

seems more reasonable to wonder why the potentials for the blue-copper systems are *so low* since X-ray crystallography of azurin<sup>4b</sup> and plastocyanin<sup>4a</sup> shows ligation of the copper by two sulfur atoms, extreme distortion from planar geometry, and the presence of an entirely hydrophobic environment about copper. Clearly, one difference is that our systems carry a greater overall charge in each oxidation state and that must contribute to a higher potential for our complexes based on electrostatic considerations. The statement that mercaptide sulfur produces a similar influence on the Cu(I)-Cu(II) potential as does a thioether sulfur<sup>8</sup> must be examined carefully therefore, since the anionic ligand will lower the overall charge on the complex and may accordingly shift the potential more negatively.

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**Supplementary Material Available:** Listings of observed and calculated structure factors and final positional and thermal parameters (50 pages). Ordering information is given on any current masthead page.

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## Mössbauer and X-ray Studies of Ferrous Malonate Dihydrate, Fe(C<sub>3</sub>H<sub>3</sub>O<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O

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Ferrous malonate dihydrate, Fe(C<sub>3</sub>H<sub>3</sub>O<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O, has been synthesized for the first time. The compound has a monomeric structure, isomorphous with magnesium malonate dihydrate with two molecules per unit cell and with space group *P*<sub>2</sub><sub>1</sub>/*c* and unit cell dimensions *a* = 4.96<sub>1</sub> Å, *b* = 11.40<sub>3</sub> Å, *c* = 9.61<sub>6</sub> Å, and β = 90.58°. The temperature dependence of quadrupole splitting and optical spectral data give ~10 400 cm<sup>-1</sup>, ~700 cm<sup>-1</sup>, ~100 cm<sup>-1</sup>, and ~1200 cm<sup>-1</sup> for the 10Dq, tetragonal field, rhombic field, and splitting of the E<sub>g</sub> level, respectively. The DTA and TGA curves indicate dehydration and decomposition to the oxide to occur at 160 and 350 °C, respectively.

### Introduction

Previous studies on the organic acid salts of divalent iron limited to formate and oxalate showed that the monobasic acid salt has a structure quite different from that of the dibasic acid salt.<sup>2</sup> A dibasic acid higher up in the series such as malonic acid may be expected to give rise to an iron compound structurally different from that of formate and oxalate on account of the separation of the two carboxylic acid groups by a -CH<sub>2</sub>- group reducing the spatial restriction in bonding. Our initial work on the malonate of iron employing Mössbauer spectroscopy provided evidence for the anticipated structural distinctions compared to those of formate and oxalate. As our own observations varied with those of Kwiatkowski et al.<sup>3,4</sup> on the iron malonic acid system, we have extended our work to an X-ray analysis of the powder pattern and established the isomorphous structure of the compound with magnesium malonate. As this system is being reported for the first time, information about the crystal field splitting of the ground state has been obtained by an analysis of the temperature dependence of quadrupole splitting.<sup>5</sup> Additional information on the crystal field splittings has been obtained by measuring the optical and photoacoustic spectra of the sample. The decomposition products of organic acid salts are of considerable interest.<sup>6</sup> Hence, DTA and TGA studies of the system have

been carried out. The possible evidence for the existence of the anhydrous form is obtained by decomposing the hydrate absorber in the Mössbauer cryofurnace under vacuum. The results of our investigations by Mössbauer, X-ray diffraction, and optical spectral studies and DTA and TGA studies are presented in this paper.

### Experimental Section

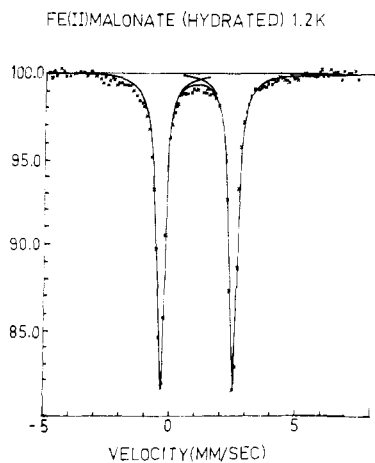
Ferrous malonate dihydrate was prepared by dissolving 500 mg of iron powder (electrolytic grade, Sarabhai Chemicals) in a hot aqueous solution containing an excess of malonic acid (Riedel) and concentrating the resultant solution to half the original volume and cooling to room temperature. Light green crystals separated out, which were filtered off on a Büchner funnel, washed with small quantities of water, and dried initially in air and then under vacuum at room temperature. Initially the preparations were carried out in a nitrogen atmosphere, but later it was found that the product is resistant to oxidation and can be conveniently prepared in the presence of air.

