Spin Cross-over and the Mössbauer Emission Spectrum of Cobalt-57-labelled Di-isothiocyanatobis(1,10-phenanthroline)-iron(II) and -cobalt(II)

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Mössbauer emission spectra of ^{57}Co-labelled [Co(phen)$_2$(NCS)$_2$] (phen = 1,10-phenanthroline) and ^{57}Co-doped [Fe(phen)$_2$(NCS)$_2$] have been recorded at room temperature and at 77 and 4 K, and compared with the absorption spectrum of [Fe(phen)$_2$(NCS)$_2$]. A large proportion, sometimes >95%, of the emission corresponds to high-spin [^{57m}Fe(phen)$_2$(NCS)$_2$], irrespective of the temperature. However, both the absorption and emission spectra of [Fe(phen)$_2$(NCS)$_2$] vary in an unexplained manner with the method of preparation of the sample.

A FEW years ago Ensling *et al.*[1] reported a complex and temperature-dependent ^{57}Fe Mössbauer emission spectrum from ^{57}Co-labelled [Co(phen)$_3$][ClO$_4$]$_2$·2H$_2$O(phen = 1,10-phenanthroline) and attributed it to the appearance of unusual spin states of the nascent iron complex. König *et al.*[2] modified the original assignments, discarding an improbable triplet state, and suggested that the three doublets observed arise from the usual low-spin $^1A_1$ state and high-spin $^5A_1$ and ^5E states of the iron complex. The $^5A_1$ doublet might also be due to a ligand-deficient species produced by the decay event.

Thus some uncertainty remains in the interpretation of the data because the only significant Mössbauer parameters available are those from absorption experiments with the normal $^1A_1$ state of the iron complex. Now the data of Nath and his co-workers [3,4] and Sanchez *et al.*[5] suggest that in complexes of aromatic ligands, like phen, a substantial fraction of the ^{57m}Fe, from the orbital electron-capture decay of the ^{57}Co, either survives as, or re-forms, the iron analogue of the parent cobalt complex. But present knowledge of the ' after effects ' is insufficient to enable one to predict with much confidence other species that might be produced.

The problem of the identification of the various products can be avoided by working with iron complexes that exhibit temperature-dependent spin cross-over. With such complexes the Mössbauer parameters can be measured by absorption for two electronic states of the complex. In addition, for some of these complexes, small changes in the lattice can make one or other electronic state become the ground state. Further, since the cobalt-57 complex can be incorporated into matrices of either the cobalt or iron complexes, there is a possibility of learning something about the role of the lattice in spin cross-over. The complex [Fe(phen)$_2$(NCS)$_2$] which shows a rather sharp spin cross-over at *ca.* 170 K seems a suitable system for such a study.

While these experiments were in progress a copy of Dr. Ensling's thesis [6] became available. The thesis records similar experiments carried out a few years ago but only recently submitted for publication.[7] Our results confirm those of Ensling and lead to similar immediate conclusions. However, we have discovered some additional unusual and curious features of these complexes.

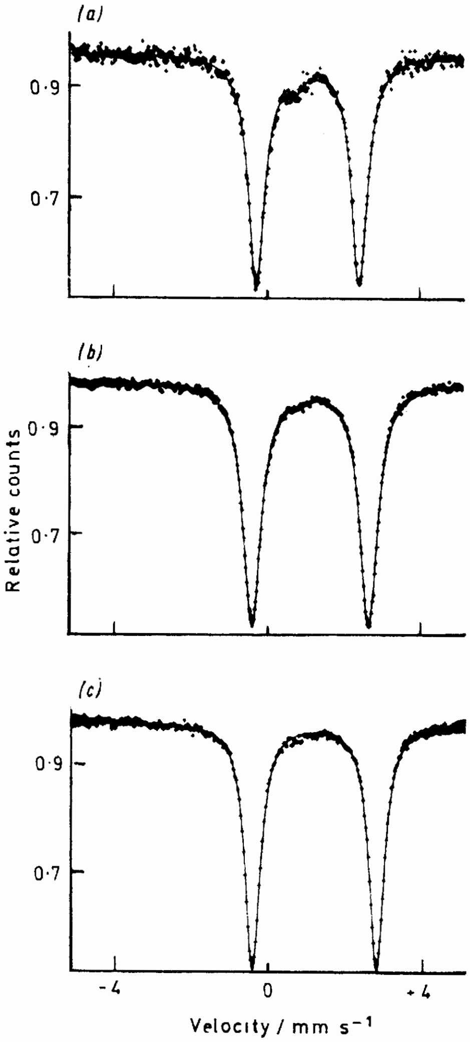

FIGURE 1 Mössbauer emission spectra of [Fe(phen)$_2$(NCS)$_2$] doped with ^{57}Co at (*a*) 293, (*b*) 77, and (*c*) 4.2 K *versus* Na$_4$[Fe(CN)$_6$]·10H$_2$O. The source was prepared by the aqueous method

