SYNTHESIS AND MOSSBAUER EFFECT STUDY OF IRON COMPLEXES OF TETRAOXALYL
PARA – PHENYLENE DIAMINE

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Tetraoxalyl para phenylene diamine (TO p-Ph D) has been synthesised. Fe(II) and Fe(III) complexes have been prepared in different media and their structures were proposed on the basis of elemental analysis, Infra-red measurements and Mossbauer studies. The study indicated that iron existed in different states of coordination and valence, where their ratio depends upon the medium used.

INTRODUCTION

Though there is a large number of inorganic compounds that contain metal ions of the same element in two formally different oxidation states, there are a very few organometalic compounds of this type known. Cowan *et al.* [1] reported the study of biferrocene [Fe(II)Fe(III)] picrate, where Vertes and Suba studied the mixed iron states in Formamide [2]. These studies clearly show the effect of electron exchange.

Generally, it is well known that the reaction between *para*-phenylene diamine and aliphatic dibasic acids depends upon the molar ratio of the reactants and the experimental conditions employed. At fusion condition, the dark infusible mass produced is said to be polymeric [3]. On the other hand, if reflux condition is employed and at molar ratio less than 1:4 (*para*-phenylene diamine: oxalic acid), acid imide, acid di-imide and various condensation products are obtained. However, at 1:4 molar ratio (*para*-phenylene diamine: oxalic acid), the tetrafunctional compound is obtained.

Tetrabasic compounds "tetrasuccinyl urea and tetra-oxalyl urea" were recently prepared [4]. The present work is mainly concerned with the reaction of *para*-phenylene diamine with oxalic acid aiming at producing tetrafunctional product tetraoxalyl *para*-phenylene diamine (TO p-Ph D). Also their ability to form iron (II) and (III) complexes is investigated by means of Mossbauer effect as well as infrared absorption spectra.

MATERIALS AND METHODS

All chemicals used throughout this work were of the

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purest grade available. The iron salts $FeSO_4$ and $FeCl_3$ are of the chemically pure grade and are the products of BDH., England.

Preparation of (TO p-Ph D). Tetraoxalyl *para*-phenylene diamine was prepared by refluxing a mixture of *para*-phenylene diamine (0.1 mole), Oxalic acid (0.4 moles) and 150 ml xylene in the Dean & Stark apparatus till the theoretical amount of water was collected. The solid obtained was washed with xylene followed by warmed ethanol, hot water and recrystallized from distilled water and dried at 50° in vacuo. The yield percentage was found to be 78.4% and the melting point of >300° Water of crystallization was estimated by heating at 140° under vacuum till constant weight.

Preparation of iron (II) and (III) complexes of (TO P-Ph D): A solution of ferrous sulphate ($FeSO_4$.$7H_2O$) (0.02 moles) in 50 ml ethanol was added dropwise to a solution of (0.1 mole) TO p-Ph D in 50 ml ethanol. The mixture was refluxed for 3 hr. in the presence of nitrogen atmosphere with stirring until the formation of a stable colour.

The product was filtered under nitrogen atmosphere, washed with absolute ethanol and dried in vacuo. The yield percentage was 85.2%. The above experiment was repeated several times using different media (ethanol: water) with different ratios (1:0); (1:1) and (1:3) and pure water [1-4]. Also the reaction was carried out with anhydrous $FeCl_3$ in the presence of distilled water as a medium [5].

The analytical data of the complexes obtained are included in Table [1].

Elemental analysis and molecular weight determination were carried out in microanalytical laboratories of El-Nasr Pharmaceutical Company and Cairo University. Iron was determined by Atomic absorption using Spectro photometer SP 191. Infra-red measurements were carried out using Pye-

Table 1. Characteristics of compounds (1-5)