**Physical Measurements.** Microanalyses of carbon and hydrogen were carried out with use of a Hewlett-Packard Model 1858 C, H, N analyzer. Iron was analyzed by decomposing the product at 500 °C and weighing as Fe<sub>2</sub>O<sub>3</sub>. The analyses were found to correspond to the formula FeC<sub>6</sub>H<sub>10</sub>O<sub>10</sub>. (Anal. Calcd: Fe, 18.74; C, 24.18; H, 3.38. Found: Fe, 18.54; C, 24.61; H, 3.52.) This suggested a molecular formula similar to that of magnesium malonate dihydrate, viz., Fe(C<sub>3</sub>H<sub>3</sub>O<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O.

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were carried out with use of a Mom-Budapest derivatograph employing a heating rate of 10 °C/min.

Mössbauer spectra were recorded with use of a constant-acceleration Elscint drive in conjunction with a multichannel analyzer (Promeda). The data were acquired in 512 channels with a mirror-image spectrum simultaneously acquired. At least 10<sup>5</sup> counts were acquired to maintain good counting statistics. Measurements close to liquid-helium temperature were carried out with use of a modified Stohr 29-105 helium cryostat.<sup>7</sup> High-temperature measurements were made under vacuum

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**Figure 1.** Mössbauer spectrum of ferrous malonate dihydrate at 1.2 K.

with use of an Elscint Model MF-2A Mössbauer furnace. In all the cases a 5-mCi  $^{57}\text{Co}/\text{Rh}$  source and an absorber containing 10 mg of natural iron/cm<sup>2</sup> were employed. The isomer shift values relative to iron foil were obtained by applying a correction factor of 0.11 mm/s for measurements at 300 and 77 K and 0.14 mm/s at very low temperatures.<sup>8</sup> The errors quoted in the Mössbauer parameters are standard deviations obtained in velocity calibrations using a laser.<sup>7,9</sup>

The photoacoustic spectra were recorded on a Princeton Applied Research Model 6001 instrument. The spectra were corrected for blank absorption and normalized with use of carbon black as reference. The normalization corrects the observed spectrum for the power variation in the source over the spectral region of interest. The optical spectra were recorded in a Cary 17 model spectrometer with use of quartz cells of path length 1 mm.

### Results and Discussion

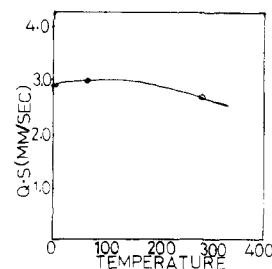
**Mössbauer Spectra.** Ferrous malonate dihydrate prepared as described earlier exhibits several features indicating structural differences from the earlier studied organic acid salts of iron. First, the malonate is quite soluble in water whereas the oxalate is known to be sparingly soluble. Second, in the case of the malonate synthesized by us, 1 mol of iron combined with 2 mol of the acid, whereas the oxalate has a metal to ligand ratio of 1:1. Our end product is different from that of Kwiatkowski et al., who have reported the formation of a compound with a 1:1 metal to ligand ratio on dissolution of iron in a hot dilute aqueous solution of malonic acid in the absence of air.<sup>3,4</sup> Third, a comparison of the Mössbauer spectrum of ferrous malonate dihydrate with that of ferrous oxalate dihydrate shows the following differences. Although both the oxalate and malonate give rise to similar quadrupole-split room-temperature spectra, the former gives rise on cooling below 18 K to an eight-line spectrum whereas the malonate retains the quadrupole-split character even on cooling to 1.2 K (Figure 1). There is however observable line broadening due to relaxation effects. These observations indicate that in the oxalate with a polymeric structure a large internal magnetic field arises presumably due to strong metal-metal interaction via a superexchange mechanism, and in the case of the malonate, poor metal-metal interaction is observed, suggesting a monomeric structure. These observations also suggest isomorphism of the iron and magnesium malonates.

The isomer shift and the quadrupole-split data obtained for the malonate in the temperature range 1.2–300 K are reproduced in Table I. In general isomer shift increases as tem-

**Table I.** Mössbauer Parameters

temp, K	IS, <sup>a</sup> mm/s (±0.01)	QS, mm/s (±0.02)	Γ, mm/s
300	1.15	2.68	0.27
77	1.23	2.98	0.27
4.2	1.09	2.87	0.39
1.2	1.12	2.90	0.39

<sup>a</sup> With respect to Fe foil.