RESULTS AND DISCUSSION

Experiments were made with (*a*) ^{57}Co-doped [Fe(phen)$_2$(NCS)$_2$] and (*b*) ^{57}Co-labelled [Co(phen)$_2$(NCS)$_2$]. The iron and cobalt complexes were prepared by the

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[1] J. Ensling, B. W. Fitzsimmons, P. Gütlich, and K. M. Hasselbach, *Angew. Chem.*, 1970, **82**, 638.

[2] E. König, P. Gütlich, and R. Link, *Chem. Phys. Letters*, 1972, **15**, 302.

[3] A. Nath, M. P. Klein, W. Kündig, and D. Lichtenstein, *Radiation Effects*, 1970, **2**, 211.

[4] T. S. Srivastava and A. Nath, *Radiochem. Radioanalyt. Letters*, 1974, **16**, 103.

[5] J. P. Sanchez, Y. Llabador, and J. M. Friedt, *J. Inorg. Nuclear Chem.*, 1973, **35**, 3557.

[6] J. Ensling, Thesis, Darmstadt, 1970.

[7] J. Ensling, P. Gütlich, K. M. Hasselbach, and B. W. Fitzsimmons, *Chem. Phys. Letters*, 1976, **42**, 232.

aqueous method described in refs. 8 and 9. The cobalt-doped material was prepared using a mixture of the iron(II) salt with a solution of $^{57}Co^{2+}$ of high specific activity. In both sources the ^{57}Co is present as [Co-(phen)$_2$(NCS)$_2$]. In addition, samples were prepared using a methanol medium [6] and also from the tris(1,10-phenanthroline) thiocyanates by leaching out one molecule of phen with boiling acetone.[10]

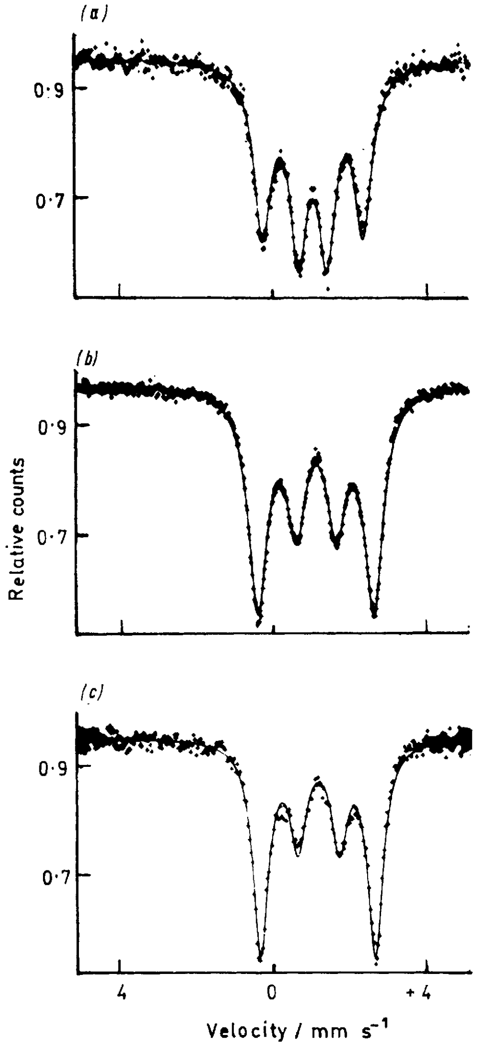

FIGURE 2 Mössbauer emission spectra of [Co(phen)$_2$(NCS)$_2$] labelled with ^{57}Co at (a) 293, (b) 77, and (c) 4.2 K *versus* $Na_4[Fe(CN)_6]\cdot10H_2O$. The source was prepared as in Figure 1

Mössbauer emission spectra were recorded using an enriched $Na_4[Fe(CN)_6]$ absorber (1 mg of ^{57}Fe per cm^2) at 300 K. The emission spectra, recorded with the source at ambient, liquid-nitrogen, and liquid-helium temperatures, are shown in Figures 1 and 2. By comparison with most emission spectra, the spectra are unusually clean and simple. Linewidths are narrow by the same standards.

