

## Studies on Metal Complexes in Aqueous Solution by Infrared Spectrophotometry

### I. A Qualitative Investigation of the Iron(III) and Aluminium Oxalate Systems

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The infrared spectra of the iron(III) and aluminium oxalate systems in aqueous solution have been recorded in the range 1 500—1 200  $\text{cm}^{-1}$ . Solutions of compositions corresponding to the first, second, and third mononuclear complexes show absorption peaks of almost the same frequency. The positions of the peaks correspond approximately to those of the third complexes in the solid state reported in the literature. Solutions in which the iron(III) concentration has been greatly increased give spectra showing two new absorption peaks. This fact is thought to indicate the existence of polynuclear complexes.

During the past few years a large amount of data has accumulated concerning the infrared light absorption of coordination compounds. The large majority of these investigations, however, has been confined to the solid state. Only in a few instances have equilibria of complex ions in aqueous solution been investigated. There is no doubt, however, that such measurements can be a valuable complement to conventional methods of investigation. This must be so much more the case when considering strongly coloured solutions of transition metals, where the Raman technique cannot be applied.

Inspired by the interesting achievements of Jones and Penneman<sup>1</sup>, we have therefore started a project of infrared absorption investigations on some metal complex systems in aqueous solution.

Owing to the strong absorption of water, measurements must be confined to ions having their characteristic vibration frequencies in those parts of the spectrum where the water absorption is not too strong.

In order to test the possibilities of the method we have made a qualitative investigation of the iron(III) and aluminium oxalate systems by studying the oxalate absorption frequencies in the region 1500—1200  $\text{cm}^{-1}$ . Solid state studies

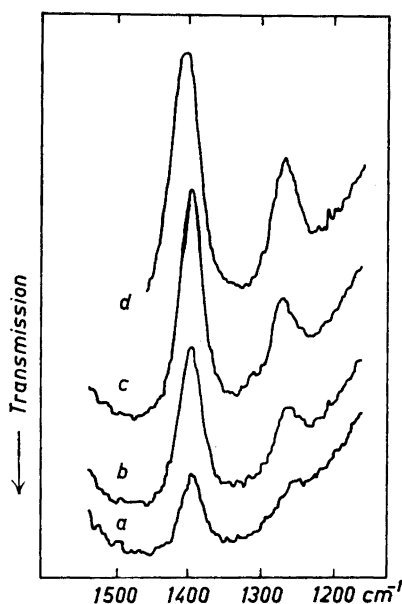


Fig. 1. Spectra of the iron (III)-oxalate system. The compositions of the solutions are found in Table 1. As in all figures of this paper the curves are arbitrarily displaced along the ordinate- (transmission-) axis to increase the readability.

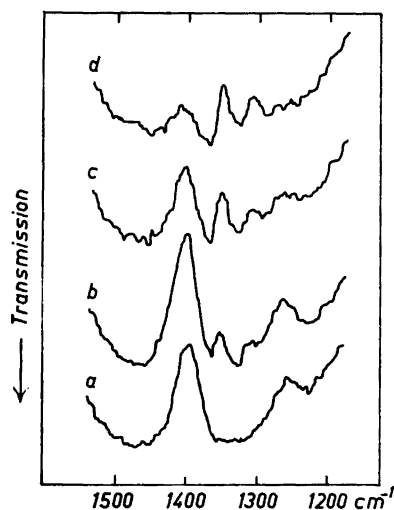


Fig. 2. Spectra of the iron (III)-oxalate system for large metal concentrations. The compositions of the solutions are found in Table 1.

<sup>2,3</sup> of these systems have shown definite shifts of the oxalate ion frequencies to occur as a result of coordination. Conventional investigations have also been reported in the literature <sup>4</sup>, the results of which indicate that the complexity is quite strong.

#### EXPERIMENTAL

*General technique.* The general procedure was that of Jones and Penneman <sup>1</sup>. The instrument was a Hilger H 800 Infrared Absorption Spectrophotometer fitted with a

Table 1. Wave numbers of the peaks of the iron(III)-oxalate system.

