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Spin State Transition in Fe(1,10-phen)(2,2′-bipy)(NCS)$_2$

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Abstract

The mixed ligand complex Fe(phen)(bipy)(NCS)$_2$ exhibiting a thermally induced spin state transition between the low spin ($^1A_1$) and high spin ($^5T_2$) states, has been synthesized and characterized by different techniques. The nature of the spin state transition has been studied by ^{57}Fe Mössbauer spectroscopy and differential scanning calorimetry techniques. At spin transition temperature $T_c \simeq 179$ K, the values of isomeric shift and quadrupole splitting for the low and high spin states are $\delta_{LS} = 0.41$, $\delta_{HS} = 1.01$, $\Delta Eq_{LS} = 0.36$ and $\Delta Eq_{HS} = 2.9$ mm s^{-1}, respectively. Although the spin state transition for this complex is of first order, the value of $\Delta H =$ 1 kJ/mol is significantly less than the values observed for single ligand complexes Fe(phen)$_2$(NCS)$_2$ and Fe(bipy)$_2$(NCS)$_2$. The possible reason for this behaviour has been pointed out.

Introduction

Spin state transitions in solid Fe(II) complexes have been the subject of numerous investigations in recent years [1–3]. Depending on the nature of the coordinating ligands both discontinuous and continuous types of spin transitions have been observed. Based on the study of a number of Fe(II) complexes [1, 2], it has been established that the discontinuous type of spin state transitions are associated with a concurrent crystallographic phase transition and a first order character has been well established from thermodynamic measurements and the study of thermal hystersis effects (ΔT_c). Unlike this, for the continuous type of transitions, the existence of an associated crystallographic phase transition and thermal hysteresis effects have not been observed. For certain systems a pseudo discontinuous character of spin state transition has been observed [4–6] either because of metal substitution effects or due to imperfactions in the lattice. For Fe(phen)$_2$(NCS)$_2$ [7–9] and Fe(bipy)$_2$(NCS)$_2$ [9, 10] a first order character of spin transition has been well demonstrated in earlier studies. It has also been reported that for Fe(phen)$_2$(NCS)$_2$ both the abrupt nature of the spin transition and the transition temperature ($T_c = \simeq 174.5$ K) are significantly affected by substitution in the phenanthroline moiety. For example both Fe[4,7(CH$_3$)$_2$phen]$_2$(NCS)$_2$ [11, 12] and Fe[4,7(CH$_3$)$_2$phen]$_2$(NCS)$_2$α-picoline [5] show a discontinuous type of spin state transition but with significantly different values of T_c and ΔT_c as compared to Fe(phen)$_2$(NCS)$_2$. Unlike this, both Fe(4-CH$_3$phen)$_2$(NCS)$_2$ [13] and Fe(5-CH$_3$phen)$_2$(NCS)$_2$ [14] show a continuous type of spin state transition. Complex Fe(2-CH$_3$phen)$_2$(NCS)$_2$ has been reported to exist only in the high spin state [15]. However, detailed substitution effects have not been reported [14, 2] for Fe(bipy)$_2$(NCS)$_2$.

Until now there has been no study about the nature of the spin state transition for Fe(II) complexes where two different types of chelating ligands are coordinated. In the present communication, we report the results of our study of the spin state transition in the Fe(phen)(bipy)(NCS)$_2$ complex. Certain unusual features observed for this complex have been discussed.

Sample Preparation and Characterization

One mole of Fe(ClO$_4$)·6H$_2$O was dissolved in ethanol and treated with slightly more than two moles of potassium thiocynate dissolved in hot acetone. The mixture was stirred well and cooled to room temperature. The precipitated KClO$_4$ was filtered off and the filtrate was added to an equimolar solution of 1,10-phenanthroline (phen) and 2,2′-bipyridine (bipy) so that the ratio of Fe:phen:bipy was 1:1:1. The mixture was stirred well and allowed to stand overnight under a slow stream of nitrogen. The precipitated complex was filtered off and purified by soxlet extraction with acetone. The extracted solid was dried under vacuum. All the above operations were carried out in a nitrogen atmosphere. *Anal.* Found: C, 58.35; N, 16.28; H, 3.24; Fe, 10.68.Calc. C, 57.62; N, 16.52; H, 3.14; Fe, 10.99%.