For each material two completely independent preparations using the aqueous method [9] were made. The products showed identical behaviour. When, however, sources of ^{57}Co-labelled [Co(phen)$_2$(NCS)$_2$] were made using a methanol medium the emission spectra showed identical parameters to those of the ^{57}Co-doped iron complex sources. In view of these differences, the identities of the complexes from the different preparations were carefully investigated. Elemental analysis is not a very sensitive indicator of the kind of differences that might be important here, but the following data (%) were typical:

	Co	S	C	N
Found	9.96	11.50	57.7	15.8
Calc. for:				
[Co(phen)$_2$(NCS)$_2$]	10.49	12.04	58.65	15.78
[Co(phen)$_2$(NCS)$_2$]·H$_2$O	10.15	11.65	56.73	15.27
[Co(phen)$_2$(NCS)$_2$]·2H$_2$O	9.82	11.28	54.94	14.78
	Fe			
Found	10.9	12.9	57.1	14.98
Calc. for:				
[Fe(phen)$_2$(NCS)$_2$]	11.00	11.97	58.32	15.69
[Fe(phen)$_2$(NCS)$_2$]·H$_2$O	10.65	11.58	56.42	15.18
[Fe(phen)$_2$(NCS)$_2$]·2H$_2$O	10.91	11.22	54.64	14.70

Examination of the i.r. absorption spectra of the complexes, using the KBr disc technique, revealed some small differences between the different products. All the preparations showed the absorptions listed by Schilt and Fritsch [9] but some showed a rather broad band at 1 040 cm^{-1} and a well resolved pair at 1 170 and 1 180 cm^{-1}. These absorptions were considerably enhanced if the complexes were stored in water vapour. They were not removed by subsequent heating *in vacuo*. Cunningham *et al.*[11] described two differently hydrated forms of [Fe(phen)$_2$(NCS)$_2$] and analogous substituted phen complexes (or, possibly, a hydrate and an anhydrous form). The more strongly hydrated form is reported to be dehydrated on heating *in vacuo* to 180 °C and the complex is believed to be stable at this temperature. We found that marked changes in the i.r. spectrum occurred on heating to 150—160 °C. New C–N stretching absorptions appeared at 2 105 and 2 130 cm^{-1} (compared with 2 060 and 2 080 cm^{-1} in the normal complex). Such behaviour may indicate a change from M–NCS to M–SCN bonding in the complex. Certainly some chemical changes take place on heating.

Cunningham *et al.*[11] found considerable differences in magnetic behaviour between their higher and lower hydrates. Using various 5-substituted 1,10-phenanthrolines, the lower hydrates, possibly anhydrous complexes, showed spin cross-over over a narrow range of temperature. The higher hydrates showed anomalous magnetic properties, and a Mössbauer absorption spectrum of one quadrupole-split pair with $\Delta \sim 0.22$ mm s^{-1} at both ambient and liquid-nitrogen temperature. Unfortunately, no data were included for the hydrated unsubstituted phen complex.

The Mössbauer absorption-spectrum parameters of

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[8] K. Madeja and E. König, *J. Inorg. Nuclear Chem.*, 1963, **25**, 377.

[9] A. A. Schilt and K. Fritsch, *J. Inorg. Nuclear Chem.*, 1966, **28**, 2677.

[10] K. Madeja, W. Wilke, and S. Schmidt, *Z. anorg. Chem.*, 1966, **346**, 306.

[11] A. J. Cunningham, J. E. Fergusson, H. J. K. Powell, E. Sinn, and H. Wong, *J.C.S. Dalton*, 1972, 2155.

some of our products are given in Table 1, together with previously reported data. We do not find any clear relation between spin cross-over characteristics, as revealed by the Mössbauer absorption spectra of our [Fe(phen)$_2$(NCS)$_2$] preparations and the appearance of the absorptions at 1 040, 1 170, and 1 180 cm^{-1}. Nor do we find much change after storage in a moist atmosphere.