No.	Medium and reactants	Colour	Analysis % Reqid/Found					Fe^{++}% by weight of total Iron from M E.	Formula
			Fe	Cl	C	H	N		
1	1 (TO p–Ph D) with $FeSO_4$ in Enthanol	pale brown	16.28 15.92	----	38.37 21.94	4.07 3.95	4.07 4.12	67 ±5	A $Fe_2(C_2H_5OH)_4$
2	1 with $FeSO_4$ in Ethanol water (1:1) by volume.		17.72 17.90	----	34.18 18.89	3.16 2.93	4.43 4.22	70 ±5	A $Fe_2(C_2H_5OH)_2 (H_2O)_2$
3	1 with $FeSO_4$ in Ethanol water (1:3) by volume.		18.54 17.79	-----	31.79 13.34	2.65 2.13	4.64 4.42	36 ±5	A $Fe_2C_2H_5OH.(H_2O)_3$
4	1 with $FeSO_4$ in distilled water	dark brown	19.44 18.32	----	29.17 13.32	2.08 1.91	4.86 4.20	34 ±5	A $Fe_2(H_2O)_4$
5	1 with anhydrous $FeCl_3$ in dist. water	reddish brown	15.53 16.10	29.54* 28.92*	23.30 11.90	1.11 1.01	3.88 3.62	Zero	$H_4A Fe_2Cl_6$

where A represents: $C_{14}N_2O_{12}$

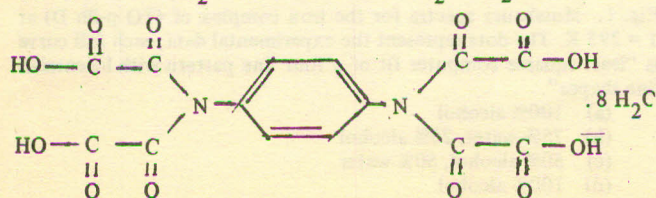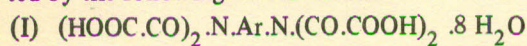* ionizable chlorine % reqd/found = 19.69/20.00
  attached chlorine % reqd/found = 9.85/10.50

Unicam SP 2000. Mossbauer spectra were recorded with a 512 multichannel analyzer, coupled to a constant acceleration driving system, the source was ^{57}Co (Rh), of 10 m Ci. Velocity calibration was done using the standard spectrum of metallic iron. Measurements were performed at room temperature. Analysis were done using a computer programme based on superposition of lorentzian lines with different position widths and intensities.

RESULTS & DISCUSSION

Recently tetrasuccinyl urea and tetraoxalyl urea were prepared by refluxing urea with succinic or oxalic acid in xylene [4, 5]. The amount of water liberated was taken as a criterion for the termination of the reaction. Similarly, TO-*para*phenylene diamine was prepared under identical experimental condition.

Structure I is suggested for this compound and is supported by the following consideration.

(I) $(HOOC.CO)_2.N.Ar.N.(CO.COOH)_2 .8 H_2O$

(i) Acid value determination, Reqd/Found: 566.77/520.70 mg KOH.

(ii) Amount of water liberated, Reqd/Found: 18/21.6 ml.

(iii) Elemental analysis.
Reqd.: C = 31.11%; H = 4.44; N = 5.19%
Found: C = 30.12%; H = 5.20; N = 5.69%

(iv) Molecular weight determination, Reqd/Found : 396/374.

(v) Potentiometric titration of I indicated that the dissociation constants of the four protons of TO-*para* phenylene diamine are $_pK_1$ = 3.00;
pK_2 = 3.65; $_pK_3$ = 8.45 and $_pK_4$ = 8.65.

(vi) X-ray analysis shows that this compound is crystalline.

(vii) Infra-red spectra show the characteristic bands of the various groups present (Table II).

The reaction of (TO p-Ph D) and $FeSO_4.7H_2O$ depends upon the medium employed. After purification, these products analysed as shown from Table I.

UV spectrum of the various Iron complexes showed a characteristic observation of the Fe-O bond at 285 nm.

It is worth mentioning that the lower values of carbon percentage in various iron complexes were observed and are attributed to the formation of metal carbides [6]. Treatments of sample No. 5 with $AgNO_3$ resulted in the precipi-

Table 2. Assignment of TO p-PH D and its iron complexes.

