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# Simple Malonate and Maleate Complexes of Oxovanadium(IV)

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Oxovanadium(IV) malonate tetrahydrate, VO(malon)·$4H_2O$ and oxovanadium(IV) maleate dihydrate, VO(mal)·$2H_2O$ are prepared and characterised. Magnetic moments agree with quadrivalent vanadium. The differential thermal analysis and infrared spectra of both the complexes have been studied. Molar conductance, molecular weight by cryoscopic method and the electronic spectrum of the malonate have also been obtained. A comparison of oxalate, malonate and maleate complexes of the type VO(LL)·$x\,H_2O$ (LL, being one of the bidentates) is attempted to arrive at a series from cryoscopic data, thermal decomposition temperature and vanadium-oxygen stretching frequency. The series obtained showing the 'stability' is: oxalate> malonate>maleate and is expected to be the same as the naphelauxetic series.

Oxovanadium(IV) is known to form complex oxalates and malonates of the type $(NH_4)_2[VO(ox)_2]\cdot 2H_2O$ and $(NH_4)_2[VO(malon)_2]\cdot 4H_2O$ (ox=oxalate ion, malon=malonate ion).[1] But no simple compounds of the type VO(LL)·$xH_2O$ (LL=$ox^{2-}$, $malon^{2-}$ or $mal^{2-}$=maleate ion) have been known. It is only recently that we reported[2] the preparation and investigations on simple oxalates of oxovanadium(IV), VO(ox)·$2H_2O$ and VO(ox)·$4H_2O$. A study of malonate and maleate corresponding to VO(ox)·$xH_2O$ is described here. Further, an attempt has been made to compare the properties of VO(malon)·$4H_2O$ and VO(mal)·$2H_2O$ with those of VO(ox)·$2H_2O$.

A 1 : 1 compound with a p$K$ value of 3.8 has been postulated from the reaction between malonic acid and $VO^{2+}$ spectrophotometrically.[3] But the complex has not been prepared in the solid state. Very recently, detailed investigations on $\alpha$, $w$-dicarboxylates of copper(II) (belonging to $d^9$ system) including oxalate and malonate have been made.[4,5] Except the malonate, they are polymeric while the compounds of oxovanadium(IV), belonging to $d^1$ system, described here are monomeric.

## Experimental

**Materials Employed.** Malonic and malaic acid were Reidel de Häen A. G. reagents. Vanadium pentoxide was obtained by heating ammonium metavanadate (Analar). Vanadyl chloride was prepared by treating the pentoxide with concentrated hydrochloric acid and a few drops of ethanol. Vanadyl hydroxide, $VO(OH)_2$, was precipitated by adding a stoichiometric amount of sodium hydroxide solution to vanadyl chloride. It was filtered, washed with water and used for the preparations.

**Preparations.** *(i) Oxovanadium(IV) Malonate Tetrahydrate.* Calculated amount of aqueous solution of malonic acid, according to the reaction $VO(OH)_2 + H_2malon \rightarrow VO(malon) + 2H_2O$, was added slowly with stirring, to vanadyl hydroxide suspended in water. Excess of malonic acid was avoided to prevent the formation of anionic malonate of oxovanadium(IV). The solution was kept on a water bath for 20 min, cooled and filtered. The clear blue filtrate was concentrated by passing dry air and then shaken with ethanol, when a blue solid crystallized out. The crystals were purified by washing with ethanol and dried *in vacuo*. Vanadium was estimated by ignition to $V_2O_5$ and malonate by oxidation with permanganate, correction being made for the oxidation of vanadium(IV).

Found: $V_2O_5$, 37.58; malon, 42.10%. Calcd for VO(malon)·$4H_2O$: $V_2O_5$, 37.76; malon, 42.33%.

*(ii) Oxovanadium(IV) Maleate Dihydrate.* It was prepared by the same procedure as given above for the malonate. In place of ethanol, acetone was used for crystallization and purification. Final washing was done with diethyl ether and the product dried *in vacuo*. The compound was analysed by the combustion method.

Found: $V_2O_5$, 42.14; mal, 52.18%. Calcd for VO(mal)·$2H_2O$: $V_2O_5$, 41.93; mal, 52.53%.

**General Properties.** The malonate is blue, slightly hygroscopic and soluble in water; while the maleate is chrome green in colour, nonhygroscopic and difficultly soluble in water followed by slow hydrolysis. The average molecular weight of the malonate in aqueous solution was found by the cryoscopic method to be 198 (the calculated value: 241) showing it to be a monomer in aqueous solution and dissociating to a small extent. The molar conductance for 0.01 to 0.001 M aqueous solutions ranged from 34 to 49 $ohm^{-1}\cdot cm^2mol^{-1}$ for the malonate which is for less than that

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[1] N. V. Sidgwick, "Chemical Elements and Their Compounds," Vol. I, Oxford University Press, Oxford (1950), p. 822.