**Figure 2.** Variation of quadrupole split as a function of temperature. Experimental data are given as points, and the line gives the theoretical fit.

perature decreases. The anomaly in the values obtained close to absolute zero may be due to relaxation effects as shown by the line broadening. One can obtain semiquantitative information on the crystal field parameters by an analysis of the temperature dependence of quadrupole splitting for the high-spin divalent iron ( $3d^6$ ) case. This was done by diagonalizing the  $15 \times 15$  matrix to obtain the energy levels arising from the  $^5T_g$  levels of the  $\text{Fe}^{2+}$  ion in an octahedral field with tetragonal ( $\delta$ ) and rhombic ( $\epsilon$ ) distortions and assuming that contributions from the  $^5E_g$  levels may be ignored. Employing a value of  $\lambda = -80 \text{ cm}^{-1}$  for the spin-orbit coupling constant,<sup>5</sup> we obtained good fit (Figure 2) for  $\delta = 700 \text{ cm}^{-1}$  and  $\epsilon = 100 \text{ cm}^{-1}$  with the orbital singlet ( $d_{xy}$ ) lying lowest. A rhombic field was introduced on the basis of isomorphism of this compound with magnesium malonate dihydrate, which has a  $D_{2h}$  symmetry as shown by our X-ray data. A fit with  $\delta = 700 \text{ cm}^{-1}$  and zero rhombic field does not alter the theoretical curve significantly. Thus the quadrupole splitting data alone are inadequate in establishing the presence or absence of rhombic distortion.

**X-ray Studies.** In order to establish the exact nature of the compound obtained, we took a powder X-ray diffractogram using nickel-filtered  $\text{Cu K}\alpha$  radiation. The powder pattern so obtained does not tally with that reported by Kwiatkowski<sup>3</sup> for  $\text{Fe}(\text{C}_3\text{H}_3\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ . Single crystals of the ferrous malonate dihydrate obtained in the present study were therefore subjected to further X-ray analysis. The cell parameters were determined from Weissenberg and precession photographs. The values are  $a = 4.96_1 \text{ \AA}$ ,  $b = 11.40_3 \text{ \AA}$ ,  $c = 9.61_6 \text{ \AA}$ , and  $\beta = 90.58^\circ$ . From the systematic absences observed the space group was determined to be  $P2_1/c$ . The density of the crystal measured with use of a density bottle is  $1.81 \text{ g/cm}^3$ . The calculated density is  $1.82 \text{ g/cm}^3$  for  $Z = 2$ . The values of these cell parameters are very close to those of  $\text{Mg}(\text{C}_3\text{H}_3\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$  as reported by Briggman and Oskarsson.<sup>10</sup> X-ray powder patterns of  $\text{Mg}(\text{C}_3\text{H}_3\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$  were taken and compared with those of the ferrous malonate dihydrate prepared by us. The indexed powder patterns of both these compounds are given in Tables II and III. From these powder data it is clearly seen that both of these compounds are isomorphous.

It may be mentioned here that the X-ray data reported for  $\text{Fe}(\text{C}_3\text{H}_3\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$  reveal certain discrepancies. On the basis of the systematic absences observed, the space group assigned

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Table II. X-ray Data of Magnesium Malonate Dihydrate

$d(\text{obsd}), \text{Å}$	$d(\text{calcd}), \text{Å}$	$I/I_0$	$hkl$
7.35	7.34	100	011
5.66	5.65	64	020
4.95	4.94	22	100
4.83	4.824	25	002
4.44	4.44	8	012
4.11	4.11	22	111
3.68	3.67	6	022
3.51	3.51	31	031
3.46	3.46	90	102
3.30	3.31	100	112
3.10	3.09	10	013
2.95	2.95	38	122
2.86	2.87	22	131
2.828	2.827	10	040
2.622	2.628	18	113
2.545	2.549	11	132
2.475	2.470	13	200
2.443	2.438	20	123
2.361	2.359	12	014
2.191	2.196	30	133
2.170	2.172	12	104
2.056	2.053	12	222
2.023	2.022	13	231
1.949	1.948	8	143
1.925	1.925	19	213
1.859	1.860	6	240
1.838	1.835	7	044
1.755	1.756	8	062
1.734	1.730	9	204
1.704	1.701	10	214
1.653	1.655	6	162
1.621	1.625	5	135
1.595	1.594	6	045