Fig: Curve	$C_{FeCl_3}$ M	$C_{Na_2C_2O_4}$ M	Observed wave numbers, $cm^{-1}$			
1:a	0.30	0.30	1 393	~1 255		
1:b	0.30	0.60	1 393	1 265		
1:c	0.30	0.90	1 393	1 268		
1:d	1.9	1.9	1 404	1 266		
2:a	1.20	0.60	1 398	1 258		
2:b	3.0	1.20	1 403	1 352	1 309	1 265
2:c	3.6	1.20	1 404	1 352	1 309	1 265
2:d	4.1	1.00	1 410	1 351	1 309	?

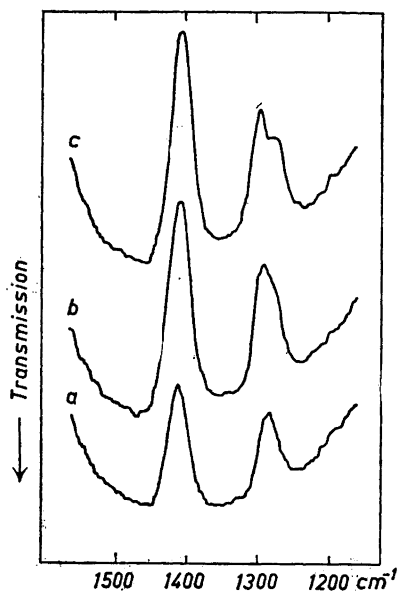


Fig. 3. Spectra of the aluminium-oxalate system. The compositions of the solutions are found in Table 2.

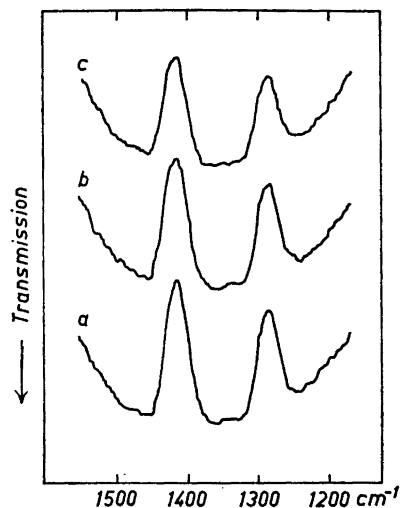


Fig. 4. Spectra of the aluminium-oxalate system for large metal concentrations. The compositions of the solutions are found in Table 2.

rocksalt prism. The window material of the cell was calcium fluoride. Platinum spacers measuring 8.8 and 12.5  $\mu$  defined the thickness of the cell. The instrument was used in the double-beam setting but without any compensation cell. The wave number setting was calibrated against benzene and toluene spectra. The reported wave numbers are correct within 2  $\text{cm}^{-1}$ .

The solutions to be investigated were made up by dissolving weighed amounts of the salts. The weighing accuracy was limited to about 1 % in view of the qualitative nature of the investigation. For the same reason chlorides were used instead of perchlorates.

Ferric chloride, sodium and potassium oxalate were of analytical grade, whereas the aluminium chloride was of purum quality.

Table 2. Wave numbers of the peaks of the aluminium-oxalate system.

Fig: Curve	$C_{\text{AlCl}_3}$ M	$C_{\text{K}_2\text{C}_2\text{O}_4}$ M	Observed wave numbers, $\text{cm}^{-1}$	
3:a	0.50	0.50	1 411	1 283
3:b	0.50	1.00	1 407	1 291
3:c	0.38	1.14	1 406	1 296 1 274
4:a	1.50	0.75	1 415	1 286
4:b	1.87	0.75	1 416	1 285
4:c	1.83	0.61	1 417	1 285

