

INFRARED ABSORPTION SPECTRA OF COPPER POTASSIUM OXALATE, COPPER SODIUM OXALATE AND COPPER AMMONIUM OXALATE

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ABSTRACT

The infrared absorption spectra of powdered copper potassium oxalate, copper sodium oxalate and copper ammonium oxalate have been obtained in the region $2-15\mu$. A tentative assignment of the recorded bands has been made.

1. INTRODUCTION

The infrared absorption spectra of a few metallic oxalates, simple and complex, have been reported by Douville *et al.* (1941, 1942). They covered the limited region $550-1,600\text{ cm.}^{-1}$. This paper presents the investigations on the infrared absorption spectra of three complex oxalates in the region $5,000-600\text{ cm.}^{-1}$

2. EXPERIMENTAL DETAILS

The substances were examined as powders mulled in paraffin oil. A Perkin-Elmer Moder 112 single beam double pass infrared spectrometer provided with NaCl optics was used to record the spectra. Atmospheric water vapour and carbon dioxide and ammonia vapour served as calibration points. The spectral slit-width employed was approximately as follows: $5,000-2,000\text{ cm.}^{-1}$ 25 cm.^{-1} ; $2,000-1,300-5\text{ cm.}^{-1}$; $1,300-800-3\text{ cm.}^{-1}$; $800-600-5\text{ cm.}^{-1}$. The true per cent. transmission curves were drawn from a point by point division of the records obtained with the mulled sample and with pure paraffin oil.

3. RESULTS

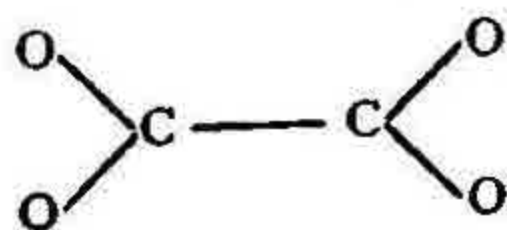
Table I gives the infrared data for these compounds. The figures written in brackets refer to the relative intensities of the different infrared frequencies and are based on the per cent. transmission of those frequencies.

TABLE I
Infrared Absorption Frequencies (cm^{-1})

Copper potassium oxalate	Copper Sodium oxalate	Copper ammonium oxalate
4726 (6)	4753 (4)	4639 (5)
3438 (8)	3603 (8)	3420 (6)
	3513 (8)	..
	3309 (5)	3178 (7)
2943 (10)	2931 (10)	2870 (10)
2877 (9)		
2739 (6)	2744 (3)	..
2592 (5)	2566 (2)	..
2251 (4)	2181 (2)	2217 (4)
1675 (9)	1674 (10)	1656 (7)
1456 (10)	1461 (9)	1453 (10)
	1414 (10)	..
1378 (10)	1377 (9)	1375 (10)
1280 (10)	1283 (10)	1280 (7)
1160 (8)	..	1156 (7)
1029 (7)	1033 (4)	1032 (6)
975 (7)	..	973 (6)
893 (7)	900 (6)	895 (5)
860 (6)	..	861 (4)
803 (9)	812 (9)	805 (6)
724 (7)	731 (4)	730 (4)
712 (8)	711 (4)	712 (6)

4. DISCUSSION

The observed infrared frequencies have to be interpreted mainly in terms of the modes of vibration of the oxalate ion group. The oxalate ion has the structure,



Infrared and Raman data (Douville *et al.*, 1941; Gupta, 1936) on the oxalates examined so far have shown a remarkable similarity to those of N_2O_4 which has

a similar structure. Sutherland (1933) has discussed the different modes of vibration of this molecule and assigned the observed infrared and Raman frequencies to these modes. Basing oneself on the parallel case of N_2O_4 and on the available infrared and Raman data on the metallic oxalates, one can write down the regions of absorption corresponding to these different modes:

$\nu_1 = 1,200-1,300 \text{ cm.}^{-1}$	$\nu_7 = \dots$
$\nu_2 = 1,300-1,400 \text{ cm.}^{-1}$	$\nu_8 = 300 \text{ cm.}^{-1}$
$\nu_3 = 750-800 \text{ cm.}^{-1}$	$\nu_9 = 370 \text{ cm.}^{-1}$
$\nu_4 = 900 \text{ cm.}^{-1}$	$\nu_{10} = 525 \text{ cm.}^{-1}$
$\nu_5 = 1,500-1,000 \text{ cm.}^{-1}$	$\nu_{11} = 650-700 \text{ cm.}^{-1}$
$\nu_6 = 1,650 \text{ cm.}^{-1}$	$\nu_{12} = 450 \text{ cm.}^{-1}$

For a simple metallic oxalate like sodium oxalate, ν_1 , ν_3 , ν_5 , ν_9 and ν_{11} are infrared active while ν_3 , ν_6 , ν_8 , ν_{10} and ν_{12} are Raman active. ν_7 is forbidden in both. This distinction vanishes in the case of complex oxalate like aluminium potassium oxalate where the two COO groups are no longer in the same plane, the centre of symmetry vanishes and consequently all the modes cited above are active in absorption and scattering (Douville *et al.*, 1941). Therefore, taking copper potassium oxalate as a representative of the substances that have been chosen for study, we can assign the recorded frequencies fairly easily.

1,280, 1,378 and 1,452, 803, 893, 1,675 and 712 cm.^{-1} bands can be assigned to the fundamentals ν_1 , ν_2 , ν_3 , ν_4 , ν_5 , ν_6 and ν_{11} respectively. The splitting of ν_2 is probably a case of resonance degeneracy. A similar splitting of the 1,360 cm.^{-1} Raman line of N_2O_4 has been attributed to this cause by Sutherland (1933). It is interesting to note that there is a further splitting in copper sodium oxalate, a strong triplet being found in this region.

Following the classification of Sutherland (1933) of frequencies near 2,700–2,900 cm.^{-1} in N_2O_4 , we can assign 2,943 and 2,739 to $\nu_1 + \nu_6$ and $\nu_1 + \nu_2$ respectively. 860 is likely to be the combination of ν_9 and ν_{10} while 1,029 and 4,700 cm.^{-1} are probably the first overtone of ν_{10} and a higher harmonic of one of the fundamentals ν_1 and ν_2 respectively.

The band at about 3,500 cm.^{-1} is due to the water hydration. Raman lines of about the same frequency have been recorded for a number of hydrated salts by Marignan and co-workers (1946, 1948). Three strong bands have been recorded in the region for copper sodium oxalate.

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