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The powder X-ray diffraction pattern for the mixed complex was found to be almost similar to that of Fe(phen)$_2$(NCS)$_2$ except some of the peaks showed a slight difference in their 2θ values. The IR studies suggested the coordination of both phen and bipy as the observed peaks corresponding to Fe–N stretching in the mixed ligand complex could be matched well with the peaks reported for single ligand complexes [16, 17]. In order to further confirm the coordination of both phen and bipy, a portion of the sample was dissolved in HNO$_3$ and the organic phase was extracted in ethyl ether. The ^{13}C NMR spectra of the organic phase recorded in CDCl$_3$ solution showed clear peaks corresponding to both phen and bipy in quantitative measure. This established that both bipy and phen are present in this compound.

Spin State Transition

Magnetic susceptibility measurements recorded at room temperature and 110 K gave $\mu_{eff} = 5.1\ \mu_\beta$ and $1.1\ \mu_\beta$ respectively which suggest the possibility of a thermally induced spin state transition. Figure 1 shows a few representative ^{57}Fe Mössbauer spectra of Fe(phen)(bipy)(NCS)$_2$ recorded in the spin transition region, which clearly establish the occurrence of a spin state transition. The value of the spin transition temperature for the heating cycle is approximately 180 K. The observed values of isomeric shift and quadrupole splitting for the low spin species, in the spin transition temperature region, are $\delta_{LS} = +0.41$ mm s^{-1} (with respect to Fe metal at 298 K) and $\Delta Eq_{LS} = 0.36$ mm s^{-1}. The corresponding values for the high spin phase are $\delta_{HS} = +1.01$ mm s^{-1} and $\Delta Eq_{HS} = 2.9$ mm s^{-1}. These values of isomeric shift and quadrupole splitting are closer to the values observed for Fe(phen)$_2$(NCS)$_2$ [6, 7] and other substituted phen complexes [11–13]. The values of ΔEq_{HS} showed a slight temperature dependence. From this figure it is clear that the spin transition is complete in the low spin state but in the high temperature region a small fraction of residual low spin phase is present.

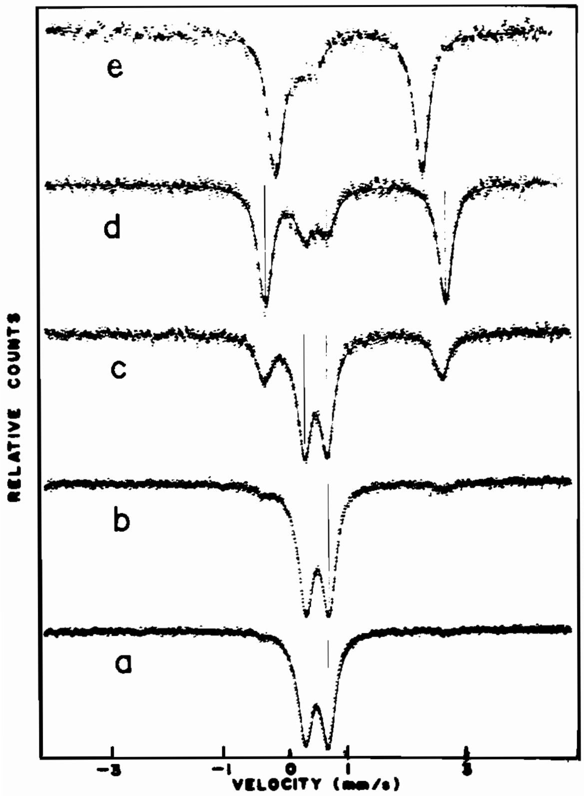

Fig. 1. Mössbauer spectra of Fe(phen)(bipy)(NCS)$_2$ in the spin transition region for the heating cycle at different temperatures (K): a, 78; b, 175; c, 178; d, 184; e, 297.

Figure 2(b) shows the differential scanning calorimetry curve for Fe(bipy)(phen)(NCS)$_2$ along with those of Fe(phen)$_2$(NCS)$_2$ and Fe(bipy)$_2$(NCS)$_2$ recorded under similar conditions. From this Figure it is clear that although the spin transition is of first order the value of ΔH for Fe(phen)(bipy)(NCS)$_2$ is very much less than that of the other two complexes. The value of the transition temperature T_c as determined from the initiation of DSC peaks for the heating and cooling cycles are $T_c\uparrow = 180$ K and $T_c\downarrow = 179$ K respectively. The observed values of transition temperatures for Fe(phen)$_2$(NCS)$_2$ and Fe(bipy)$_2$(NCS)$_2$ are $T_c\uparrow = 175.5$ K, $T_c\downarrow = 174.4$ K, $T_c\uparrow = 211$ K and $T_c\downarrow = 210.5$ K, respectively, and match extremely well with the values reported by earlier authors using different techniques [6–10]. From peak area measurements the value of ΔH is approximately 1 kJ mol^{-1}. The observed values of ΔH for phen and bipy complexes are approximately 8 and 6.5 kJ mol^{-1} respectively. The derived value of ΔS for Fe(phen)(bipy)(NCS)$_2$ is approximately 5.5 J mol^{-1} K^{-1} which is much smaller than the value of $\Delta S_{spin} = 13.4$ J mol^{-1} K^{-1} expected to arise due to a change in the spin state alone. For all discontinuous type of spin transitions, the observed value of ΔS has been found to be more than 13.4 J mol^{-1} K^{-1}. The additional contribution arises due to a change in the phonon state of the system [1, 2]. The present results suggest that the spin state transition for the present complex may not be associated with a concurrent crystallographic phase transition and is very sensitive to steric effects.