TO p-PH D	Fe complex	Vibration assignment
3200-3400[b]	3280[b]	C=C–H
1690-1720[m]	1720[m]	C=O belonging to EDTA (7)
1520[m]	1520[m]	C=C stretch
1320[s]	1360, 1310[s]	C–N st,
930[s]	945[s]	Carboxyl group
850[s]	860[s]	Para substitution in benzene ring
---	248[m]	(Fe)
---	830-780[s]	Fe–O band.
---	1580[s]	COO. . .Fe

tation of 4 equivalent moles of AgCl indicating that only ionic chlorine atoms are present outside the complex. On the other hand, the treatment of 5 with NaOH followed by neutralisation with HNO_3 prior to the addition of $AgNO_3$ resulted in the precipitation of 6 equivalent moles of AgCl. Both treatments indicated that the molecule contains two attached chlorine atoms in the inner sphere of the complex ion and 4 ionizable chlorine atoms outside the sphere.

It has been observed visually that the brownish colour density increases from sample 1 to 4 indicating an increase in the amount of ferric ion on increasing the water content in the medium.

The oxidizing properties of the (TO p-Ph D) can also be seen from the discharge of the colour of permenganate solution.

Infra-red measurements for (TO p-Ph D) and its iron complexes showed the characteristic bands for carbonyl, carboxy, *para* sbstitution in benzene ring, C=C–H and C–N as illustrated in Table 2.

The infra-red spectra of different iron complexes show a band in the region 1400-1300 cm^{-1} which is attributed to the coordinated oxalate groups. This is in agreement with Fornacous's work [8] who stated that CO stretching bands of the coordinated oxalate groups appear in the 1500-1200 cm^{-1} region for many oxalate complexes.

Mossbauer spectroscopy has been known in the last two decades as a powerful tool for identifying the state,

electronic structure, electron exchange, site preference and degree of site distortion in iron complexes. Fig. 1 shows the Mossbauer spectra of iron complexes of tetra-oxalyl *para*-phenylene diamine which were prepared in different media. It is clearly observed that iron is located in three different states which are octahedrally coordinated.

On the other hand the spectrum of sample 5 (cf. Fig. 2) shows iron to be as high spin Fe^{3+} in octahedral site. Such
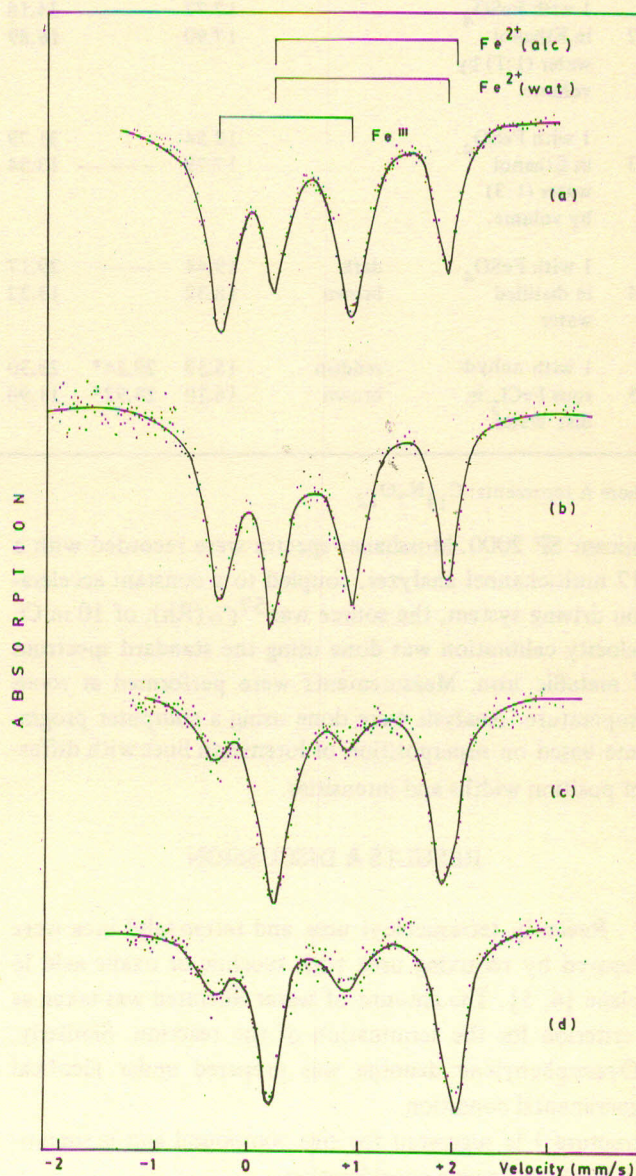

Fig. 1. Mossbauer spectra for the iron complex of (TO p-Ph D) at T = 295 K. The dots represent the experimental data; each full curve is "least squares computer fit of a four line pattern with lorentzian line shapes".
    (a)   100% alcohol
    (b)   75% water, 25% alcohol
    (c)   50% alcohol, 50% water
    (d)   100% alcohol

a result is expected on the basis of the strong oxidizing properties of tetraoxalyl *para*-phenylene diamine, as stated before, which does not affect the state of iron valence.

