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Malonates of Bi- and Ter-valent Metal Ions

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Some complexes and salts of malonic, ethylmalonic and benzyl malonic acids have been prepared and characterised. The following metal ions have been used in this study; Al(III), Co(III), Fe(III), Cr(III), Cu(II), Co(II), Ni(II), Zn(II), Cd(II). The literature concerning the correlation of physical properties with structure has been reviewed, for the malonates. In particular, the correlations between the CO_2 stretching bands in the infrared spectrum, the structure and the effective ionic radius is discussed. The results indicate that stronger metal–oxygen bonding is produced with ethylmalonic acid, than with either of the other two acids.

Introduction

Crystallographic work has shown that the conformation of the six-membered malonate ring is dependent upon its environment in the solid state [1]. In solution, using n.m.r. methods, the acidity of the α-protons of free malonic- [2], ethylmalonic- [2], benzyl-malonic acids [3], and of malonate ligands chelated to Co(III) have been demonstrated [2, 4–7]. This paper presents a further investigation of the compounds of these three acids with bi- and tervalent metal ions.

Experimental

Preparation of the Compounds Aluminium(III) Complexes

$K_3[Almal_3]6H_2O$, $K_3[Al(etmal)_3]6H_2O$ and $K_3[Al(bzylmal)_3]3H_2O$ were prepared as described previously [3]. Analyses are given in Table I. Crystal data for the malonato complex is as follows: $K_3[Almal_3]6H_2O$, monoclinic, $a = 8.26_3$, $b = 13.01_8$, $c = 14.24_0$, $\beta = 67.99$, $U = 1420.19$ Å^3, $Z = 4$, $D = 2.6$ g cm^{-3}, space group $P2_1/c$.

Iron(III) Complexes

$Na_3[Femal_3]4H_2O$, $Na_3[Fe(etmal)_3]2H_2O$ and $Na_3[Fe(bzylmal)_3]2H_2O$ were prepared by the method of Scholtz [8] for the malonato complex, and analysis are given in Table I. The green, air- and moisture-sensitive compounds were stored in a desiccator in the dark.

Cobalt(III) Complexes

$K_2[Comal_3]4H_2O$ was prepared by the method of Lohmiller [9], at the final crystallisation stage, absolute ethanol was added to the green oil to induce crystallisation. The compound was sensitive to light and moisture and decomposed to the pink cobalt(II) compound. Although the analysis results gave low values for carbon (Table I) crystal data agreed with the literature (10): $K_3[Comal_3]4H_2O$, orthorhombic, $a = 12.31_7$, $b = 12.06_7$, $c = 14.05_0$, $\alpha = \beta = \gamma = 90°$, $U = 391.137$ Å^3, $Z = 8$, space group $Pna2_1$.

Attempts to isolate the tris(ethylmalonato)- and tris(benzylmalonato)cobalt(III) complexes proved unsuccessful, neither complexes could be prepared although modifications of the literature methods for the malonato complexes [9, 11] were tried. In each case the complexes could be obtained as green oils at low temperatures, but on crystallisation they rapidly converted to pink Co(II) species.

Chromium(III) Complex

Trans $K[Crmal_2(OH)_2)_2]$ was prepared by the method of Chang [12]. In the solid state the bands in the visible region were at 18.200 cm^{-1} (550 nm) and 24.450 cm^{-1} (409 nm) near the literature values for aqueous solution [12, 13].

Malonates of Bivalent Metals

All simple malonates, except that of Ni(II) which was prepared by Ive's method [14], were prepared in the following way. A slight excess of the metal carbonate was added to a solution of malonic acid. The mixture was stirred and heated for 2 h at 35 °C. The excess of carbonate was filtered off and the filtrate was concentrated using a rotary evaporator. The concentrate was set aside to crystallise, and finally the products were filtered off and air dried. The crystal data for Zn mal $2H_2O$ was as follows: monoclinic, $a = 11.062_5$, $b = 7.422_1$, $c = 7.290_1$, $\alpha = \gamma = 90.000$, $\beta = 92.27_5$, $U = 596.03$ Å^3, $Z = 4$, space group I2/m. These values are in good agreement with those in the literature [15]. $Na_2[Cumal_2(OH)_2)_2]$ was prepared by the method of Riley [16].

