. J. Basto, M. Abbate, H. Petersen and J. C. Fuggle, *Phys. Chem. Min.*, 1992, **19**, 140; G. Cressey, C. M. B. Henderson and G. van der Laan, *Phys. Chem. Min.*, 1993, **20**, 111; P. F. Schofield, C. M. B. Henderson, S. A. T. Redfern and G. van der Laan, *Phys. Chem. Min.*, 1993, **20**, 375; R. A. D. Pattrick, G. van der Laan, D. J. Vaughan and C. M. B. Henderson, *Phys. Chem. Min.*, 1993, **20**, 395; R. Brydson, L. A. J. Garvie, A. J. Craven, H. Sauer, F. Hofer and G. Cressey, *J. Phys. Condensed Matter*, 1993, **5**, 9379; J. F. W. Mosselmans, R. A. D. Pattrick, G. van der Laan, J. M. Charnock, D. J. Vaughan, C. M. B. Henderson and C. D. Garner, *Phys. Chem. Min.*, 1995, **22**, 311; P. F. Schofield, C. M. B. Henderson, G. Cressey and G. van der Laan, *J. Synchr. Rad.*, 1995, **2**, 93; G. van der Laan, P. F. Schofield, G. Cressey and C. M. B. Henderson, *Chem. Phys. Lett.*, 1996, **252**, 272; J. M. Charnock, C. M. B. Henderson, J. F. W. Mosselmans and R. A. D. Pattrick, *Phys. Chem. Min.*, 1996, **23**, 403.

44 (*a*) S. P. Cramer, F. M. F. de Groot, Y. Ma, C.-T. Chen, F. Sette, C. A. Kipke, D. M. Eichhorn, M. K. Chan, W. H. Armstrong, E. Libby, G. Christou, S. Brooker, V. McKee, O. C. Mullins and J. C. Fuggle, *J. Am. Chem. Soc.*, 1991, **113**, 7937; (*b*) S. J. George, J. van Elp, J. Chen, Y. Ma, C.-T. Chen, J.-B. Park, M. W. W. Adams, B. G. Searle, F. M. F. de Groot, J. C. Fuggle and S. P. Cramer, *J. Am. Chem. Soc.*, 1992, **114**, 4426; (*c*) S. J. George, M. D. Lowery, E. I. Solomon and S. P. Cramer, *J. Am. Chem. Soc.*, 1993, **115**, 2968; (*d*) J. van Elp, G. Peng, B. G. Searle, S. Mitra-Kirtley, Y.-H. Huang, M. K. Johnson, Z. H. Zhou, M. W. W. Adams, M. J. Maroney and S. P. Cramer, *J. Am. Chem. Soc.*, 1994, **116**, 1918; (*e*) J. van Elp, G. Peng, Z. H. Zhou, M. W. W. Adams, N. Baidya, P. K. Mascharak and S. P. Cramer, *Inorg. Chem.*, 1995, **34**, 2501; (*f*) G. Peng, J. van Elp, H. Jang, L. Que, W. H. Armstrong and S. P. Cramer, *J. Am. Chem. Soc.*, 1995, **117**, 2515; (*g*) M. M. Grush, J. Chen, T. L. Stemmler, S. J. George, C. Y. Ralston, R. T. Stibrany, A. Gelasco, G. Christou, S. M. Gorun, J. E. Penner-Hahn and S. P. Cramer, *J. Am. Chem. Soc.*, 1996, **118**, 65; (*h*) H. Wang, G. Peng, L. M. Miller, E. M. Scheuring, S. J. George, M. R. Chance and S. P. Cramer, *J. Am. Chem. Soc.*, 1997, **119**, 4921.

45 M. A. Arrio, Ph. Sainctavit, Ch. Cartier dit Moulin, T. Mallah, M. Verdaguer, E. Pellegrin and C.-T. Chen, *J. Am. Chem. Soc.*, 1996, **118**, 6422.

46 M. J. Ashcroft, D. Collison, C. D. Garner, J. F. W. Mosselmans, E. Pidcock and N. A. Young, *Physica B*, 1995, **208** and **209**, 725.

47 F. M. F. de Groot, *J. Electron Spectrosc. Relat. Phenom.*, 1994, **67**, 529.

48 C. S. Mythen, G. van der Laan and H. A. Padmore, *Rev. Sci. Instrum.*, 1992, **63**, 1313.

49 See, for example, B. Wallbank, C. E. Johnson and I. G. Main, *J. Electron Spectrosc. Relat. Phenom.*, 1974, **4**, 263; B. A. de Angelis, *J. Electron Spectrosc. Relat. Phenom.*, 1976, **9**, 81; R. G. Copperthwaite, *Surf. Interface Anal.*, 1980, **2**, 17; S. Storp, *Spectrochim. Acta, Part B*, 1985, **40**, 745; M. Oku, *J. Chem. Soc., Faraday Trans.*, 1993, 743; M. Oku, *J. Electron Spectrosc. Relat. Phenom.*, 1994, **67**, 401; M. Oku, H. Matsuta, K. Wagatsuma, *J. Chem. Soc., Faraday Trans.*, 1997, 1061.

50 V. Kiryukhin, D. Casa, J. P. Hill, B. Kelmer, A. Vigliante, Y. Tomloka and Y. Tokura, *Nature* (*London*), 1997, **386**, 813.

Received 29*th May* 1997; *Paper* 7/03728G