[2] D. N. Sathyanarayana and C. C. Patel, *J. Inorg. Nucl. Chem.*, **27**, 297 (1965).

[3] P. K. Bhattacharya and S. M. Banerji, *Curr. Sci. (India)*, **29**, 147 (1960).

[4] L. Dubick, C. M. Harris, E. Kokot and R. L. Martin, *Inorg. Chem.*, **5**, 93 (1966).

[5] B. N. Figgis and D. J. Martin, *ibid.*, **5**, 100 (1966).

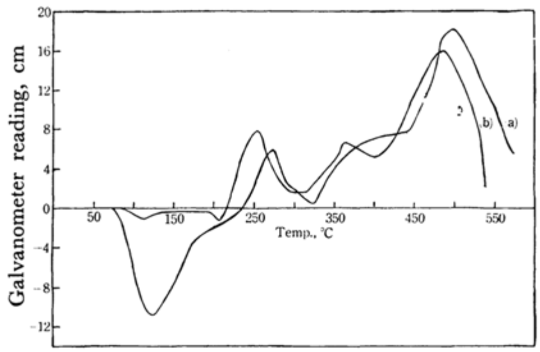
expected for a bi-divalent electrolyte of 1 : 1 type.[6,7] It may also be taken to show the slight dissociation of oxovanadium(IV) malonate in water as indicated by the cryoscopic study. The molecular weight and conductance data could not be obtained for the maleate because of its low solubility.

**Apparatus.** The infrared spectra of the complexes were taken in Nujol mull with a Carl Zeiss UR-10 spectrophotometer using LiF and NaCl prisms. The apparatus and procedure used for other studies are given in an earlier paper.[8]

### Results and Discussion

Magnetic susceptibility data for the solid samples obtained by the Gouy method at room temperature (23°C) are given in Table 1. The diamagnetic corrections are also given. The magnetic moments for both the complexes are as expected and indicate one unpaired spin per vanadium.

Differential thermal analysis (DTA) of malonate and maleate was carried out in an atmosphere of air at a heating rate, 6°C per min, and the DTA curves are given in Fig. 1.



Figl 1. Differential thermograms of (a) VO(malon)·$4H_2O$ and (b) VO(mal)·$2H_2O$.

VO(malon)·$4H_2O$ gives an endothermic peak at 125°C and exothermic peaks at 275, 380 (shoulder) and 500°C. The endothermic peak at 125°C is

Table 1. Magnetic susceptibilities of the malonate and maleate of oxavanadium(IV)

| Complex | $\chi_g \times 10^6$ | $\chi_M \times 10^6$ | $-\chi_g \times 10^6$ Dia. corr. | $\chi_M' \times 10^6$ | Mag. moment BM |
|---|---|---|---|---|---|
| VO(malon)·$4H_2O$ | 5.30 | 1277 | 99 | 1376 | 1.78 |
| VO(mal)·$2H_2O$ | 5.32 | 1155 | 84 | 1239 | 1.72 |

$\chi_g$ is gram susceptibility; $\chi_M$ is molar susceptibility without diamagnetic correction and $\chi_M'$ is the corrected susceptibility.

Table 2. Assignment of the infrared frequencies of malonate and maleate

| VO(malon)·$4H_2O$* | | VO(mal)·$2H_2O$* | |
|---|---|---|---|
| Frequency, $cm^{-1}$ | Assignment | Frequency, $cm^{-1}$ | Assignment |
| 3620—3180 m, br | $\nu(H_2O)$ | 3400 m, br | $\nu(H_2O)$ |
| 1620 vs, br | $\nu_a$(C=O)<br>$\delta(H_2O)$(coord.) | 1730 m<br>1710 m | $\nu_a$(C=O) |
| 1580 vs | $\delta(H_2O)$(free) | 1635 m | $\delta(H_2O)$ |
| 1465** vs | $CH_2$ bend | 1540 s | $\nu_a$(C=O) |
| 1380** vs | $\nu_s$(C-O) | 1372** s | CH rock |
| 1280 s | $CH_2$ wag. | 1330 m | $\nu_s$(C-O) |
| 1180 w, br | $\nu_a$(C-C) | 1248 w | CH bend |
| 1100 vw<br>1040 w, sh | — | 1180 w, sh<br>1000 m | $\nu_a$(C-C)<br>$\nu$(V=O) |
| 990 vs<br>965 m, sh | $\nu$(V=O)<br>$\nu_s$(C-C) | 900 s<br>870 m | CH wag. |
| | | 830 w | $H_2O$ rock |
| 850 w | $H_2O$ rock | | |
| | | 810 w | $\delta$(O-C=O) |
| 800 w | $\delta$(O-C=O) | 730 w | |
| 740 s | | | |

v=very, s=strong, m=medium, w=weak, sh=shoulder, $\nu$=stretching, $\nu_s$=sym. str., $\nu_a$=asym. str. and $\delta$=in-plane bending

* C-H str. is overlapped by Nujol band. ** Overlapped by Nujol bands.