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TABLE I. Analysis Results for Some Compounds of Malonic, Ethylmalonic and Benzylmalonic Acids.

No.	Compound	% Found				% Theory			
		C	H	K/Na[a]	*M*[b]	C	H	K/Na	M
1	$K_3[Al\,mal_3]6H_2O$	19.2	3.1	20.8	–	19.3	3.2	21.0	–
2	$K_3[Co\,mal_3]4H_2O$	17.0	2.5	21.6	–	19.5	2.5	21.8	–
3	$Na_3[Fe\,mal_3]4H_2O$	21.7	2.7	13.6	11.1	21.5	2.8	13.7	11.1
4	$K[Cr\,mal_2(OH_2)_2]3H_2O$	18.7	3.5	10.15	13.8	18.7	3.6	10.15	13.5
5	$Na_2[Cu\,mal_2(OH_2)_2]$	20.7	2.3	–	18.3	20.6	2.3	–	18.2
6	Co mal $2H_2O$	18.8	3.0	–	29.6	18.3	3.1	–	29.9
7	Ni mal $2H_2O$	18.2	3.0	–	30.3	18.3	3.1	–	29.8
8	Zn mal $2H_2O$	17.5	2.9	–	32.2	17.7	2.9	–	32.1
9	Cu mal $2.5H_2O$	17.0	3.3	–	29.9	17.1	3.3	–	30.1
10	Cd mal H_2O	15.2	1.6	–	48.2	15.4	1.7	–	48.4
11	$K_3[Al(etmal)_3]6H_2O$	30.6	4.3	19.3	–	30.6	4.1	19.9	–
12	$Na_3[Fe(etmal)_3]2H_2O$	32.8	4.0	12.5	9.9	32.7	4.0	12.5	10.1
13	Co etmal $2H_2O$	26.8	4.7	–	26.0	26.7	4.5	–	26.2
14	Ni etmal$\cdot Ni(OH)_2 3H_2O$	23.1	4.0	–	34.2	22.9	3.8	–	33.6
15	Zn etmal $2H_2O$	25.6	4.5	–	28.0	25.9	4.3	–	28.2
16	Cu etmal $2H_2O$	26.1	4.6	–	27.45	26.1	4.4	–	27.7
17	Cd etmal H_2O	23.1	3.0	–	43.1	23.1	3.1	–	43.2
18	$K_3[Al(bzylmal)_3]3H_2O$	46.1	3.8	15.0	–	46.5	3.9	15.1	–
19	$Na_3[Fe(bzylmal)_3]2H_2O$	48.8	3.8	9.2	7.4	48.9	3.8	9.4	7.6
20	Co bzylmal $2H_2O$	42.1	3.5	–	20.4	41.8	4.2	–	20.5
21	Ni bzylmal $2H_2O$	41.4	4.5	–	20.3	41.8	4.2	–	20.5
22	Zn bzylmal $2.5H_2O$	39.7	4.2	–	21.0	39.7	4.3	–	21.0
23	Cd bzylmal H_2O	37.0	3.1	–	34.4	37.2	3.1	–	34.8
24	Cu bzylmal $0.5H_2O$	44.9	3.2	–	23.95	45.4	3.4	–	24.0

[a] By flame photometry. [b] By atomic absorption.

Ethylmalonates of Bivalent Metals

These compounds were prepared in the same way as the malonates. The Ni(II) compound was prepared bu Ive's method [14], and analysis (Table I) showed that it was the basic salt. Difficulty was encountered in the filtration of the ethylmalonates, Whatman paper 5V and suction was used in all cases.

Benzylmalonates of Bivalent Metals

These compounds were prepared in a similar way, but it was found that considerable foaming occurs during the preparation, and again difficulty was found at the filtration step. The reactions took much longer than in the cases of the malonato and ethylmalonato compounds, and the mixtures were stirred for a number of days at room temperature before the excess of carbonate was filtered off. Analysis results are shown in Table I.

Spectroscopic Measurements

Infrared spectra were measured using a Perkin-Elmer 457 spectrometer, samples were as nujol or hexachlorbutadiene mulls or as KBr discs. The electronic spectra of freshly ground solid sample were measured using a Pye-Unicam SP700 recording spectrophotometer fitted with the SP735 solid state attachment, and with freshly prepared MgO as reference.