Table III. X-ray Data of Ferrous Malonate Dihydrate

$d(\text{obsd}), \text{Å}$	$d(\text{calcd}), \text{Å}$	$hkl$	$I/I_0$
7.37	7.35	011	100
5.72	5.70	020	15
4.95	4.96	100	13
4.82	4.81	002	17
4.10	4.13	111	33
3.69	3.68	022	12
3.52	3.53	031	30
3.45	3.47	102	100
3.29	3.29	112	100
3.10	3.09	013	5
2.97	2.96	122	10
2.894	2.88	131	10
2.855	2.850	040	15
2.610	2.608	113	25
2.548	2.548	132	5
2.495	2.480	200	3
2.440	2.443	123	3
2.350	2.352	014	3
2.206	2.204	133	7
2.200	2.203	142	10
2.050	2.048	222	12
2.025	2.027	151	7
1.926	1.924	213	22
1.841	1.839	241	7
1.752	1.748	242	5
1.740	1.743	153	5
1.704	1.705	125	4
1.658	1.659	224	2
1.610	1.611	243	2

was  $P2_12_12$ . It is stated by the authors that  $h0l$  reflections are present only if  $h = 2n$ , a condition that is not consistent with the space group assigned, viz.,  $P2_12_12$ . The unit cell lengths reported by Kwiatkowski et al. are close to those of the monoclinic calcium malonate dihydrate reported by Briggman and Oskarsson.<sup>11</sup> The possibility of isomorphism

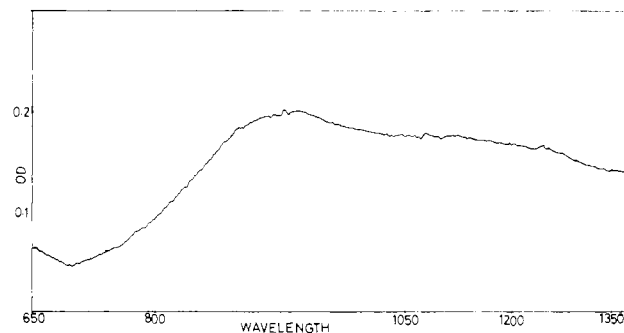


Figure 3. Optical spectrum of a solution of ferrous malonate dihydrate ( $\sim 0.06 \text{ M}$ ) (wavelength in nm).

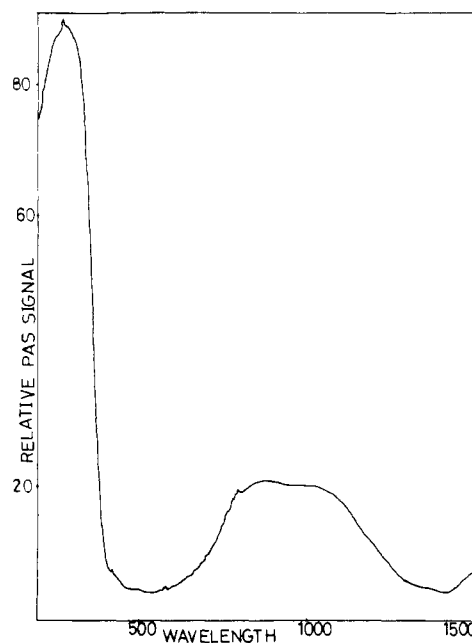


Figure 4. Photoacoustic spectrum of solid ferrous malonate dihydrate (wavelength in nm).

of these two forms needs further investigation.

