TABLE II

QUANTITATIVE ELECTRON DIFFRACTION DATA FOR CARBON SUBOXIDE

Feature Max.	Feature Min.	q_0	q_c/q_0 1	q_c/q_0 2	q_c/q_0 3
	1	14.08	1.010	0.999	0.983
1		18.38	1.004	1.001	.998
	4	30.50	1.003	0.995	.982
4		34.61	1.004	.998	.995
5		37.86	1.011	.999	.998
	7	47.04	0.995	.992	.981
7		50.75	1.008	1.001	.998
8		54.52	1.007	0.995	.988
	10	63.15	1.006	0.994	.987
10		66.66	1.003	1.000	1.002
12		75.81	1.016	1.004	0.983
	13	79.80	...	0.994	0.983
14		92.65	1.026	1.020	...
15		108.80	1.029	1.025	1.016
		Mean	1.009	1.001	0.992
Av. dev. from the mean			0.007	0.006	0.009

TABLE III

PRINCIPAL PARAMETERS FROM ACCEPTABLE MODELS

Parameter, Å.	1	2	3
C–O	1.15_0	1.16_1	1.17_1
C–C	1.29_2	1.28_1	1.27_0

experimental curve is a visual curve, they were considered as barely acceptable. The quantitative electron diffraction data are shown in Table II. The parameters calculated from the three models are listed in Table III. The final parameters of carbon suboxide by the radial distribution curve and the correlation procedure are

$$\text{C–O} = 1.16 \pm 0.015 \text{ Å.}$$
$$\text{C–C} = 1.28 \pm 0.015 \text{ Å.}$$

It should be noted that the uncertainties determined in this investigation are much smaller than those reported in the earlier investigations[3-5] which employed the visual method with non-sectored plates with the data extending to about $q = 70$ at the most.

The C–C distance obtained in this investigation is smaller than the C–C distance in ethylenes and ketene.[15] This is possibly because of the greater multiple bonding in carbon suboxide. The C–O distance in C_3O_2 agrees very well with the C–O distances in ketene and carbonyl fluoride[15] but is less than the C–O distance in aliphatic ketones.[16]

Acknowledgments.—The authors' thanks are due to Professor Henry Feuer and Mr. R. Miller for their assistance and advice in the preparation of carbon suboxide.

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LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Infrared Absorption Spectra of Inorganic Coördination Complexes. XVIII. Infrared Studies of Malonato Metal Complexes[1]

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The infrared spectra of malonic acid and simple metal malonates have been measured in the NaCl region. The observed bands are assigned by comparison with the frequencies reported for simpler molecules of similar structure for which normal vibration calculations are available. The spectra of the malonato metal complexes of Fe(III), Cr(III), Al(III), Cu(II) and Pd(II) are interpreted by correlation with the spectra of the alkali metal malonate salts. The nature of the oxygen-to-metal bonds present in these complexes can be determined indirectly from the observed values of the O–C–O stretching frequencies.

Introduction

A variety of organic chelating agents are known which involve one or more carboxylate ions as donor centers. Previous studies[3] indicate that in nickel(II), copper(II) and zinc(II) complexes with glycine the resonance structure of the carboxylate ion is essentially maintained and the bonding between the central metal and the carboxylate ion is essentially ionic in nature. Similarly, EDTA[4] and aspartic acid complexes[5] of copper(II) show relatively small shifts in the O–C–O vibrations from those observed for the simple ionic salts of these ligands. The infrared spectra of the oxalato complexes, of Fe(III), Cr(III), Al(III) Pd(II) and Cu(II),[6] however, reveal that the oxygen-to-metal bond present in these compounds is approximately 50% covalent in character.

The present investigation reports an infrared study of the complexes formed by these same metal ions with the bidentate malonate ion; the chelate malonato ligand is not rigid and planar like the oxalato group. The infrared absorption bands of malonic acid and its simple salts are assigned and the spectra of the malonato metal complexes are explained by comparison with these. Earlier work on malonate salts includes the infrared stud-

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ies of Duval, *et al.*,[7] and the Raman measurements made by Edsall[8] for malonic acid, the malonate ion and the deuterated malonates in aqueous solution.

Experimental

Preparation of Compounds.—Potassium tris-(malonato)-aluminate(III) trihydrate, $K_3[Al(C_3H_2O_4)_3]\cdot 3H_2O$, was prepared as described by Bailar and Jones[9] for the corresponding tris-(oxalato)-complex.