Magnetic measurements were made by the Gouy method using a Newport variable temperature balance with $Hg[Co(NCS)_4]$ as calibrant.

Powder pattern diffraction traces were recorded using a Philips PW1011 X-ray diffractometer, with Ni-filtered CuK radiation ($\lambda = 1.54178$ Å^3). Computations were performed using the programmes of Langford and Marriner [17, 18].

Mössbauer spectra were measured at Birkbeck College using a $^{57}Co(Pd)$ source and a Harwell Research Proportional counter. Powdered samples of the Fe(III) complexes were measured at 290.5 and 60 K.

Results

Infrared Spectra

Positions of the bands in the CO_2 stretching regions are shown in Table II.

Visible Spectra

Bands in the solid state diffuse reflectance spectra are shown in Table III.

TABLE II. Bands (cm^{-1}) in the CO_2 Stretching Region^a.

Malonates						
1 Al(III)	2 Co(III)	3 Fe(III)	4 Cr(III)	5 Cu(II)		
1640, sb^b	1570, sb	1625, sb	1595, sb	1610, s	ν_a	
				1580, s		
1370, s	1360, sb	1390, s	1385, m	1405, m	ν_s	
			1338, m	1365, m		
270	210	235	–	–	Δ^c	
6 Co(II)	7 Ni(II)	8 Zn(II)	9 Cu(II)	10 Cd(II)		
1570, sb	1580, sb	1565, sb	1590, sb	1560, sb	ν_a	
1375, s	1380, s	1375, s	1370, s	1380, s	ν_s	
195	200	190	220	180	Δ	
Ethylmalonates						
11 Al(III)	12 Fe(III)	13 Co(II)	14 Ni(II)			
1640–1610, sb	1615, sb	1580–1540, sb	1600–1550, sb	ν_a		
1340, m	1345, s	1360, s	1355, m	ν_s		
285^d	270	200^d	270^d	Δ		
15 Zn(II)	16 Cu(II)	17 Cd(II)				
1620–1560, sb	1610–1540, sb	1555, sb	ν_a			
1360, s	1360, s	1380, s	ν_s			
230^d	215^d	175	Δ			
Benzylmalonates						
18 Al(III)	19 Fe(III)	21 Ni(II)	22 Zn(II)	23 Cd(II)	24 Cu(II)	
1635, vs b	1610, vs b	1570, vs b	1600, vs b	1560, sb	1610, s	ν_a
					1590, s	
1400, s	1390, s	1355, m	1415, s	1370, vs	1350, vs	ν_s
235	220	215	185	190	250^d	Δ

Malonates						
1 Al(III)	2 Co(III)	3 Fe(III)	4 Cr(III)	5 Cu(II)		
1640, sb^b	1570, sb	1625, sb	1595, sb	1610, s	ν_a	
				1580, s		
1370, s	1360, sb	1390, s	1385, m	1405, m	ν_s	
			1338, m	1365, m		
270	210	235	–	–	Δ^c	
6 Co(II)	7 Ni(II)	8 Zn(II)	9 Cu(II)	10 Cd(II)		
1570, sb	1580, sb	1565, sb	1590, sb	1560, sb	ν_a	
1375, s	1380, s	1375, s	1370, s	1380, s	ν_s	
195	200	190	220	180	Δ	
Ethylmalonates						
11 Al(III)	12 Fe(III)	13 Co(II)	14 Ni(II)			
1640–1610, sb	1615, sb	1580–1540, sb	1600–1550, sb	ν_a		
1340, m	1345, s	1360, s	1355, m	ν_s		
285^d	270	200^d	270^d	Δ		
15 Zn(II)	16 Cu(II)	17 Cd(II)				
1620–1560, sb	1610–1540, sb	1555, sb	ν_a			
1360, s	1360, s	1380, s	ν_s			
230^d	215^d	175	Δ			
Benzylmalonates						
18 Al(III)	19 Fe(III)	21 Ni(II)	22 Zn(II)	23 Cd(II)	24 Cu(II)	
1635, vs b	1610, vs b	1570, vs b	1600, vs b	1560, sb	1610, s	ν_a
					1590, s	
1400, s	1390, s	1355, m	1415, s	1370, vs	1350, vs	ν_s
235	220	215	185	190	250^d	Δ

(continued overleaf)

TABLE II *(continued)*

Acids		
malonic	ethylmalonic	benzylmalonic
1730, vs	1740–1700, vs b	1760, vs
1710, vs		1735, s
1439, s	1420, s	1452, vs
1310, s	1300, s	
	1270, s	

^a^Compound numbers from Table I. ^b^s = strong, b = broad, m = medium, v = very. ^c^$\Delta = (\nu_a - \nu_s)$. ^d^Average value.

