RAMAN SPECTRA OF OXALATES AND OXALATO-COMPLEXES : VIBRATIONS OF DICARBOXYL.

By JAGANNATH GUPTA,
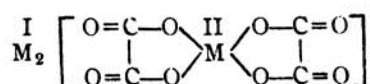
Palit Research Scholar in Chemistry.

ABSTRACT.—In continuation of the author's work on the Raman spectra of oxalic acid and metallic oxalates, the oxalato complexes of aluminium and titanium have been examined with a view to testing the validity of the views on the structure of the ionised carboxyl group put forward in previous papers. A general confirmation has been obtained, in view of certain remarkable changes observed in the spectra of the oxalate group, such as the disappearance of the line 1306 and the band 1620 of the oxalate ion, and the appearance of two lines 1680 and 1730, in the spectrum of potassium alumino-oxalate. The spectra also reveal the less stable character of the titanium complex. An attempt has been made to characterise the modes of oscillations of the (C_2O_4) ion and identify them with the Raman lines of the oxalates, on the basis of vibrations of the ethylene molecule, analysed by other workers. Also, from the appearance of two lines 1680 and 1730 in the spectra of the complexes, in place of only one observed in the case of the esters, it is suggested that in the complex, the two carbonyl linkages are of different energy contents, and hence the possibility of existence of an interesting form of isomerism is pointed out.

The crystal structures of anhydrous oxalic acid,[1] its dihydrate,[2] and several metallic oxalates, both normal and acid, have been studied by the usual methods of X'ray analysis. The general conclusion arrived at, from a detailed study of the Weissenberg photographs is that, except in the case of ammonium oxalate[3] which is slightly exceptional, the six atoms of the ionic group (C_2O_4) lie in the same plane. In oxalic acid dihydrate, Zachariasen's measurements show that the four oxygen atoms are equivalent, the distances being $C-C = 1.59\text{Å}$, and $C-O = 1.25\text{Å}$. The possibility of co-ordination of each of the hydrogen atoms between two oxygen atoms in anhydrous oxalic acid has been pointed out by Hendricks.

Similar conclusions were arrived at by the present author from the study of the Raman spectra of oxalic acid and metallic oxalates in solution, and have

J. Gupta

been discussed in a previous paper.[4] The structure $\left[\begin{array}{c}O \\ O\end{array}\right\rangle C-C \left\langle\begin{array}{c}O \\ O\end{array}\right]^{-}$ was attri-

buted to the ion, and Raman lines at 1306 1460, 1485, and 1620 wavenumbers were attributed to the vibrations of the group. It was considered that the validity of the hypothesis could be examined if one of the oxygen atoms in each of the (COO) group could be linked with a covalent bond with some element or group of elements; because, under such circumstances, the other oxygen is thereby linked to carbon in no other way than as C=O, which group should show its characteristic Raman lines, not originally observed in the spectra of the oxalates. Such a type of linking, besides existing in the esters, is precisely the one present in Werner's oxalato-complexes, which may be generally represented as

$$\text{I} \quad M_2 \left[\begin{array}{c} O=C-O \\ | \\ O=C-O \end{array}\right\rangle \text{II} \quad M \left\langle\begin{array}{c} O-C=O \\ | \\ O-C=O \end{array}\right]$$

in the particular case where the central atom is divalent, and 4-covalent. These complexes are, however, of varying degrees of stability in solutions, and it was thought if the progressive stabilities of such complexes could be followed with the help of Raman spectra of these solutions, and to the differences in spectra, if any, which might follow as a result of such co-ordination. The present paper contains the results for potassium titani-oxalate $K_2[Ti\,O(C_2O_4)_2]$ and potassium alumino-oxalate $K_3[Al\,(C_2O_4)_3]$, as also for potassium acid oxalate, which stands intermediate between oxalic acid and the normal oxalate. It was observed that the titani-oxalate crystallises well, but its aqueous solution gives strongly acid reactions from which calcium oxalate is immediately precipitated on adding calcium chloride, which indicates that the salt is hydrolytically dissociated to a large extent in solution. The alumino-oxalate is far more stable, inasmuch as its aqueous solution is rather feebly acid and gives very small amounts of precipitate with calcium chloride. This salt is therefore remarkably stable among the oxalato-complexes, as is also evinced by the isolation of its optically active stereo-isomers by Wahl.[5]

EXPERIMENTAL.