TABLE 1

Parameters[a] of the Mössbauer absorption spectra of [Fe(phen)$_2$(NCS)$_2$]

(*i*) Aqueous preparation

T / K	δ / mm s^{-1}	Δ / mm s^{-1}	DIP (%)	Γ / mm s^{-1}	Ref.
293	1.008 ± 0.01	2.82 ± 0.01			*b*
	0.98 ± 0.03	2.67 ± 0.03		0.40 ± 0.02	*c*
	1.27	2.7			*d*
	1.22 ± 0.1	3.09 ± 0.1			*e*
	1.03 ± 0.05	2.60 ± 0.03	0.7 ± 0.2	0.35 ± 0.03	*f*
77	0.37 ± 0.05	0.34 ± 0.06		0.71 ± 0.05	*c*
	0.73	0.35			*d*
	0.43 ± 0.05	0.35 ± 0.03	3.9 ± 0.1	0.28 ± 0.03	*f*

(*ii*) Acetone-extraction preparation (this work)

	T / K	δ / mm s^{-1}	Δ / mm s^{-1}	DIP (%)	Γ / mm s^{-1}
Initial material	77	1.04 ± 0.05	2.96 ± 0.05	1.16 ± 0.2	0.32 ± 0.03
After storage over water	77	0.43 ± 0.05	0.33 ± 0.03	3.86 ± 0.1	0.32 ± 0.03
	293	0.98 ± 0.05	2.62 ± 0.03	0.5 ± 0.2	0.33 ± 0.03

[a] δ = Isomer shift with respect to iron metal; Δ = quadrupole splitting; DIP = maximum absorption; and Γ = line width. [b] R. L. Collins, R. Pettit, and W. A. Baker, *J. Inorg. Nuclear Chem.*, 1966, **28**, 1001. [c] E. König and K. Madeja, *Chem. Comm.*, 1966, **3**, 61; E. König, S. Hüfner, E. Steichele, and K. Madeja, *Z. Naturforsch.*, 1967, **A22**, 1543. [d] I. Dezsi, B. Molnar, T. Tarnoczi, and K. Tompa, *J. Inorg. Nuclear Chem.*, 1967, **29**, 2490. [e] J. F. Duncan and K. F. Mok, *J. Chem. Soc.* (*A*), 1966, 1493. [f] This work.

TABLE 2

Parameters[a] of the emission spectra

(*a*) [Fe(phen)$_2$(NCS)$_2$] doped with ^{57}Co

T / K	δ_1 / mm s^{-1}	Δ_1 / mm s^{-1}	DIP$_1$ (%)	δ_2 / mm s^{-1}	Δ_2 / mm s^{-1}	DIP$_2$ (%)	Γ / mm s^{-1}	DIP$_T$ (%)	DIP$_1$/DIP$_T$ (%)
293	1.12	2.70	5.53	0.43	0.35	0.37	0.51	5.9	93.7
173	1.11	3.01	10.19	0.43	0.35	0.46	0.62	10.7	95.7
77	1.18	3.05	17.5	0.43	0.35	0.37	0.56	17.8	98.0
4.2	1.20	3.04					0.45	52.2	

(*b*) [Co(phen)$_2$(NCS)$_2$] labelled with ^{57}Co

T / K	δ_1 / mm s^{-1}	Δ_1 / mm s^{-1}	DIP$_1$ (%)	δ_2 / mm s^{-1}	Δ_2 / mm s^{-1}	DIP$_2$ (%)	Γ / mm s^{-1}	DIP$_T$ (%)	DIP$_1$/DIP$_T$ (%)
293	1.11	2.64	2.8	1.11	0.74	3.0	0.56	5.9	48.0
173	1.17	3.00	6.8	1.17	0.92	5.1	0.55	11.9	57.0
77	1.19	3.04	11.3	1.20	1.05	6.8	0.59	18.1	62.5
4.2	1.20	3.01	4.4	1.22	1.09	2	0.50	6.5	68.2
293[b]	1.01	2.64	2.8	0.42	0.34	0.1	0.6	2.9	96.5
77[b]	1.10	3.10	20.8				0.21		

[a] The computed probable error in δ is ±0.05 mm s^{-1} and in Δ is ±0.03 mm s^{-1}. [b] The sample was prepared in methanol solution; all the other samples were prepared in aqueous solution.