Table 3 gives the Mossbauer effect parameters at room temperature, where it can be seen that at site 1 the iron is in the low spin ferric state [9] where its concentration decreases on increasing alcohol content as given in Table 1. On the other hand two different high spin ferrous states are present in different ratios depending on the water content in the medium (alcohol, water mixture). Another observation is the relatively broad line width specially of the ferric state spectrum. Such a broadening indicates an electron exchange interaction. This will be further discussed in a later section.

It is most convenient to subdivide our discussion in to two different sub headings concerning the Mossbauer parameters.

(1) *Isomer shift*. The isomer shift arises because of the electron density at the nucleus interacting with the positive nuclear charge, and the relative energies of the ground and excited nuclear states are affected in much the same way, as the positive nuclear charge affects the energy of the

Fig. 2. Mossbauer spectrum of the ferric state complex of (TO p-Ph D) at T = 295 K.

electrons. Only electron density in the s-orbitals has a finite value at the nucleus. So electrons in *p* and *d* orbitals can affect the isomer shift only by screening the s electrons from the nuclear charge.

It is well established that in iron complexes [10] two main mechanisms affect the isomer shift:

(A) In high spin complexes where the s electron density in the 4s orbital is most important, i.e. the electron density decreases with increasing tendency of the ligands to withdraw electrons from the iron atom, the isomer shift is increased [11].

(B) In low spin complexes the main factor is the strength of the π bonding between the central atom and the ligands. Strong π bonding decreases the electron density in the metal *d*-orbitals and hence the screening of the s-electrons, which lowers the isomer shift. Simultaneously with this effect there is a contribution from σ bonding of the ligand, which has the opposite effect; the withdrawal of electrons increases the isomer shift.

Generally it is hard to distinguish between low spin iron (II) and iron (III) compounds from isomer shift alone. Nevertheless, a distinction in such cases can be made by considering the data of quadruple splitting in addition (see Table 3).
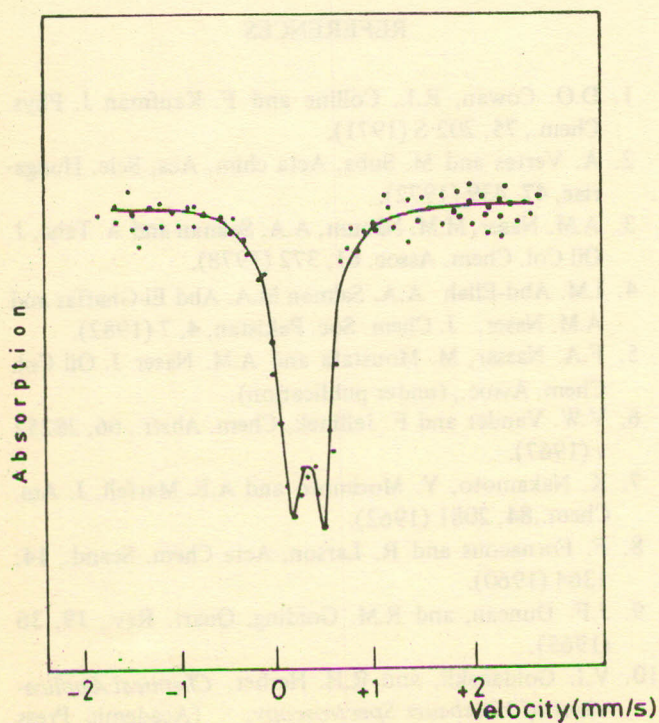
Table 3. Mossbauer effect parameters at room temperature

State	Fe (III)	Fe (II) Alchol	Fe (II) Water	Fe^{3+} sample 5
I.S* (mm/Sec)	+0.365	1.257	1.151	0.320
Q.S (mm/Sec)	+1.387	1.945	1.716	0.360
Line width (mm/Sec)	0.400	0.257	0.260	0.290