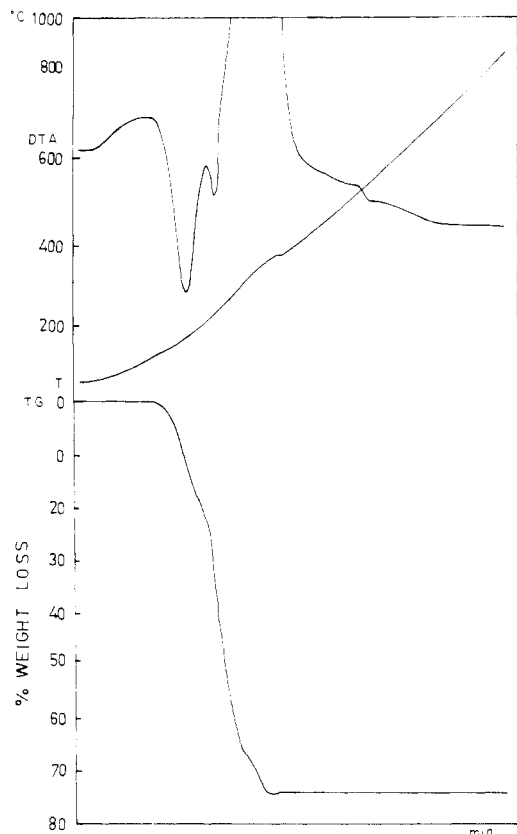
**Optical Spectra.** Optical spectra can give information about lower ligand fields. The solution spectrum of ferrous malonate dihydrate, which is reproduced in Figure 3, gives a broad asymmetric absorption maximum around  $10400 \text{ cm}^{-1}$  with an extinction coefficient of  $\sim 4.8$ , indicating that the absorption arises due to  $d-d$  transitions.<sup>12</sup> For the achievement of more precise absorption maxima, the solid-state spectrum was recorded with use of a photoacoustic spectrometer and is reproduced in Figure 4. The spectrum shows a charge-transfer band at  $\sim 25000 \text{ cm}^{-1}$  and an asymmetric absorption band with shoulders, the center of gravity of which was found to be at  $\sim 10500 \text{ cm}^{-1}$ . The band has a definite doublet structure with a peak separation of  $\sim 1200 \text{ cm}^{-1}$ . The spectrum is very similar to those reported earlier for high-spin  $\text{Fe}^{2+}$  cases<sup>13</sup> and arises due to  ${}^5T_{2g} \rightarrow {}^5E_g$  transition. The splitting can arise either due to the splitting of the excited state in a permanently distorted ligand field as in the case of ferrous ammonium sulfate or due to Jahn-Teller distortions.<sup>13,14</sup> If we go by the magnesium malonate dihydrate structure, the metal ion is situated at M-O distances  $2.063 \text{ Å}$  and O-M-O angles  $90 \pm 3^\circ$ , signifying considerably less distortion than encountered in ferrous ammonium sulfate.<sup>14</sup> A final conclusion on the reasons for splitting can therefore be made only after detailed

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**Figure 5.** DTA and TGA curves of ferrous malonate dihydrate. X-ray data become available.

**Decomposition Studies.** The DTA and TGA curves obtained for ferrous malonate dihydrate are reproduced in Figure 5. The compound starts decomposing at 120 °C and gives rise to an exothermic peak between 120 and 210 °C. The weight loss corresponding to the anhydrous product (15.4%) has been found to occur at 160 °C. Thus it appears that in the presence of air in the above temperature region both dehydration and decomposition take place simultaneously as in the case of oxalate.<sup>6</sup> After 350 °C no significant weight loss took place beyond 75%, a value corresponding to the formation of  $\text{Fe}_2\text{O}_3$  (73.19%). The profile is significantly different from that of the oxalate in that the second peak in the 380–538 °C region attributed to amorphous to crystalline transformation of the

oxide is not observed. The decomposition product heated to 550 °C for 2 h gave rise to a six-line Mössbauer spectrum characteristic of  $\alpha\text{-Fe}_2\text{O}_3$  free from any detectable impurities. So that the existence of the anhydrous malonate might be established, the material kept in the form of a Mössbauer absorber is heated under vacuum. It was found that even at 106 °C this material gave rise to a significantly different two-line spectrum with an isomer shift of 1.04 mm/s (Fe) and a quadrupole splitting of 1.70 mm/s. When the absorber was cooled to room temperature, the isomer shift remained unchanged but the quadrupole splitting changed to 2.00 mm/s. The isomer shift observed is close to values reported for  $\text{Fe}^{2+}$  surrounded by oxide ions in a tetrahedral geometry.<sup>15</sup> Further support for a tetrahedral geometry is obtained from the fact that the change in the quadrupole splitting as a function of temperature is as much as 0.003 mm/(s deg), a value characteristic for tetrahedral high-spin iron.<sup>5,16</sup>

### Conclusions

Malonic acid and iron are found to combine to form a compound of the formula  $\text{Fe}(\text{C}_3\text{H}_3\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ . X-ray studies show that the material prepared by us is isomorphous with magnesium malonate dihydrate. Mössbauer spectra do not show Zeeman splittings even up to 1.2 K in accordance with the monomeric structure. The temperature dependence of quadrupole splitting and optical spectra give rise to crystal field parameters of  $\sim 10\,400$ ,  $\sim 700$ , and  $\sim 100\text{ cm}^{-1}$  for  $10Dq$ , tetragonal field, and rhombic field, respectively, and a splitting of  $\sim 1200\text{ cm}^{-1}$  for the excited-state splitting.

Decomposition studies by DTA and TGA indicate dehydration and decomposition to the oxide form to take place at 120 and 350 °C, respectively. Vacuum decomposition at 106 °C gives rise to a Mössbauer spectrum characteristic of high-spin divalent iron in a tetrahedral site, which may be attributed to the anhydrous malonate.

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**Registry No.**  $\text{Fe}(\text{C}_3\text{H}_3\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ , 79855-57-5.

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