Potassium acid oxalate—Molecular proportions of chemically pure oxalic acid dihydrate and normal potassium oxalate were dissolved separately in water. The solutions were mixed with further addition of water, heated to boiling and crystallised.

PLATE XXII
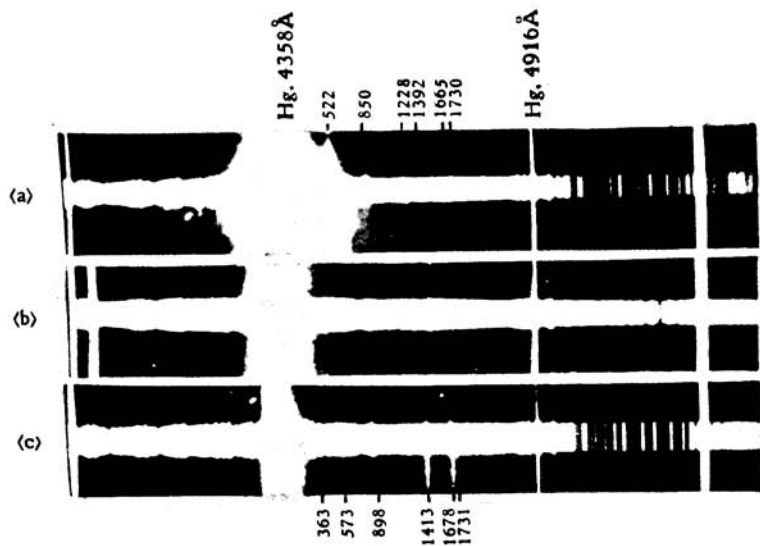
Raman spectra of aqueous solutions.

(a) Potassium titani-oxalate.
(b) Potassium oxalate.
(c) Potassium alumino-oxalate.

Potassium alumino-oxalate—The method of preparation is according to Wahl. Freshly precipitated pure aluminium hydroxide was heated to boiling for over an hour with just a little less than the calculated amount of a molecular mixture of oxalic acid and normal potassium oxalate. It was filtered from the small amount of the unreacted hydroxide and the filtrate evaporated on the water bath to a very small volume. This concentrated solution was allowed to crystallise in a desiccator over sulphuric acid. The crystals thus obtained were dissolved in the least quantity of water and recrystallised. The recrystallised product was pure, as shown by testing with litmus paper and calcium chloride.

Potassium titani-oxalate—Schuchardt's pure sample of the oxalate was recrystallised from warm water.

Distilled water, thrice redistilled in vacuum, was used for preparing the solutions. The crystals were washed with small quantities of this water, after which they were dissolved, and the solutions filtered repeatedly through gravimetric filter papers and finally run directly into Wood's tubes. The condenser method of illumination was employed, and a 4% solution of *m*-dinitrobenzene in benzene used as a filter for removing the 4046 Å group of mercury lines.

Table I shows the results for oxalic acid with its normal and acid salt, and table II for the complex oxalato-compounds along with those for diethyl oxalate, the latter being included for convenience of comparison.

Raman Spectra of aqueous solutions.

TABLE I.

Oxalic acid (G).	KHC_2O_4.	$K_2C_2O_4$ (G).	$(NH_4)_2C_2O_4$ (G).
		175 (1)	
		294 (1)	
450 (2)	450 (½)	452 (2)	442 (1)
847 (4)	870 (½)	898 (4)	895 (3)
1372 (½b)	1310 (0)	1306 (4)	1302 (3)
1460 (1)	1440 (1)	1460 (3)	1460 (2)
		1485 (3)	1485 (2)
1631 (2b)	1635 (1b)	1600±30 (3b)	1610±30 (3b)
1740 (4)	1715 (½)		

9

J. Gupta

TABLE II.

Potassium titani-oxalate	Potassium alumino-oxalate.	Diethyl oxalate pure (500 – 2000) cm⁻¹ (K – P).
	160 (1)	
283 (1b)	258 (1)	
365 (½)	363 (1)	
522 (4)	573 (2)	
850 (1b)	898 (2)	868 (10 b)
		904 (½ b)
1228 (2)		1018 (7 b)
		1106 (7 b)
1392 (1)	1413 (5)	1294 (4 sb)
		1351 (½)
		1393 (4)
1665 (1b)	1678 (2)	1451 (10 b)
1730 (1)	1731 (1)	1761 ± 7 (9 b)

K – P = Kohlrausch and Pongratz, *Ber. deut. chem. Gesel.*, **66**, 1355 (1933).

