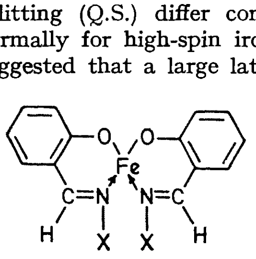
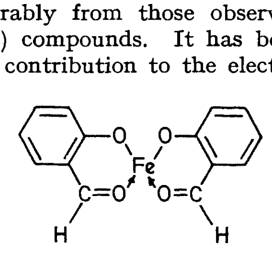
Mössbauer Spectra of High-spin Iron(II) Chelates of Salicylaldoxime, Salicylaldehyde, and Some Schiff Bases

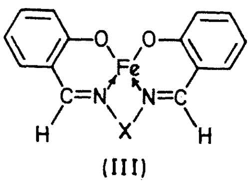
By J. L. K. F. DE VRIES,* J. M. TROOSTER, and E. DE BOER
(*Department of Physical Chemistry, University of Nijmegen, Nijmegen, The Netherlands*)

Summary Mössbauer spectra of the above mentioned chelates were found to be characteristic for high-spin iron(II) compounds, and previously reported deviations by other authors are not observed if the spectra are recorded under anaerobic conditions.

IN several articles Mössbauer spectra of high-spin iron(II) chelates have been reported,[1–5] especially those of salicylaldoxime (I; X = OH), salicylaldehyde (II), and Schiff bases derived from salicylaldehyde (I; X = H, III; X = CH_2–CH_2, III; X = o-C_6H_4). For all these compounds the reported values of the isomer shift (I.S.) and quadrupole splitting (Q.S.) differ considerably from those observed normally for high-spin iron(II) compounds. It has been suggested that a large lattice contribution to the electric field gradient[1] and back-donation[4,5] are responsible for these discrepancies. Since it was not clear to us why just these compounds should give deviating Mössbauer spectra, we re-investigated them, using a new preparation technique. The results show that normal iron(II) spectra can be obtained if absolute oxygen-free conditions are maintained during the preparation and while measuring the Mössbauer spectra. After exposing the compounds to air, Mössbauer spectra are obtained similar to those reported in the literature and characteristic for high-spin iron(III) compounds.


(I)


(II)


(III)

The chelates were prepared using a vacuum technique. In a Pyrex glass apparatus consisting of two interconnected tubes, an aqueous solution of iron(II) sulphate and an alcoholic solution of the ligand were thoroughly degassed. The apparatus was then sealed off the vacuum line. Upon mixing the solutions at room temperature a brightly-coloured precipitate (see Table) was immediately formed. The solid was dried by distilling the solvent into the adjacent tube which was then sealed off. Absorbers for the Mössbauer measurements were prepared in a glovebox (VAC lab dri-train) by sealing the dry iron compound in a

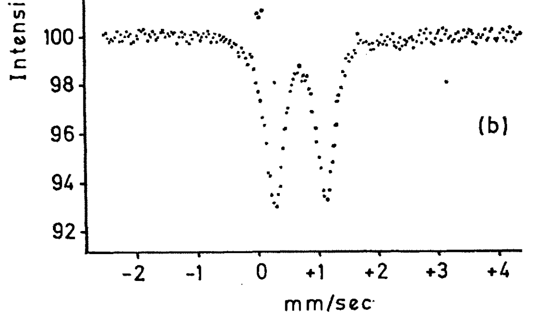


FIGURE. *Mössbauer spectra of* NN′-*ethylenebis(salicylideneiminato)iron*(II) (III; X = CH_2–CH_2) *at liquid nitrogen temperature* (a) *iron*(II) *chelate* (b) *after exposure to air.*

Mössbauer parameters in mm/sec measured at liquid nitrogen temperature

Compound	Colour	This work I.S.	Q.S.	Exposed to air I.S.	Q.S.	Literature I.S.	Q.S.	
(I; X = OH)	Grey–purple	1·56	2·53	0·64	0·86	0·56	0·85	(ref. 4)
(II)	Violet	1·43	2·51	0·68	0·82	0·65	0·70	(ref. 2)
(I; X = H)	Purple	1·47	2·53	0·69	0·91	0·71	0·70	(ref. 2)
(III; X = CH_2–CH_2)	Lilac	1·24	2·50	0·65	0·82	0·60	0·81	(ref. 2)
(III; X = *o*-C_6H_4)	Green	1·20	2·42	0·63	0·81	0·66	0·76	(ref. 2)

polypropylene capsule. The Mössbauer spectra did not alter, when the potassium salts of the ligand were used as starting materials, showing the irrelevance of the pH of the solution. The iron(II) salicylaldoxime chelate (I) could not be prepared completely pure: the Mössbauer spectrum always showed the presence of a second species having nearly the same parameters as the air-exposed product. By measuring the volume of oxygen uptake at room temperature and atmospheric pressure, we found that all the complexes consumed $\frac{1}{4}O_2$ per iron atom, indicating normal oxidation to iron(III). Oxidation was particularly rapid in nonpolar solvents.

The Mössbauer spectra were taken with a constant acceleration spectrometer using a source of ^{57}Co in palladium. The absorption intensity of all compounds varied between 10—14% at liquid nitrogen temperature; a typical spectrum is given in the Figure. The Table lists the I.S. and Q.S. parameters; the I.S. values are given with respect to $Na_2Fe(CN)_5NO,2H_2O$; the accuracy is 0·03 mm/sec.

The observed Mössbauer parameters all fall in the range expected for high-spin iron(II) compounds and no special effects[1,2,4,5] need be invoked to rationalise them. After exposing the complexes to air the observed spectra are similar to those given by Stukan *et al.*[1] and Burger *et al.*[4] (see Table) and typical for iron(III) compounds. This observation stresses the importance of working under anaerobic conditions. In the presence of air, oxidation of iron(II) to iron(III) complexes might occur; the latter cannot unequivocally be distinguished from the iron(II) chelates by elemental analysis or magnetic measurements.[4,6] This work illustrates once more that Mössbauer spectroscopy is a powerful tool for determining oxidation states of metal atoms in co-ordination compounds. Deviations of Mössbauer parameters from expected values might be taken as evidence for the occurrence of undesirable reactions.

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