Anal. Calcd. for $K_3[Al(C_3H_2O_4)_3]\cdot 3H_2O$: $C_3H_2O_4$, 60.68. Found: $C_3H_2O_4$, 60.45.

Potassium tris-(malonato)-ferrate(III) tetrahydrate, $K_3[Fe(C_3H_2O_4)_3]\cdot 4H_2O$, was prepared by the method of Scholz.[10]

Anal. Calcd. for $K_3[Fe(C_3H_2O_4)_3]\cdot 4H_2O$: $C_3H_2O_4$, 55.53. Found: $C_3H_2O_4$, 55.81.

Potassium tris-(malonato)-chromate(III) trihydrate, $K_3[Cr(C_3H_2O_4)_3]\cdot 3H_2O$ was prepared by the method of Lapraik.[11]

Anal. Calcd. for $K_3[Cr(C_3H_2O_4)_3]\cdot 3H_2O$: Cr, 9.82. Found: Cr, 10.08.

Sodium bis-(malonato)-diaquocuprate(II), $Na_2[Cu(C_3H_2O_4)_2(H_2O)_2]$, was prepared by the method of Riley.[12]

Anal. Calcd. for $Na_2[Cu(C_3H_2O_4)_2(H_2O)_2]$: Cu, 18.18. Found: Cu, 18.09.

Potassium bis-(malonato)-palladate(II) monohydrate, $K_2[Pd(C_3H_2O_4)_2]\cdot H_2O$, was prepared by adding solid palladium(II) chloride to a concentrated solution of potassium malonate and warming gently until dissolved. The complex precipitated on cooling.

Anal. Calcd. for $K_2[Pd(C_3H_2O_4)_2]\cdot H_2O$: $C_3H_2O_4$, 51.02. Found: $C_3H_2O_4$, 50.97.

Malonic acid and its sodium and calcium salts were Eastman Kodak products. Potassium malonate was prepared by neutralization of malonic acid with potassium hydroxide; the solution was evaporated to dryness and the salt was recrystallized from water. Deuterated samples were prepared by recrystallization from 99.5% D_2O.

Absorption Measurements.—The infrared spectra were obtained by means of a Perkin–Elmer infrared spectrophotometer model 21 with a sodium chloride prism. The spectra of the solid complexes were obtained by the potassium bromide disk technique[13,14] and checked in Nujol mulls.

Results

The experimental results are shown in Fig. 1 and Tables I and II. The assignments listed in the last columns of the tables are explained in the Discussion.

TABLE I[a]

OBSERVED FREQUENCIES IN CM.$^{-1}$ OF SIMPLE MALONATES AND MALONIC ACID

$K_2(C_3H_2O_4)\cdot xH_2O$	$Na_2(C_3H_2O_4)\cdot H_2O$	$CH_2(COOH)_2$	Assignment
3460s 3300w 3200m	3420m 3120m		$\nu(H_2O)$[b]
2950sh	2970sh	2980s,b	$\nu(CH)$
		2680m,sh,b	$\nu(OH)$
		2575m,sh,b	$\nu(OH)$
2230vw	2230vw		
		1735vs 1705vs	$\nu(C{=}O)$
1645m	1650s		$\delta(H_2O)$[c]
1563vs,b	1600vs		$\nu(OCO)$ antisym.
	1562s		$\nu(OCO)$ antisym.
		1439s	$\nu(CO) + \delta(OH)$
1436s	1445sh	1418s	CH_2 bending
	1428m		
1405s	1390m		$\nu(OCO)$ sym.
1370s	1370s		$\nu(OCO)$ sym.
		1314s	$\delta(OH) + \nu(CO)$
1268s	1268s	1219s	CH_2 wagging
1190m	1200m 1195m	1174s	$\nu(CC)$antisym.
	973w		
955m	962m	960m,sh	$\nu(CC)$sym.
937w	936w 924w	933m,sh	CH_2 rocking
		918s,b	$\pi(OH)$
816w	813m 790m		OCO bending
		768m	$\delta(COOH)$
700s 660m	705s	654s	OCO wagging $\pi(COOH)$

[a] s = strong; m = medium; w = weak; v = very; sh = shoulder; b = broad; ν, δ and π denote stretching, in-plane deformation and out-of-plane deformation vibrations, respectively. [b] The stretching vibration of H_2O. [c] The deformation vibration of H_2O.