G = Gupta, *Ind. J. Phys.*, **10**, 199 (1936).

DISCUSSION OF RESULTS.

It may be observed that in the perfect complex, potassium alumino-oxalate, (1) the line 1306 cm⁻¹ has completely disappeared; (2) the doublet at 1470 cm⁻¹ has appeared as a single line of lower frequency shift at 1413 cm⁻¹; the broad band at 1610 cm⁻¹ observed in the spectra of the oxalates has disappeared, and two lines at about 1680 and 1730 cm⁻¹ appeared instead; (4) a new sharp line at 573 cm⁻¹ has appeared, which was not present in the spectra of the oxalate solutions. Similar changes have been observed in the spectrum of the titani-oxalate also, except that the lines have different frequency shifts, generally smaller, presumably owing to the greater mass of the central atom, and that the line 1306 cm⁻¹ observed in the spectra of the oxalates is present in this case as a line at 1228 cm⁻¹.

A thorough interpretation of such changes requires an exact analysis of the modes of vibrations of the (C_2O_4) group itself, and frequencies resulting therefrom, which does not appear to have been worked out. In the light of the views put forward by the present author in two earlier papers [1][8], as well as on the

strength of Zachariasen's and Hendricks's measurements, the oxalate ion may be represented as $\left(\begin{smallmatrix} O \\ O \end{smallmatrix} \right.\!\!\!\!>\!\!C\!\!-\!\!C\!\!<\!\!\left.\begin{smallmatrix} O \\ O \end{smallmatrix}\right)^{=}$ having in some cases a symmetry element V_h and in other cases the two (COO) groups lying in different planes. It is immediately apparent that the group possesses a higher degree of complexity than the carboxyl ion in the salts of monobasic carboxylic acids, and a larger number of modes of vibration is expected for such a grouping. An attempt is being made here to attribute several prominent lines to several modes of vibration of the group, following the line of assignment of Mecke [7] and of Dennison and Sutherland [8] in the case of the ethylene molecule, which possesses a similar element of symmetry. It may be pointed out that Sutherland and Dennison's assignments do not always agree with Mecke's, so that an absolute finality in the assignments attempted here cannot be claimed.

The more important modes of vibration of the ethylene molecule may be represented by the following figures :
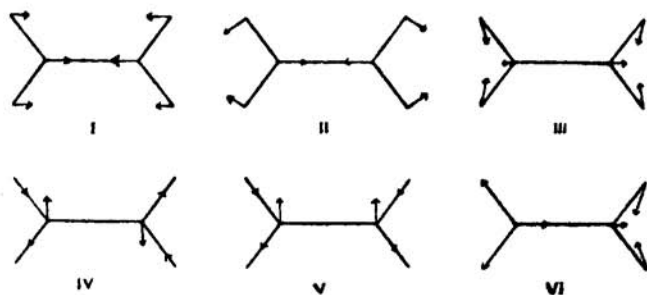

FIGURE 1.

Some normal vibrations of Ethylene (after Sutherland and Dennison).

Some of these vibrations are undoubtedly the origin of several Raman lines in the spectra of the oxalate ion also. The following assignments may be made :—

Mode I—The frequency 1342 has been attributed to this mode of vibration by Sutherland and Dennison. In this mode, the diagram indicates that the two CH_2 groups are oscillating against each other. The value of the frequency is therefore expected to be greatly diminished when the hydrogen atoms are replaced by heavier atoms. For this reason, in the Raman spectra of tetrachlorethylene, which contains as many Raman lines as ethylene itself, there is no Raman line of a greater frequency shift than 510 cm^{-1}, except one at 1570 cm^{-1}, which is to be attributed to a mode of vibration represented by II, as will be seen. When therefore, the hydrogen atoms are replaced by oxygen, and the

linkage between the two carbon atoms single, as in the case of the oxalate ion, the expected frequency can be roughly calculated. Taking Kohlrausch's values for the force constants of $C-C$ and $C=C$ links, this leads to

$$1342 \times \sqrt{\frac{4 \cdot 31}{9 \cdot 36}} \times \frac{14}{44} = 514,$$ a little over 500. The corresponding Raman line in the oxalate ion is therefore probably $\Delta \nu$ 450.

