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Mössbauer Study of Iron–Cystein and Methylcystein Complexes

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Introduction

Cystein complexes of light transition metals have been diversely studied as models for metal–protein systems, such as non haem iron proteins (ferredoxins, rubredoxins) [1–3] or blue copper proteins [4]. Similar derivatives (penicilamin, N-acetylpenicilamin) have therapeutic uses in heavy metals poisonning (Wilson desease) or cancer therapy [5–7].

An improved synthesis and the characterisation of the binding sites of cristalline complexes labelled FeL, FeL_2, FeL'_2, (L = cystein, L' = methylcystein) by infrared and Raman spectroscopies has been published [8].

To date, most of the physical data on these complexes are interpreted in terms of high spin ferrous state perturbated by exchange interactions [9], but no clear conclusion is drawn on the dimeric or polymeric nature of these species [9, 10].

We report Mössbauer data on iron(II)–cystein complexes compared to ferrous complexes of synthetic sulfur donor ligands [11, 12].

Experimental

Acidic or neutral conditions yield a solid light brown complex with a 1:1 stoicheiometry (FeL).

In alkaline solutions a 2:1 compound (FeL_2) is isolated. The methyl ester of cystein gives a red-brown precipitate (FeL'_2). Accurate conditions described in a former paper [8] are necessary to isolate pure species. The synthesis of FeL_2 performed in a CO atmosphere yields red crystalline $FeL_2(CO)_2$.

Mössbauer spectra have been recorded at various temperatures from microcrystalline samples with an equivalent natural iron density of 5 mg/cm^2 placed in a cryostat.

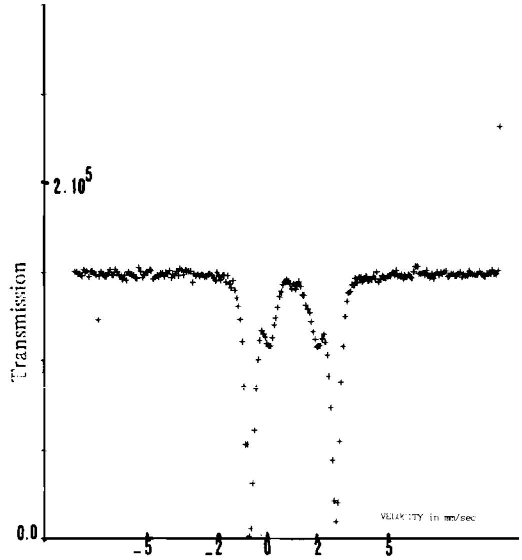

Fig. 1. Mössbauer spectra of FeL_2 at 77 K.

The spectrometer was a constant acceleration device with an electromechanical transducer. The source was at room temperature (12 mCi, ^{57}Co in Pd matrix). Signals referred to metallic iron were recorded from a 256 channels analyser.

Results

Mössbauer parameters, isomeric shifts (δ) and quadrupole splittings (ΔE_q) are grouped in Table I. A typical spectrum is shown in Fig. 1 as an example. FeL_2 spectra consist of a single quadrupolar split signal, while for FeL'_2 spectra give evidence for two different quadrupolar couplings.

The mean values of the isomeric shift and of the quadrupole splitting for non carbonyl compounds are consistent with high spin Fe(II) and are similar to those of related high spin ferrous complexes of sulfur [11, 15–17] or nitrogen donor ligands [14]. $FeL_2(CO)_2$ appears to be quite different.

Measurements have been made from room to liquid nitrogen temperatures and while FeL, FeL'_2 and $FeL_2(CO)_2$ show no variation in the whole range, Mössbauer parameters for FeL_2 are temperature dependent.

Discussion and Concluding Remarks

Isomeric shifts are rather similar and denote little influence of the nature of the bonding of the cystein

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TABLE I. Mössbauer Parameters[a] of the Different Compounds.

Temperature (K)		77	103	149	229	298
FeL	Δ	3.14				3.11
	δ	1.05				0.93
FeL_2	Δ	3.59	3.47	3.35	3.16	2.99
	δ	1.05	0.96	1.04	0.96	0.96
$FeL_2(CO)_2$	Δ	0.24				0.24
	δ	0.12				0.12
	Δ_1	2.78				2.78
	δ_1	0.66				0.66
FeL_2'	Δ_2	3.14				3.14
	δ_2	0.84				0.84

[a] In mm/sec.

molecule on the gross population around iron atom for FeL, FeL_2 and FeL_2'. In contrast with this, $FeL_2(CO)_2$ has a much lower δ value which demonstrate stronger covalent character for the complex with a low spin configuration for ferrous iron.

Quadrupole splitting is much reduced in $FeL_2(CO)_2$ which can be interpreted by a nearly octahedral symmetry for this compound.