## RESULTS

In Fig. 1 are given the absorption curves for some solutions of iron(III) chloride and sodium oxalate in various proportions. Because of the strong complexity we can assume that the curves correspond to the first, second and third complexes, respectively. The wave numbers of the peaks of the third complex agree rather well with those given by Schmelz *et al.*<sup>2</sup> and by Fujita *et al.*<sup>3</sup>

In Fig. 1 is also included the absorption curve of the first complex at a much higher concentration. A shift of the absorption peak at 1 400  $\text{cm}^{-1}$  towards a somewhat higher wave number is observed. This fact led us to investigate some solutions in which the ratio between the iron(III) and the oxalate concentration was successively increased. The results given in Fig. 2 indicate the very interesting fact that, in addition to the above-mentioned shift of the 1 400  $\text{cm}^{-1}$  peak, two new peaks appear.

Analogous experiments were performed with aluminium in place of iron(III). The results are reported in Figs. 3 and 4. In this case as well (Table 2 and Fig. 3, curve c) the agreement with solid state data<sup>2,3</sup> is fairly good. An examination of Fig. 4 shows that no new peaks appear at high aluminium concentrations, although the shift of the 1 400  $\text{cm}^{-1}$  peak towards higher wave numbers is quite obvious.

## DISCUSSION

The first point of interest emerging from the presented observations is the very small variation of the position of the absorption peaks as the number of coordinated ligands is increased (Figs. 1 and 3). This fact is quite contrary to the findings of Jones and Penneman<sup>1</sup> for the silver cyanide system. To explain this difference we suggest that a significant wave-number shift will be observed only when the total enthalpy of coordination per ligand is appreciably different for the sequence of complexes with increasing ligand number. For all so-called normally built complex systems the enthalpy of addition of a ligand is almost constant within a given system (*cf.* Bjerrum<sup>5,6</sup>). The total coordination enthalpy per ligand will then also be approximately constant.

For the silver cyanide system, having a "characteristic coordination number" of two and maximum coordination number of four, we can with confidence assume a large difference in the enthalpy of addition of the two last ligands compared to that of the first two. Hence a considerable difference in the positions of the peaks of the second, third and fourth complexes might be expected, as is in fact observed.<sup>1</sup>

The oxalate systems investigated here are most probably quite normally built. The variation in the consecutive formation constants<sup>4</sup> is what might be expected for such a highly charged ligand. The absence of a pronounced shift of the peaks of successive complexes is thus understood.

Hence we conclude that, in general, there is little hope of using infrared spectroscopy as a "finger-print method" to prove the existence of step-wise complex formation.

The second point of interest is the effects produced by increasing the iron(III) concentration. The appearance of two new peaks at 1 352  $\text{cm}^{-1}$  and

1 309  $\text{cm}^{-1}$  is obviously an indication of a new molecular species (Fig. 2). We assume that this is a polynuclear complex. Whether the displacement of the peak at about 1 400  $\text{cm}^{-1}$  is also an indication of polynuclear complex formation or if it is some kind of a "medium effect" is difficult to say. It might be noted, however, that the shift is away from the position of the peak in question for the solid complexes <sup>3,4</sup>. If the first alternative is true, two kinds of polynuclear complexes must be considered. A confirmative correlation between metal — oxalate structure and the infrared spectrum of the oxalate ligand may — in a way — be obtained by a comparison between the solid-state spectra <sup>7,2</sup> of  $\text{CuC}_2\text{O}_4$  and  $\text{Na}_2\text{Cu}(\text{C}_2\text{O}_4)_2$ . Whereas the first compound shows oxalate peaks that coincide approximately with the peaks ascribed here to polynuclear complexes, the latter one shows a spectrum similar to that of the mononuclear complexes.

The Hilger spectrophotometer used was put at our disposal on loan for a considerable period of time by Messrs. Hilger & Watts, Ltd., London. We wish to express our appreciation of the generosity of this Company as well as of the kind cooperation of its Swedish representatives, Messrs. Bergman & Beving AB, Stockholm.

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