TABLE II

OBSERVED FREQUENCIES IN CM.$^{-1}$ OF MALONATO COMPLEXES

$K_2[Pd(C_3H_2O_4)_2]\cdot H_2O$	$Na_2[Cu(C_3H_2O_4)_2(H_2O)_2]$	$K_3[Fe(C_3H_2O_4)_3]\cdot 4H_2O$	$K_3[Al(C_3H_2O_4)_3]\cdot 3H_2O$	$K_3[Cr(C_3H_2O_4)_3]\cdot 3H_2O$	Assignment
3400w	3300m 3200m	3440m	3400m 3250sh	3420m	$\nu(H_2O)$
	2900w	2900w	2900w	2900w	$\nu(CH)$
1695m	1725w				
1666s	1610s	1625s,b	1625s,b	1625s,b	$\nu(OCO)$ antisym.
1640s	1580s				and $\delta(H_2O)$
1405m	1440s		1440s	1410m	CH_2 bend
1380m	1410m	1390s	1400m	1390s	$\nu(OCO)$ sym.
	1370m		1375s	1360m	$\nu(OCO)$ sym.
				1325sh	
1285m	1290m	1310m	1290m	1260m	CH_2 wagging
		1280m,sh			
1128w	1185w	1210w		1180w	$\nu(CC)$ antisym.
983vw	990vw			980m,sh	
957w	972m	973m 960m	1000m	962m	$\nu(CC)$ sym.
935m	938m	930m	962m	935m	CH_2 rocking
			860vw		
836w	830m	790w	795w	795w	OCO bending
753m	740m	726m	742m	742m	OCO bending
		717sh		716sh	

Discussion

A. Assignment of the Observed Frequencies of Simple Malonates and Malonic Acid.—The twenty-one normal vibrations of the malonate ion with the point group C_{2v} are as follows: two CH_2 stretching (A_1,B_2), CH_2 bending (A_1), CH_2 wagging (B_1), CH_2 twisting (A_2), CH_2 rocking (B_2), symmetric and antisymmetric CC stretching (A_1, B_1 respectively), two symmetric OCO stretching (A_1, B_1), two antisymmetric OCO stretching (A_1, B_1), CCC bending (A_1), two OCO bending (A_1, B_1), two OCO wagging (A_2, B_2), two OCO rocking (A_1, B_1) and two OCO twisting (A_2, B_2) vibrations. The A_2 type vibrations are infrared-inactive. The symmetric and antisymmetric OCO stretching vibrations of the malonate ion become the C=O stretching and C–O stretching vibrations of the acid, the latter couples with the in-plane OH de-

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formation vibration.[15,16] The out-of-plane deformation vibrations also must be taken into account. In other respects the vibrations of the malonate ion and malonic acid are quite similar.

The CH_2 deformation vibrations of the malonate ion and malonic acid can be assigned readily by comparison with the CH_2 deformation vibrations of $CH_2(CN)_2$ (bending 1422, wagging 1322, twisting 1214, (infrared inactive) and rocking 936 cm.$^{-1}$).[17,18] Thus the three absorption bands observed in the spectrum of $K_2(C_3H_2O_4)\cdot xH_2O$ at 1436, 1268 and 937 cm.$^{-1}$ can be assigned to CH_2 bending, wagging and rocking vibrations, respectively. Similarly the corresponding bands present in the spectra of $Na_2(C_3H_2O_4)\cdot H_2O$ and malonic acid easily can be identified (see Table I).

A very strong band at about 1600 cm.$^{-1}$ and another strong band at about 1400 cm.$^{-1}$ observed in the spectrum of the malonate ion can be assigned, respectively, to the antisymmetric and symmetric OCO stretching vibrations. The corresponding frequencies also have been found in the spectra of the CH_3COO^- and $HCOO^-$ ions.[19,20] In the spectrum of the malonate ion each of these frequencies appears as a doublet, the separations being of the order of 20 to 40 cm.$^{-1}$

As referred to above, these carbon–oxygen stretching vibrations of the malonate ion correspond to the C=O and C–O stretching vibrations of malonic acid. The C=O stretching vibrations can be assigned to the 1735 and 1705 cm.$^{-1}$ bands; the C–O vibrations, coupled with the in-plane OH deformation vibration, can be assigned to the 1439 and 1314 cm.$^{-1}$ bands, respectively. This assignment is compatible with the corresponding assignments made for acetic, propionic, chloroacetic, succinic and oxalic acids.[17] The broad band observed in the spectrum of malonic acid at about 920 cm.$^{-1}$ corresponds to the out-of-plane OH deformation vibration.