Mode II—The Raman line at $\Delta \nu$ 1620 has been assigned to this vibration in the case of ethylene. It may be seen that in this mode, involving a deformation oscillation of the hydrogen atoms, the value of the frequency normally attributed to $C = C$ oscillation remains unchanged. In the oxalate ion therefore, the corresponding Raman line is $\Delta \nu$ 898. As in the case of tetrachlorethylene, where the corresponding Raman line is $\Delta \nu$ 1570, the usual value of the frequency of vibration is diminished to some extent, presumably owing to the heavier masses of the atoms attached to carbon.

Mode III—This mode of vibration is expected to give rise to a strong Raman line, owing to its symmetrical character, and has been identified with the intense Raman line at 3020 cm^{-1} in the spectrum of ethylene. It is almost certain, therefore, that in the case of the oxalate ion, the corresponding line is one of the intense doublet in the region of 1470 cm^{-1}, which forms the most intense pair of lines in the Raman spectra of the oxalates. The appearance of a doublet in place of a single sharp line may be attributed to the close approach in the values of this frequency and of the combination frequency $175 + 1306$, both of which are observed in the spectra of the oxalates, and the consequent resonance degeneracy owing to perturbation between the two energy levels, as in the case of the 770 line of carbon tetrachloride. It must be confessed that this explanation of the origin of the doublet is to a high degree tentative; but it is a significant point to note that where the line at 1460 has shifted to other regions, as in the case of the complexes, the line appears single.

It may be also remarked in this connection that this mode of vibration is not prohibited even in the oxalato-complexes, where one of the oxygen atoms in each (COO) group is co-ordinated with a metal atom to form a 5-ring, as can be seen from Reitz's analysis[10] of the mode of vibration of five-membered rings. The mode of vibration represented as ω_5 by Reitz, involves within itself a vibration of this type, with the result that the Raman line arising from this mode of vibration persists even after co-ordination.

Modes IV and V—Of these two, mode V is not allowed in Raman effect owing to its asymmetric nature of oscillation with respect to the centre of symmetry. The vibration represented by IV may be identified with the broad band at 1620 cm^{-1} of the oxalates.

Mode VI—This mode of vibration is also 'forbidden' in Raman effect in the case of ethylene. In the case of the oxalate ion in solution, however, where a free rotation of each of the groups (COO) about the axis C—C is permissible, this vibration is no longer forbidden ; for, although when all the carbon and oxygen atoms are in one plane, the change in the polarisability of the molecule as a result of this vibration is zero, it is no longer so when the planes containing each of the (COO) groups make some angle with each other, as for example, in the crystals of ammonium oxalate. Since the two (COO) groups are free to rotate about the axis in solutions, the average value of the change in the polarisability will be quite large, and the corresponding Raman line will be quite intense. To this mode of vibration can therefore be attributed the strong Raman line at 1305 cm^{-1} in the spectra of the oxalates.

It is an extremely interesting fact that in the spectrum of the stable complex, potassium alumino-oxalate, this line has totally disappeared. It immediately indicates that a free rotation in the oxalato group is no longer permissible, as must essentially be the case if two of the oxygen atoms of the group are co-ordinated with the aluminium atom, in the way indicated by Werner. The persistence of this line at 1228 cm^{-1} in the case of the titani-oxalate indicates the more labile nature of the metal-oxalato ring postulated in this case, which is also supported by the chemical properties of the salt, previously mentioned.
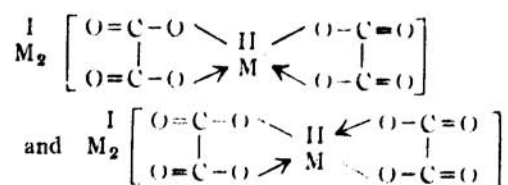
Whatever may be the alternative explanation of the modes of oscillation of the (C_2O_4) group and frequencies resulting therefrom, the fact that some remarkable changes have taken place in the structure of the (C_2O_4) group as a result of co-ordination is beyond doubt. The hypothesis of chelation also appears to be well established from a theoretical consideration of the changes observed.