TABLE III. Diffuse Reflectance Spectra of Malonates. Band Maxima (cm^{-1}).

Fe(III) complexes	3 mal	12 etmal	19 bzylmal	
	10,400	10,500	11,900	$^6A_{1g} \rightarrow {}^4T_{1g}$
	15,400	14,400	16,500	$\rightarrow {}^4T_{2g}$
	22,600	22,500	25,700	$\rightarrow {}^4A_{1g}$
	25,700	25,600	25,700	$\rightarrow {}^4T_{2g}$
Co(II) compounds	6 mal	13 etmal	20 bzylmal	
	8,200	11,500	8,100	$^4T_{1g}(F) \rightarrow {}^4T_{2g}$
	16,600	16,700	15,400	$\rightarrow {}^4A_{2g}$
	20,000	19,500	19,100	$\rightarrow {}^4T_{1g}(p)$
Ni(II) compounds	7 mal	14 etmal	21 bzylmal	
	8,300	8,300	8,100	$^3A_{2g} \rightarrow {}^3T_{2g}$
	14,600	14,400	14,500	$\rightarrow {}^3T_{1g}(F)$
	25,300	24,800	24,900	$\rightarrow {}^3T_{1g}(p)$
Cu(II) compounds	9 mal	16 etmal	24 bzylmal	
	13,800	9,400	14,400	

Magnetic Moments

Magnetic moments over a range of temperatures are shown in Table IV. The diamagnetic corrections were measured at room temperature for the three acids and the results are shown in Table V.

Mossbauer Spectra

The mossbauer spectra of the three FeIII complexes were as follows: malonato, 0.45 mm s^{-1}; benzylmalonato, 0.42 mm s^{-1}; ethylmalonato, 0.36 mm s^{-1}.

Discussion

Few of the structures of the compounds in this study have been determined. No structures of the ethylmalonates nor of the benzylmalonates have been investigated. The malonate ligand is extremely versatile in its mode of bonding to metal ions, this point has been discussed by Karipides *et al.* [24]. The group can form a six-membered ring with two unidentate carboxyl groups, four-membered rings with bidentate carboxyl groups, or combinations of these modes of bonding. Of the malonates of bivalent metals in this study, the structure of the Cd(II) compound alone has been determined [25]. The structure is unusual in that each malonate forms one six-membered ring and two four-membered rings. Each cadmium is seven-coordinate. Similar bonding is found in $Eu_2(mal)_3 8H_2O$ [26].

The molecular structures of the compounds of the type M mal $2H_2O$ (M = Co, Ni, Zn) have not been determined, but these compounds have been found to be isomorphous, all are monoclinic with space group I2/m [15]. Our crystal data for Zn mal $2H_2O$ are in agreement with those of Walter–Levy *et al.* [15], (See experimental section).

As well as its versatility in its mode of coordination to metal centres [24], the six-membered chelate ring appears in different conformations (see Fig. 2 in that article) which have been discussed by Butler and Snow [1], with particular reference to M(III) malonates. The structures of Cr(III) [10, 27, 28], Mn(III) [29–31] and Co(III) [1, 32, 33] complexes have been reported. These structural studies have revealed that the malonate chelate ring shows a high degree of conformational flexibility. In

TABLE IV. Magnetic Moments of Some Metal Malonates[a] (Bohr Magnetons).