The CC stretching frequencies in malonic acid as well as in the malonate ion are considered to appear as a double band with a separation of some 200 cm.$^{-1}$ The 955 and 1190 cm.$^{-1}$ bands observed in the spectrum of $K_2(C_3H_2O_4)\cdot xH_2O$ and the 960 and 1174 cm.$^{-1}$ bands observed in the spectrum of malonic acid undoubtedly can be assigned to the symmetric and antisymmetric CC stretching vibrations.

Several bands have been observed in the NaCl region below 800 cm.$^{-1}$. From the normal vibration calculations made for simpler molecules with similar structure,[20–23] these bands can be assigned to the OCO bending and wagging vibrations of the malonate ion and the COOH in-plane and out-of-plane deformation vibrations of malonic acid as shown in Table I. This assignment is compatible with those made for the CH_3COO^-, $HCOO^-$ and $NH_2CH_2COO^-$ ions.[24]

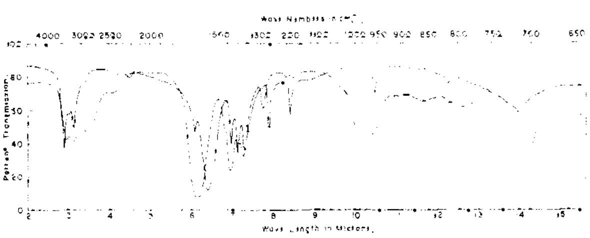

Fig. 1.— ———, potassium malonate hydrate, $K_2C_3H_2O_4\cdot xH_2O$; – – – –, potassium tris-(malonato)-aluminate trihydrate, $K_3[Al(C_3H_2O_4)_3]\cdot 3H_2O$.

B. Assignment of the Observed Frequencies of the Malonato Metal Complexes.—Strictly speaking, the vibrations of the bis- and tris-(malonato)-metal complexes should be treated as nineteen-body and twenty-eight-body problems, respectively. The bis-(malonato)-metal complex ion has a point group V_h and the tris complex ion has a point group D_3. Therefore, the symmetry species of the vibrations of these metal complexes are different from those of the simple metal malonates.

For the bis-(malonato)-metal complex ions with symmetry V_h, all the vibrations symmetric to the center are infrared-inactive. Therefore no band of the complex ion arising from a specific vibration of the simple malonato group will be observed as a doublet.

For tris-(malonato)-metal complex ions with the point group D_3, the vibrations corresponding to the B_1 and B_2 type vibrations of a single malonato group are classed as symmetric to the trigonal axis (A_2) or degenerate (E), both infrared-active. Therefore, these vibrations are expected to appear as double bands. However, only a single broad band which could not be resolved is observed in the spectra.

On the other hand, those vibrations of the metal complex, corresponding to the A_1 type vibrations of a single malonato group which are symmetric to the trigonal axis (A_1) are inactive, and those which are degenerate (E) are active. Consequently the A_1 vibrations of the group appear as single bands.

Although the selection rules for the metal complexes are as stated above, values of many normal frequencies will not be much different from those of a single coördinated malonato group. Thus the assignment of malonic acid and its simple salts listed in Table I can be used to interpret the spectra of the metal coördination complexes.

The absorption bands of the metal complexes near 1380 cm.$^{-1}$ correspond to the 1405 cm.$^{-1}$ band of the simple malonate ion (potassium salt) assigned to the OCO symmetric stretching vibration. In the complex ions the two C–O bonds are no longer equivalent and strictly speaking cannot be designated as OCO symmetric. However, we have used this expression (Table II) for the in-phase OCO stretching vibrations, because the difference in the bond order is small. The strong absorption bands observed near 1630 cm.$^{-1}$ in the spectra of the complexes correspond to the broad band at 1563 cm.$^{-1}$ present in the spectrum of the

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simple malonate ion in the potassium salt. This band has been assigned to the OCO antisymmetric stretching vibration.

A previous investigation[6] showed that the nature of the metal-to-ligand bond (M–O) may be determined indirectly from the values of the CO stretching frequencies, without determining the low frequencies characteristic of the M–O stretching vibration. The in-phase OCO frequency in malonato metal complexes is lower than the corresponding OCO symmetric frequency of the simple malonate ion, and the out-of-phase frequency is higher than the corresponding antisymmetric frequency. However, these differences are less than those observed for the oxalato metal complexes. Consequently we may conclude that the metal-to-ligand bond of the malonato metal complexes is more ionic than that of the oxalato metal complexes.

Although the OCO bending vibrations are also affected by coördination, the observed frequencies can reasonably be assigned as shown in Table II.