It is an extremely interesting point to consider why two lines at about 1670 and 1730 cm^{-1}s, attributed to the $C=O$ grouping, appear in the Raman spectra of the oxalato complexes, unlike one, observed in the esters. If the oxalato complex is formulated as

$$K_3 \left[\begin{matrix} O=C-O \\ | \\ O=C-O \end{matrix} \searrow Al \overset{\nwarrow}{\underset{\swarrow}{\subset}} \left(C_2O_4\right)_2 \right]$$
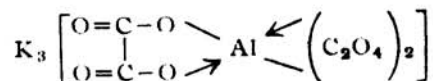
in conformation to the mode of preparation of the salt, it appears that the two bonds of the chelate are of different energy contents, as is quite likely, since their electron terms are different. This implies a difference in the binding energies of the two $C-O$ links, from which it follows that the two oxygen atoms in the two $C=O$ groups may be held with different energies. The two Raman lines of slightly different frequency shifts may be attributed to the two different energy contents of the two $C=O$ bonds of each oxalato group. Assuming the non-identical nature of the two links, it becomes an interesting possibility to obtain isomers

of the cis-trans type in such oxalato complexes where the central atom is 4-covalent and the valence bonds lie in the same plane, the isomers being represented as

$$M_2 \begin{bmatrix} O=C-O \diagdown & \diagup O-C=O \\ | & \diagup M \diagdown & | \\ O=C-O \diagup & \diagdown O-C=O \end{bmatrix}$$

$$\text{and} \quad M_2 \begin{bmatrix} O=C-O \diagdown & \diagdown O-C=O \\ | & & | \\ O=C-O \diagup & M \diagdown O-C=O \end{bmatrix}$$

An undoubtedly 4-covalent element having planar distribution of valencies is divalent platinum, as supported both by X'ray and stereochemical evidences.[11] Soderbaum's platoso-oxalic acid[12] $H_2 [Pt (COO)_2]$, $2H_2O$, gives rise to two series of salts having different colours and solubilities. The potassium salt, in particular, shows this isomerism even in the anhydrous state. With the free acid, concentrated aqueous solutions are blue, which change to yellow on dilution or on heating. Investigations are being made to decide whether this isomerism is due to the formation of polymers like Vernon's dimethyl telluro-iodide[13] and Kraus and Brodkorb's diammine palladous chloride,[14] or to a kind of isomerism depicted above, although it should be admitted that isomers of this type are not expected to show such sharp differences in properties.

In conclusion, the author wishes to express his respectful thanks to Sir P. C. Ray and Dr. P. B. Sarkar for their kind interests in the work, and to Prof. D. M. Bose for his kindly allowing the author to work in the Palit Laboratory of Physics. The work was carried out under the kind guidance of Dr. S. C. Sirkar, to whom also the author's best thanks are due.

Palit Chemical Laboratories,
University College of Science
and Technology, Calcutta.

REFERENCES.

[1] Hendricks, *Z. Krist*, **91**, 48 (1935).

[2] Zachariasen, *Z. Krist*, **89**, 442 (1934).

[3] Hendricks, *J. Chem. Phys.*, **5**, 102 (1936).

[4] Gupta, *Ind. J. Phys.*, **10**, 199 (1936).

[5] Wahl, *Ber. deut. chem. Ges.*, **60B**, 399 (1927).

[6] Gupta, *Ind. J. Phys.*, **10**, 117 (1936).

[7] Mecke, *Z. Phys.*, **64**, 173 (1930) ; *Z. phys. Chem.*, **17B**, 1 (1932).

[8] Sutherland and Dennison, *Proc. Roy. Soc.*, **148A**, 250 (1935).

[9] Kohlrausch, *Smekal-Raman Effect*, 1931, p. 154.

[10] Reitz, *Z. phys. Chem.*, **33B**, 179 (1936).

[11] Sidgwick, *Cornell University Lectures*, 1933, Chap 6.

[12] Söderbaum, *Bull. Soc. Chim.*, **46**, 188 (1886).

[13] Vernon, *J. Chem. Soc.*, **117**, 26, 889 (1920).

[14] Kraus and Brodkorb, *Z. anorg. allg. Chem.*, **165**, 73 (1927).