	T/K	112	132.5	152	171.5	212	233	253	273	293			
3 Fe(III)	μ_{eff}/BM	5.91	5.94	5.94	5.91	5.91	5.91	5.92	5.92	5.92			
	T/K	112.5	132.5	152	172	192.5	212	233	253.5	273	293		
12 Fe(III)	μ_{eff}/BM	5.92	5.92	5.92	5.93	5.94	5.94	5.96	5.96	5.93	5.94		
	T/K	113	133	153	173	193	213	233	253	273	293		
19 Fe(III)	μ_{eff}/BM	5.73	5.75	5.77	5.77	5.77	5.80	5.83	5.83	5.83	5.84		
	T/K	113	133	153	173	193	213	233	253	273	293		
6 Co(II)	μ_{eff}/BM	4.74	4.72	4.74	4.75	4.75	4.74	4.75	4.75	4.74	4.75		
	T/K	112.5	132.5	152	171.5	191.5	212.5	233	253.5	273	293	313	
13 Co(II)	μ_{eff}/BM	4.72	4.73	4.72	4.72	4.71	4.72	4.72	4.72	4.72	4.72	4.73	
	T/K	113	133	153	173	193	213	233	253	273	293		
20 Co(II)	μ_{eff}/BM	4.88	4.89	4.90	4.91	4.92	4.93	4.95	4.96	5.00	5.03		
	T/K	112.5	132.5	152	172	192.5	212	233	253.5	273	293	313	
7 Ni(II)	μ_{eff}/BM	3.18	3.2	3.20	3.21	3.21	3.19	3.20	3.21	3.21	3.22	3.22	
	T/K	112	132.5	152	171	191.5	212.5	233	253.5	273	293	313	
14 Ni(II)	μ_{eff}/BM	3.12	3.12	3.11	3.10	3.10	3.12	3.12	3.11	3.10	3.11	3.10	
	T/K	112.5	132.5	152	172	192.5	212	233	253.5	273	293	313	
21 Ni(II)	μ_{eff}/BM	3.14	3.15	3.15	3.15	3.15	3.15	3.15	3.15	3.15	3.15	3.16	
	T/K	113	133	153	173	193	213	233	253	273	293		
5 Cu(II)	μ_{eff}/BM	1.95	1.94	1.93	1.93	1.93	1.92	1.91	1.90	1.90	1.88		
	T/K	112.5	132.5	152	172	192.5	212	233	153.5	273	293	313	323
9 Cu(II)	μ_{eff}/BM	1.91	1.91	1.91	1.91	1.91	1.90	1.91	1.91	1.90	1.91	1.89	1.98
	T/K	112.5	132.5	152	171.5	191.5	212.5	233	153.5	273	293	313	323
16 Cu(II)	μ_{eff}/BM	1.88	1.89	1.89	1.88	1.88	1.88	1.88	1.87	1.96	1.97	1.87	1.86

[a]Compound numbers from Table I.

TABLE V. Values of Diamagnetic Susceptibility (-10^6 c g s Units)

	χ_{obs} (293 K)	Literature values
malH$_2$	51.5	45.5, 52, 53[a]; 46[b]; 56[c]; 34[d]; 40[e]
etmalH$_2$	75.0	63[e]
bzylmalH$_2$	112.0	101[e]

[a]Graphical method from series of observations [19]. [b]Observed value [20]. [c]Observed value [21]. [d]Calculated value [22]. [e]Calculated from Pascal's constants given in [23].

[Co(-pn)$_3$][Cr mal$_3$]3H$_2$O, the three malonate rings are equivalent and have the envelope conformation only the methylene groups are significantly displaced from the ring planes [27]. However, in the two salts of the [Co en mal$_2$]$^-$ ion, the malonate ring has been shown to have different conformations: in $(-)_{589}$-[Co en(NO$_2$)$_2$]$(+)_{546}$[Co en mal$_2$] the malonate rings are planar with distortions towards the skew-boat form; whereas in the sodium salt dihydrate, the malonate rings are folded toward each other and non-equivalent [1]. This observation was explained in terms of the maximisation of interactions with the Na$^+$ ion and the lattice water.

No data are available for structures of Fe(III) or Al(III) malonato complexes, except for the crystal data for K$_3$[Al mal$_3$]6H$_2$O (see experimental section). Similarly no data are available for compounds of C-substituted malonic acids, except for some preliminary results [34].