The quadrupole splitting was observed to be temperature-dependent in the case of FeL_2. These values denote that thermally available excited states are present and a rather important departure from cubic symmetry [18, 19].

The ΔE_q value of FeL seems to indicate a less distorted structure for this compound. This is consistent with the ligation by the carboxylate group [8], and with our observation of a relative stability towards atmospheric oxidation for this complex.

Two different quadrupolar couplings are detected for FeL_2'. As analytical and spectral checks performed on the products exclude major iron impurities, these split doublets could be due to the existence of several crystallographic modifications present in the sample, or to a polymetallic unit cell containing non equivalent iron atoms.

A check for the latter hypothesis may be done by recording Mössbauer spectra of a glassy frozen solution.

Structural conclusions from the established data can be summarized as follows:

(a), high spin configuration for ferrous iron is confirmed for both acid phase (FeL) and alkaline phase (FeL_2) precipitates in aqueous solution;

(b), rather important departure from cubic symmetry corresponds to large quadrupole splittings but no bridging thiol group is present.

(c), temperature dependence of ΔE_q values singles out FeL_2 in which low lying excited states would correspond to lesser stability.

(d), $FeL_2(CO)_2$ appears to be spin coupled as a result of synergetic stabilization through π-type back-donation both towards CO and thiol coordinating groups.

Murray and Newman [9] conclude that there exists antiferromagnetic coupling in the polymeric network from their magnetic susceptibility data on FeL_2, while Karlin and Lippard [11] by analogy with their synthetic sulfur ligand ferrous complexes, suggest a thiolate-bridged dimeric complex.

Current investigation by X.P.S. [20] has shown us that $S_{2p_{1/2,3/2}}$ photopeaks allow to exclude the latter hypothesis, as we observe for FeL_2 lower binding energies than in free cysteine, whereas S-bridged complexes will have higher binding energies [21].

References

1 G. R. Moore and R. J. P. Williams, *Coord. Chem. Rev., 18,* 125 (1976).

2 R. H. Holm, 'Endeavour', *34,* 38 (1975).

3 W. Lovenberg, Ed., 'Iron-Sulfur Proteins', Vol. 1 and II, Academic Press, N.Y. (1973).

4 J. A. Fee, 'Copper Proteins', in *Structure and Bonding,* Vol. 23, Berlin (1975).

5 a) J. M. Walshe, *Lancet, 2,* 775 (1978).
b) D. Bahnemann, H. Basaga, J. R. Dunlop, A. J. F. Searle and R. L. Wilson, *Br. J. Cancer, 37,* Supp. III, 16 (1978).

6 K. F. Swaiman and D. G. Falger, *Pediatrics, 48,* 639 (1971).

7 T. D. Zucconi, G. E. Janauer, S. Donahe and C. Lewkowick, *J. Pharmaceutical Sciences,* Vol. 68, No 4 (1979).

8 R. Panossian, G. Terzian and M. Guiliano, *Spectroscopy Letters,* 12 *(10), (1979).*

9 K. S. Murray and P. J. Newman, *Aust. J. Chem., 28,* 773 (1975).

10 H. B. Mathur, M. P. Gupta and C. V. Kavedia, *Ind. J. Chem., 4,* 337 (1966).

11 K. D. Karlin and S. J. Lippard, *J. Am. Chem. Soc., 98,* (22) 6951 (1976).

12 O. A. Ileparuma and R. D. Feltham, *Inorg. Chem., 14,* 3042 (1975).

13 G. M. Bancroft and R. H. Platt, *Adv. Inorg. Chem. Radiochem., 15,* 59 (1972).

14 D. P. Riley, P. H. Merrell, J. A. Stone and D. H. Bush, *Inorg. Chem., 14,* 490 (1975).

15 L. F. Larkworthy, B. W. Fitzsimmons and R. R. Patel, *J. Chem. Soc., Chem. Comm.,* 902 (1973).

16 B. W. Fitzsimmons, S. E. Al-Mukhtar, L. F. Larkworthy and R. R. Patel, *J. Chem. Soc., Dalton Trans.,* 1969 (1975).

17 J. L. K. F. de Vries, J. M. Trooster and E. de Boer, *Inorg. Chem., 12,* 2730 (1973).

18 M. Bond, R. L. Martin and I. A. G.Roos, *Aust. J. Chem., 27,* 2307 (1974).

19 P. R. Edwards, C. E. Johnson and R. J. P. Williams, J. Chem. Phys., 37, 2074 (1974).

20 G. Terzian and R. Panossian, unpublished data.

21 S. Best, P. Brant, R. D. Feltham, T. B. Rauchfuss, D. M. Roundhill and R. A. Walton, *Inorg. Chem., 16,* 1976 (1977).