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7) P. G. Simpson, A. Vinciguerra and J. V. Quagliano, *Inorg. Chem.*, **2**, 282 (1963).

8) D. N. Sathyanarayana and C. C. Patel, This Bulletin, **37**, 1736 (1964).

due to the loss of two water molecules, which are perhaps lattice held. The exothermic peak at 275°C is due to the decomposition of dihydrate giving $VO_2$ as the solid product. The peak near 380°C is due to the oxidation of $VO_2$ to $V_2O_5$.²⁾ The exothermic peak at 500°C is due to the oxidation of carbon produced by the decomposition of malonate. The lower temperature for the oxidation of carbon may be due to the catalytic effect of $V_2O_5$. The DTA curve of maleate resembles that of malonate dihydrate and the exothermic peaks near 255, 360 and 490°C are due to the decomposition of maleate, oxidation of $VO_2$ and the oxidation of carbon respectively.

The electronic spectrum of oxovanadium(IV) malonate in aqueous solution has in the visible region, a band at 12800 $cm^{-1}$ ($\varepsilon$, 38) and a shoulder at 16200 $cm^{-1}$ ($\varepsilon$, 13) both assignable to d-d transitions. The electronic spectrum of the maleate could not be observed owing to its low solubility in solvents.

The electronic spectrum of the malonate, resembles that of the oxalate, $VO(ox)\cdot 2H_2O$, showing that the malonate compound in solution has a distorted octahedral structure with roughly $C_{4v}$ symmetry.²⁾ The bands at 12800 and 16200 $cm^{-1}$ can be assigned to $d_{xy}\rightarrow d_{xz}$, $d_{yz}$ and $d_{xy}\rightarrow d_{x^2-y^2}$ respectively. The $d_{xy}\rightarrow d_{z^2}$ band is probably overlapped with the electron transfer bands of $VO^{2+}$, occuring in the ultraviolet region. The value of 10 $D_q$ for the malonate is 16200 $cm^{-1}$, while for the oxalate, 16670 $cm^{-1}$.

The infrared frequencies, together with their assignments, are given in Table 2.

A detailed normal coordinate treatment, like the one made for metal oxalate complexes by Fujita *et al.*⁹⁾ have been made neither for the malonate ion nor for the malonate complexes. However, Schmelz *et al.*¹⁰⁾ have classified the normal vibrations of the malonate ion into different species of the point group $C_{2v}$ and assigned to infrared bands of malonic acid, its sodium and potassium salts and some metal complexes. The infrared spectrum of $VO(malon)\cdot 4H_2O$ was assigned according to Schmelz *et al.*¹⁰⁾

Maleic acid has two carboxylic acid groups attached to C=C in the cis-position and the molecule is planar. The maleate ion thus belongs to the point group $C_{2v}$. On coordination, the symmetry of the maleate ion does not change. No vibrational analysis of either maleate or its complexes with metals has been done. However, the Raman spectrum of maleic acid taken by Edsall¹¹⁾ and the infrared spectra of maleic acid and maleate complexes of some metals by Duval *et al.*¹²⁾ have been reported. The infrared spectrum of $VO(mal)\cdot 2H_2O$ has been assigned by comparing it with those of the malonate and oxalate.

The occurrence of a strong and sharp infrared absorption near 990 $cm^{-1}$ for V=O stretch indicates monomer V=O units in both the complexes. The infrared frequencies assigned for the water molecules clearly indicate coordinated nature of water molecules. Also, $VO(malon)\cdot 4H_2O$ is likely to contain lattice held water in addition to the coordinated water molecules as shown by the 1580 $cm^{-1}$ infrared band, assignable to the bending of lattice water. The loss of only two water molecules from the malonate complex at 125°C, as shown by the differential thermal analysis, may indicate that the two water molecules are lattice held while the other two are coordinated.

**A Comparison of Oxalate, Malonate and Maleate Complexes.** An attempt is made here to compare the properties of the complexes of the type $VO(LL)\cdot xH_2O$, where $LL=ox^{2-}$, $malon^{2-}$ or $mal^{2-}$, The ease of formation of the compounds seems to be in the order: oxalate>malonate> maleate. The solubility of the complexes decreases in the same order. The same series holds well for the stability of the complexes in water; the oxalate complex is not dissociated as judged by the cryoscopic data²⁾ while malonate dissociates to a small extent and maleate hydrolyses a little. Differential thermal analysis curves of oxalate, malonate and maleate have an exothermic decomposition peak at 285, 275 and 255°C respectively. The thermal stability of these complexes as obtained from the peak temperatures in the curves is also in the same order as given above.