Infrared Studies

The infrared spectra of carboxylic acids [35] and metal carboxylates [36] have been discussed extensively. The characteristic absorptions of the carboxyl group occur in the 1700 cm^{-1} region (C–O stretch); near 1400 and 1250 cm^{-1}, bands associated with the C–O stretch and/or OH deformations; and around 900–950 cm^{-1} (assigned to OH out-of-plane deformations). In malonic acid, two bands are shown at 1740 and 1710 cm^{-1}. Succinic acid shows a strong absorption at 1700 and only a weak band at 1780 cm^{-1}. Higher members of the series show only the band at 1700 cm^{-1} [37]. Ethylmalonic acid (Table II) shows a broad unresolved band at 1700–1740 cm^{-1}, while benzylmalonic acid shows two strong bands at 1760 and 1735 cm^{-1}.

In the carboxylate ion the carbonyl absorption of the acid is replaced by the antisymmetrical $\nu_a(CO_2)$ and symmetrical $\nu_s(CO_2)$ vibrations of the CO_2^- group, which appear in the regions 1610–1550 cm^{-1}

and 1400–1300 cm^{-1}. Correlations have been made between various properties of the metal ions and the carboxylate frequencies in salts and complexes. For example, a linear relationship between the electronegativity of M and the position of the antisymmetric stretch was found for M(I) and M(II) carboxylates [38]. $\nu_a(CO_2)$ increases and $\nu_s(CO_2)$ decreases as the strength of the M–O bond increases. Thus in a series of monochloracetates.$\nu_a(CO_2)$ increases in the order Ba < Sr < Ca < Cu and Δ ($\Delta = \nu_a - \nu_s$) increases in the same order [39]; in the trichloracetates the order is reversed [40] possibly indicating that structures in the two series are different [36]. Nakamoto [41] has suggested that in amino complexes, the order Ni(II) < Zn(II) < Cu(II) < Co(II) < Pd(II) ≈ Pt(II) < Cr(III) represents a sequence in which there is increasing metal-oxygen interactions; $\nu_s(CO_2)$ decreases, $\nu_a(CO_2)$ increases and Δ, the separation between the two, increase along the series.

Robinson and Uttley [42] have characterised unidentate and bidentate modes of bonding by the CO_2 group frequencies. They found that $\nu_a(CO_2)$ and Δ values are closer to those in the free ion for chelate, four-membered ring coordination, while Δ values for unidentate coordination are much larger, and $\nu_a(CO_2)$ bands appear at higher frequencies (Table VI).

TABLE VI. Data (cm^{-1}) for CO_2 Stretching Frequencies in Carboxylate Complexes [42].

	$\nu_a(CO_2)$	$\nu_s(CO_2)$	
chelate (4 m ring)	1490–1540	1400–1470	40–120
unidentate	1580–1650	1310–1390	210–170

The infrared spectra of compounds of malonic ethylmalonic and benzylmalonic acids are shown in Table II. Δ values increase along the series: Cd(II) < Zn(II) < Co(II) < Ni(II) < Co(III) < Cu(II) < Fe(III) < Al(III) for malonates. Figure 1 shows the plots of the Δ values *versus* the effective ionic radii of Shannon [43]. The effective ionic radii, which might be expected to give an indication of the metal-ligand interaction, correlate with the Δ values, except for three species: $[Co\ mal_3]^{3-}$, Cd mal H_2O and Cu mal $2.5H_2O$. The Cd complex contains both chelated and bridged carboxylate groups, and the low value of Δ would be in agreement with the predictions of Robertson and Uttley [42]. It seems reasonable to assume that the other compounds contain unidentate carboxylate groups with six-membered chelate rings, as in the M(III) complexes [27–33] and in $[Cu\ mal(OH_2)_2]^{2-}$ [44].

The cobalt(III) compound appears to have a smaller Δ value, and possibly to be less covalent than expected. $\nu_a(CO_2)$ is at a lower frequency and Δ is smaller than the corresponding figures for the Al(III)

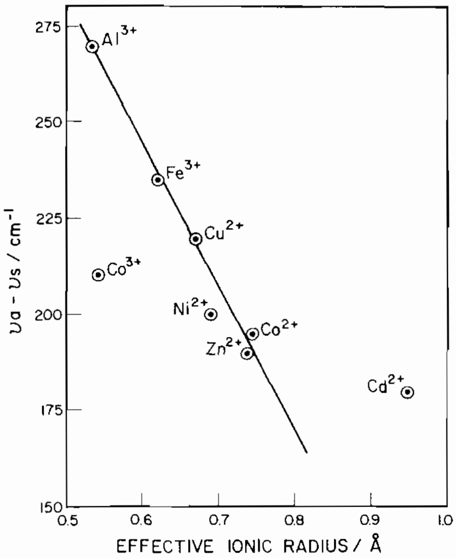

Fig. 1. Values plotted *versus* the effective ionic radii of Shannon [43], except that of Cu^{2+}, for which Kawamura's value [47] was used.