From the above it can be said that the ferric ions at sites 1 are connected with oxygen of the ligand with sigma bond which is enhanced by the presence of the benzene ring, where a relatively large isomer shift is observed for a low spin state [9]. Such bonding can be explained according to the valence bond theory where mixing the 3d, 4s and 4p orbitals of the central iron atom in the complex $Fe[(C_2O_4)(H_2O)_2]^{III}$ with nearly pure σ interaction as predicted from the above discussion yields six equivalent d^2sp^3 hybrid orbitals which form six σ bonds with different attached groups. This configuration forced the 3d electrons to spin pair against Hund's rule.

On the other hand, high spin ferrous ions presented at two different unequivalent sites depending upon the medium used. It is seen from the isomer shift values and according to W.W.J. Plott [11] the ferrous at site 2 is more ionic than in site 3. This indicates a tendency of the alcohol molecule to withdraw electrons from the outer shell of iron than water molecules, i.e. the isomer shift is more positive with increasing electronegativity of the ligand. It is possible to realize such variation in the isomer shift on the basis of valence bond theory assuming 4 ($sp^3 d^2$) hybrid orbitals in bond formation. Therefore, the removal of valence electrons of 4 ($sp^3 d^2$) character by electronegative ligand will effectively reduce the electron density at the nucleus which leads to increase the isomer shift.

(2) *Quadruple Splitting:* We may express the quadruple interaction (V_{zz}) as:

$$q_{zz} = V_{zz}/e = (1-R)q_{val} + (1-\gamma_\infty)q_{lat}$$

where R and γ_∞ are the sternheimer shielding and antishilding factors; q_{lat} is the electric field gradient (EFG) contribution from the charge of the nearest neighbours and q_{val} can be divided into two parts, $q_{CF} + q_{MO}$, where q_{CF} is due to EFG from the crystal field and q_{MO} is due to EFG of the non-spherical electron distribution in the valence molecular orbit.

Generally q_{CF} is significant in slightly distorted octahedron complexes of low spin ferric, with some admixture of q_{MO} as well as in high spin ferrous. At site 1 the observed quadruple splitting is relatively high with a broad line width and can be explained as follows:

In a ligand field of a regular octahedron symmetry the five fold degenerate set of *d* orbitals is split into a doubly degenerate set (e_g) and three fold degenerate (t_{2g}). The two degenerate groups are assymetrical in the presence of site distortion, where the t_{2g} state has lower energy and suffers a tetragonal compression which leads to a removal of the degeneracy and causing electrons to jump between the successive levels due to the thermal agitation. Such exchange between the orbits of t_{2g} should cause a distribution in the valence of q_{CF}. This is observed as a broadening in the experimental line width, where electron exchange are expected to affect profoundly the shape and intensity of the absorption curve. Systems that are exchanging at a rate faster than 10^8 sec^{-1} can show a broad Mossbauer line, since the mean life time of the Mossbauer active nuclear excited state is 1.4×10^{-7} sec.

At sites 2 and 3 we have six 3d electrons, i.e. one electron over and above the spherical $3d^5$ configuration, which has been confirmed as 5.6 Bohr magnetons. This will lead to significant contribution of q_{MO}.

To a first approximation one assumes that:

(a) Any quadruple splitting arises mainly from an unbalanced 3d orbital population, (b) any change in EFG is due to the varied ligand and not to a change in the bonding properties and (c) lattice contributions (q_{lat}) from neighbouring anions and cations are negligible. This should lead us to say that the ligand of site 2 is different than that of site 3 as observed by different quadruple splitting.

In conclusion we might say that the iron complexes of (TO p-Ph D) contains three different states (one of low spin ferric and two of high spin ferrous which are competing on taking places of different ligand forces and coordination symmetry). It is evident that we have a mixed valent inorganic solid where trapped valencies occupy one of the three unequivalent octahedral sites. The quantitative features of the spectra confirm that total oxidation number if assigned to the metal where there is no indication of a strong metal-metal interaction. The relatively broad Mossbauer line at site 1 probably indicates the existence of electron exchange between successive t_{2g} levels due to thermal agitation which take place at a rate less than 10^7 sec^{-1}.

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