NOTRE DAME, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF INORGANIC CHEMISTRY, JOHN CURTIN SCHOOL OF MEDICAL RESEARCH, AUSTRALIAN NATIONAL UNIVERSITY]

Stereospecific Influences in Metal Complexes Containing Optically Active Ligands. Part I. Some of the Optical Isomers of Tris-(propylenediamine)-cobalt(III) Ion

BY FRANCIS P. DWYER, FRANCIS L. GARVAN AND ALBERT SHULMAN

RECEIVED JULY 21, 1958

Oxidation of a mixture of a cobalt(II) salt and *levo*-propylenediamine in the presence of some acid gave two isomeric tris-compounds for which $[\alpha]_{\mathrm{D}}$ $-24°$ and $+214°$. The optical antipodes were prepared from *dextro*-propylenediamine. The base recovered from each isomer was optically pure, $[\alpha]_{\mathrm{D}}$ (in dry benzene) $\pm 34.4°$. The isomers for which $[\alpha]_{\mathrm{D}}$ $\pm 214°$ are believed to be the D-*lll* and L-*ddd* isomers. For the reaction D-*lll* $\rightleftarrows$ L-*lll* using charcoal as catalyst the equilibrium constant was found to be 5.75 whence $\Delta F^0 = -1.02 \pm 0.05$ kcal./g. mole. The preparation of optically pure *d*- and *l*-propylenediamine is described and also the resolution of DL-$[\mathrm{Co}(dl\text{-pn})_3]^{3+}$ ion.

Introduction

The introduction of asymmetric groups or molecules into metal complexes, that themselves are capable of existence in enantiomeric forms, increases very considerably the number of theoretically possible optical isomers. The bis-(ethylenediamine)-(*d,l*-propylenediamine)-cobalt(III) ion may exist in four possible optical forms designated simply D-*d*, D-*l*, L-*l*, L-*d*,[1] while eight isomers are possible for the tris-(*d,l-trans*-1,2-cyclopentanediamine)-cobalt(III) ion, ($[\mathrm{Co(cptdin)_3}]^{3+}$). However, in practice it is believed that the interaction of the ligands with themselves and with the asymmetrical field of the whole complex provide a stereospecific limiting factor that excludes many of the isomers. It is believed that a single asymmetric ligand occasions but partial stereospecificity and certain forms (usually D-*d* and L-*l*), predominate in the mixture of isomers.[2,3] More pronounced stereospecificity appears to be encountered in the synthesis of complexes with two asymmetric donor groups, and isomers containing both optical forms of the donor groups, such as D-*dl* and L-*dl*, have not been detected.[2,4] Very great limitation causing the exclusion of most of the theroretically possible isomers has been claimed to occur in the synthesis of complexes with three asymmetric ligands. Two forms only, designated L-*ddd* and D-*lll*, have been obtained for $[\mathrm{Co(cptdin)_3}]^{3+}$, $[\mathrm{Rh(cptdin)_3}]^{3+}$ and $[\mathrm{Pt(pn)_3}]^{4+}$, when the racemic base was used for the synthesis. Since propylenediamine, (pn), is unsymmetrical as well, each of the optical isomers can exist in *cis* and *trans* forms, making a total of twenty-four theoretical isomers. Frequently, in order to simplify the system in the tris-complexes, one optical form only of the ligand has been used. The number of theoretical isomers is reduced thereby to two (D-*ddd* and L-*ddd*) with symmetrical ligands. With one exception, one isomer only has been isolated. Three forms of the possible four have been obtained of tris-(*d*-alanine)-cobalt(III), of which one presumably is the unusual. thermodynamically unstable form.[5]

Detailed discussions of the principle of stereospecificity will be found in recent reviews and text books.[6-9]

It is unfortunate that the evidence for the principle of stereospecificity is largely negative and that this aspect of the theory has not been sufficiently emphasized. Critical evaluation of the experimental detail of much of the work shows that little quantitative information is available and, as Bailar and Johnson[10] have pointed out in relation to the tris-(propylenediamine)-platinum(IV) complex, that much of the chemical material is un-

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(1) The symbol D or L specifies the theoretical configuration of the whole complex which is not necessarily related to the sign of the rotation in a convenient wave length of light. As the absolute configuration neither of the optical forms of propylenediamine nor of any of its metal complexes is known, the arbitrary designation suggested by Jaeger and used constantly by all authors subsequently has been used in this paper. The capitals refer to the sign of the rotation of the whole complex and the small letters to that of the ligand, usually at the D-line of sodium.

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