and Fe(III) complexes. When two ethylenediamine ligands are present, in $[Co\ en_2\ mal]^+$, the Δ value is 210 cm^{-1} ($\nu_s(CO_2) = 1630\ cm^{-1}$; $\nu_a(CO_2) = 1420\ cm^{-1}$). A similar, low value for Δ is found in $[Co\ phen_2\ mal]^+$, where Δ is 220 cm^{-1} ($\nu_s(CO_2) = 1610\ cm^{-1}$; $\nu_a(CO_2) = 1390\ cm^{-1}$) [45]. The electron withdrawing power of the phenanthroline ligands should produce stronger M–O bonding than in the $[Co\ en_2\ mal]^+$ or the $[Co\ mal_3]^{3-}$ ions, however the Δ value is not much larger. In the isoelectronic $[Fe\ phen_2\ mal]$ the Δ value is 235 cm^{-1} [46]. This iron species is in intermediate spin state ($\mu_{eff} = 3.80$ B.M., 293 K) [46], thus the Δ value for the Co(III) analogue would be expected to be higher, since it has one positive charge and t_{2g}^6 configuration, both tending to produce stronger M–O bonding than in the Fe complex.

The Δ value for the copper compound Cu mal $2.5H_2O$ appears to be higher than would be expected. It proved impossible to obtain the Δ value for the other Cu complex; both $[Cu\ mal_2(OH_2)_2]^{2-}$ and $[Cr\ mal_2(OH_2)]_2^+$ which have *trans* chelated malonate groups [44, 12, 13] show splitting of the carboxyl stretching bands (Table II).

Kawamura *et al.* [47] have suggested that the effective ionic radius for Cu^{2+} which is given by Shannon [43] as 0.73 Å should in fact be 0.67 Å. Using this figure and Δ for Cu mal $2.5H_2O$, copper then falls on the line. Kawamura has further suggested [47] that Cu(II) can substitute for Fe(III) and Cr(III) in octahedral sites, and that the Cu–O distance is usually around 1.96 Å. This is very similar to the Cr–O distance in Cr(III) malonates. Some bond length data for malonato complexes are collected in Table VII. A few generalisations can be

TABLE VII. Bond Distances in Some Malonato Complexes (Å).

	M–O	O–C	C–O	C–C	eir[a]	ref.
$[Cu\ mal_2(OH_2)_2]^{2-}$	1.95, 1.96	1.29	1.25	1.52	0.67[b]	44
$[Mn\ mal_2(OH_2)_2]^-$	1.90	1.28	1.22, 1.24	1.53	0.65[c]	31
$[Mn\ mal_2(CH_3OH)]^-$	1.90, 1.92	1.30, 1.28	1.22	1.50, 1.52		30
$[Mn\ mal_3]^{3-}$	1.90, 2.0	1.27, 1.28, 1.3	1.22, 1.24	1.51, 1.52		29
$[Cr\ mal_3]^{3-}$	1.95	1.26	1.20, 1.33	1.56, 1.61	0.665[c]	10
$[Cr\ mal_2OH]_2^{4-}$	1.96	1.276	1.233	1.526		27
$[Cr\ en\ mal\ OH]_2$	1.94, 1.95	1.24, 1.26	1.26, 1.28	1.49, 1.53		28
$[Co\ mal_2\ en]^-$ [d]	1.90(mean)	1.29	1.24	1.475	0.545[c]	32
$[Co(CN)_2mal(NH_3)_2]^-$	1.92, 1.93	1.277, 1.267	1.23, 1.247	1.519, 1.535		33
$[Co\ mal_2\ en]^-$ [e]	1.897(mean)	1.281	1.24	1.50		1

[a] Effective ionic radius. [b] Value from ref. 47. [c] Value from ref. 43. [d] $[Co\ en_2(NO_2)_2]^+$ salt. [e] Na^+ salt.