However, preparations giving products of different crystal size showed marked differences in behaviour, although it should be noted that the products were pulverised before measurement of the Mössbauer spectra. Thus the well crystallised product from the acetone-extraction preparation[10] showed no cross-over and maintained high-spin characteristics down to the temperature of liquid nitrogen (Table 1). On storage of this material over water it eventually showed the normal cross-over characteristics (compare König and Madeja).[12] Other preparations of the formally anhydrous material showed only partial spin cross-over (survival of some high-spin form at liquid-nitrogen temperature).

The parameters of the emission spectra are shown in Table 2. Our data show that in both the matrices of the iron and cobalt complex sources, and at both high and low temperatures, a substantial part of the emission seems to take place from the high-spin iron species whose Mössbauer parameters are known from absorption measurements on the iron complex at >170 K. At liquid-helium temperature the ^{57}Co in a matrix of the iron complex gave almost entirely (at least >93%) a high-spin emission. This result is almost as surprising as the discovery that a proportion of the ^{57}Co decays yield the corresponding iron complex. Under these conditions, notwithstanding the Auger cascade that must accompany the orbital electron capture, coulombic rupture of the molecule[13,14] does not occur and the

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[12] E. König and K. Madeja, *Inorg. Chem.*, 1969, **3**, 48.

[13] J. L. Magee and E. F. Gurnee, *J. Chem. Phys.*, 1952, **20**, 894.

[14] A. A. Gordus and J. E. Willard, *J. Amer. Chem. Soc.*, 1957, **79**, 4609.

electrons emitted are not trapped by radiolysis of the ligands but are recaptured without decomposition of the complex containing the nascent iron atom. No appreciable proportion of oxidised species survives and the excitation of the molecule and its surroundings only leads to the affected molecule emitting while in the high-spin state.

At higher temperatures a small proportion of the emission (*ca.* 5%) occurred from another species, possibly the low-spin form or the iron(III) complex. In previous studies of cobalt complexes with this kind of ligand the spectra have become more complex at lower temperatures when emissions from two or more iron environments have generally become apparent.[1,5] In the matrix of the iron complex the emission is from the high-spin high-temperature form irrespective of source temperature.

It should be noted that the cobalt complex exists only in the high-spin form[15] and therefore the nascent ^{57m}Fe will be formed in an environment with metal–ligand distances closer to those in the high-spin form of the iron complex. The appearance of the high-spin emission at source temperatures appropriate to the low-spin form suggests that the ligands cannot relax to positions stabilising the low-spin form within the lifetime of the ^{57m}Fe.

The ^{57}Co-doped iron complex sources used did not show the 1 040, 1 170, and 1 180 cm^{-1} absorptions. But the ^{57}Co-labelled complexes prepared in both aqueous and methanol media showed these absorptions. Although the emissions from the two sorts of ^{57}Co-labelled complex sources were very different, no differences in analysis or i.r. spectra were noticeable. In both cases a substantial emission from the normal high-spin form of $[Fe(phen)_2(NCS)_2]$ seems to occur. The other emission from the sources prepared by the aqueous method has not been identified. It also appears to arise from a high-spin iron(II) species, possibly another low-lying state of $[Fe(phen)_2(NCS)_2]$ since the low symmetry of this species removes all the orbital degeneracy. It may also arise from a high-spin isomer of the iron complex or a ligand-deficient product. We hope to identify this latter species in more extended studies and to learn more about the role of the lattice in the cross-over by using mixed crystals of the cobalt and iron complexes.

We conclude: (*i*) that in a high proportion of the orbital electron-capture events by ^{57}Co in $[Fe(phen)_2(NCS)_2]$ the iron-57 complex is produced, very little oxidation or disruption occurring; (*ii*) the iron-57 complex exists during the lifetime of the ^{57m}Fe as the high-spin species irrespective of the ground state of $[Fe(phen)_2(NCS)_2]$ under the prevailing conditions; and (*iii*) spin cross-over characteristics are sensitive to the physical state of the complex. We suggest that (*ii*) may be because the ligand–metal distances in the high-spin parent $[Co(phen)_2(NCS)_2]$ cannot relax to low-spin values within the lifetime of ^{57m}Fe.

We thank Professor Gütlich, Dr. Ensling, and their co-workers for discussions and for a preprint of ref. 7.

[6/1641 *Received, 24th August*, 1976]

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[15] L. Cambi and E. Paglia, *Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1956, **21** 372.