Both Mössbauer spectroscopy and differential scanning calorimetry measurements establish that our sample is indeed a single phase mixed ligand complex and not a mixture of Fe(phen)$_2$(NCS)$_2$ and Fe(bipy)$_2$(NCS)$_2$ as the values of ΔEq_{HS} and T_c for these two complexes are appreciably different. For example the values of ΔEq_{HS} at 300 K for phen and bipy complexes are 2.70 mm s^{-1} and 2.15 mm s^{-1}

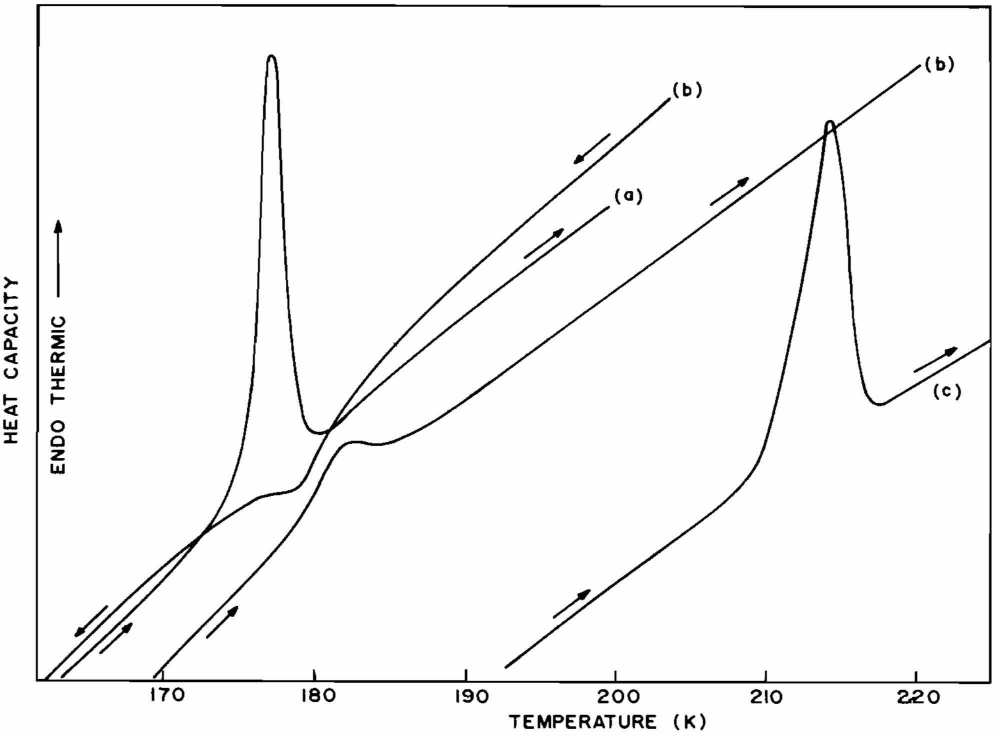

Fig. 2. DSC curves for (a) $Fe(phen)_2(NCS)_2$ 4.25 mg; (b) $Fe(phen)(bipy)(NCS)_2$ 4.89 mg; (c) $Fe(bipy)_2(NCS)_2$ 4.72 mg; for increasing and decreasing temperature cycles with a heating/cooling rate of 10 K min^{-1}. Arrows indicate the direction of temperature variation.

respectively. The value of ΔEq_{HS} for $Fe(phen)(bipy)(NCS)_2$ is approximately 2.48 mm s^{-1}.

In conclusion we would like to mention that in the present communication we have reported the preparation of a mixed ligand complex $Fe(phen)(bipy)(NCS)_2$ which exhibits a spin state transition between the low spin ($^1A_1$) and high spin ($^5T_2$) states. The transition is of first order but the values of ΔH and ΔS are very small as compared to the values observed for single ligand complexes $Fe(phen)_2(NCS)_2$ and $Fe(bipy)_2(NCS)_2$.

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