made from the very limited data; (i) The Mn–O and Co–O bond distances are shorter than those in the Cr and Cu compounds. (ii) There is little correlation between the M–O distance and the geometry of the carboxyl group. (iii) In the Cr(III) complexes the Cr–O bonds are relatively long, but the carboxyl group is quite symmetrical. This point is in agreement with the infrared results of Nakamoto [41], for the carboxyl group in amino acid complexes, where Cr(III) complexes showed the largest Δ values, which was attributed to the most covalent M–O bonding and thus the most symmetrical CO_2 group. (iv) The dimensions of the malonate group coordinated to Co(III) are very similar to those in Mn(III) and Cu(II) complexes in spite of the much smaller ionic radius of octahedral Co(III).

There are few Δ values available for compounds of substituted malonic acids, since in many cases the bands are broad (Table II). In both Al(III) and Fe(III) complexes, the infrared results indicate that stronger metal–oxygen bonds are formed in the series: ethylmalonato > malonato > benzylmalonato.

Mossbauer Spectra

Mossbauer spectra of the tris(malonato)ferrate(III) complexes are typical of high spin d^5 complexes. The isomer shifts are as follows: ethylmalonato, 0.36 mm s^{-1}; benzylmalonato, 0.42 mm s^{-1}, malonato, 0.45 mm s^{-1}. Thus the Mossbauer spectra also indicate greater covalent bonding in the Fe(III) ethylmalonato complexes than in complexes of the other two acids. This is in agreement with the infrared results although these indicated that malonate formed stronger M–O bonds than benzylmalonate.

Mossbauer spectra have been reported [48] for a postulated trimeric Fe(III) complex with bridging malonato groups and a common central oxygen atom. The isomer shift in this molecule was 0.41 mm s^{-1}, and the broadness of the line was attributed to the variety of iron environments which results from the polymeric nature of the complex.

Magnetic Moments

The magnetic data for paramagnetic compounds are shown in Table IV. Values for the Ni(II) compounds are typical of d^8 octahedral species, and are in agreement with those in the literature for Ni mal $2H_2O$ [49, 50]. Co(II) compounds are high-spin octahedral. The observed moments range between 4.74 and 4.76 B.M. for the malonate, 4.72 and 4.75 B.M. for the ethylmalonate, and 4.8 and 5.0 B.M. for the benzylmalonate. The Weiss constants are –24 K (malonate), –12 K (ethylmalonate), and –20 K (benzylmalonate). The malonate has been reported to have a room temperature moment of 5.2 B.M. [50], a value nearer to the expected value than ours, since Co(II) octahedral species are expected to have a considerable orbital contribution to the moment. The visible spectrum (Table III) shows that the compound is octahedral and the reasons for the difference are not clear.

The Fe(III) complexes are typical high-spin d^5, with zero Weiss constants. The magnetic moment of the sodium tris(malonato)ferrate(III) is similar to that in the literature for the potassium salt [51], which was 5.87 B.M. at room temperature.

The magnetic moments of the copper malonates are typical of d^9 complexes, some values are collected in Table VIII. There is some variation in the moments, the moments of copper complexes may vary

TABLE VIII. Magnetic Moments of Some Cu(II) Malonates (B.M.) at Room Temperature.

	μ_{eff}	Ref.
Cu mal $2.5H_2O$	1.89	this work
Cu mal $2.5H_2O$	1.77	21
Cu mal H_2O	1.86	22
Cu mal H_2O	1.76	20
Cu mal $3H_2O$	1.84	50
Cu mal	1.75	21
$Na_2[Cu\ mal_2(OH_2)_2]$	1.88	this work

with the history of particular preparations. Malonate-copper compounds do not show the type of temperature dependence associated with bridged complexes [22]. Room temperature magnetic moments for malonates and substituted malonates are shown in Table IX.

TABLE IX. Magnetic Moments of Some Malonates (μ_{eff} in B.M. at Room Temperature).

	mal	etmal	bzylmal
Ni(II)	3.22	3.11	3.16
Co(II)	4.75	4.74	5.02
Fe(III)	5.92	5.94	5.98
Cu(II)	1.89, 1.88	1.86	1.89

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