Vanadium-oxygen bond is a multiple covalent bond, and is formed by the $p_\pi$-$d_\pi$ donation from oxygen to vanadium and superimposed upon the sigma bond. The amount of $p_\pi$-$d_\pi$ donation may be expected to depend upon the donor and acceptor abilities of oxygen and vanadium respectively. The coordination of ligands which donate sigma electron pairs will increase the electron density in the metal d-orbitals and as a result, $p_\pi$-$d_\pi$ donation from oxygen to vanadium is expected to decrease and consequently lower the V=O stretching frequency. The decrease in the V=O stretching frequency may be expected to depend upon the coordinating or donor ability of the ligands.¹³⁾ The comparison of the donor ability, among the compounds, oxalate, malonate and maleate should be fairly good. For this purpose, $VO(malon)\cdot 4H_2O$ is taken to be five-coordinated, two molecules of water being lattice held as already explained. The V=O stretching frequency for $[VO(ox)\cdot 2H_2O]$, $[VO(malon)\cdot$

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9) J. Fujita, A. E. Martell and K. Nakamoto, *J. Chem. Phys.*, **36**, 324, 331 (1962).

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11) J. T. Edsall, *J. Chem. Phys.*, **5**, 508 (1937).

12) G. Duval, J. Lecomte and M. A. Delay, *Bull. Soc. Chim. France*, **11**, 180 (1944).

13) J. Selbin, L. H. Holmes, Jr., and S. P. McGlynn, *J. Inorg. Nucl. Chem.*, **25**, 1359 (1963).

$2H_2O$] and [VO(mal)$\cdot 2H_2O$] occurs at 986, 990 and 1000 cm$^{-1}$, showing that the ability of the ligands to coordinate decreases in the order, $\mathrm{ox}^{2-} > \mathrm{malon}^{2-} > \mathrm{mal}^{2-}$, implying that the metal-ligand bond strength decreases from oxalate to maleate.

Since the decrease in V=O stretching frequency depends upon the donor capacity of the ligands, we feel that the series (obtained from V=O stretch) should resemble the nephelauxetic series,[14] which indicates the covalent tendency of the ligands. Therefore, the nephelauxetic series would be: $\mathrm{ox}^{2-} > \mathrm{molon}^{2-} > \mathrm{mal}^{2-}$. The position of malonate and oxalate ions in the naphelauxetic series is known from the electronic spectra and the position of malonate ion is very near to the oxalate ion, indicating that the covalent character of the metal-malonate bond is very nearly the same as that of the metal-oxalate bond.[15] The position of maleate ion is known neither in the nephelauxetic nor in the spectrochemical series. It is clear from V=O stretching frequency of the maleate that the maleate ion is lower than the malonate ion in the nephelauxetic series. But the spectrochemical series obtained from $D_q$ values of VO(LL)$\cdot x H_2O$ and $[\mathrm{VO(LL)_2}]^{2-}\cdot x H_2O$, except for VO(mal)$\cdot 2H_2O$ which spectrum could not be obtained is: $\mathrm{mal}^{2-} > \mathrm{ox}^{2-} \geqslant \mathrm{malon}^{2-}$. This series is not in accordance with the series obtained from V=O stretching.

Asymmetric carbonyl stretch which is raised to a higher frequency in oxalate, malonate and maleate cannot be taken to indicate the strength of the coordinating ability, since $\nu_a$(C=O) occurs near 1720, 1620 and (1710, 1730) cm$^{-1}$ respectively, implying that the stability is in the order: oxalate $\geqslant$ maleate $>$ malonate, which is not quite true as already discussed from other considerations.

There is not much difference in the stability constants[16,17] of metal oxalate and malonate complexes although the oxalate complexes are slightly more stable than the malonate complexes. In general, there is a decrease in the thermodynamic stability of the complexes from five to higher membered ring structures.[18] Since maleate forms seven membered ring, they form weaker complexes than malonate. However, it may be noted that in peroxy titanium complexes the stability in the order, oxalate > maleate > malonate has been noticed.[19]

Five coordinated, VO(malon)$\cdot 2H_2O$ and VO(mal)$\cdot 2H_2O$, can have tetragonal pyramidal structure very similar to VO(ox)$\cdot 2H_2O$.[2] VO(malon)$\cdot 4H_2O$ can have the same type of structure with two water molecules in the lattice. In solution, the five coordinated square pyraamidal molecules are likely to take up a solvent molecule at a much longer distance in the vacant position trans to vanadyl oxygen, completing the distorted octahedral arrangement.

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