On the Far Infrared Spectra of the Tris-oxinato Complexes of

Al(III), Fe(III), and Co(III) in Chloroform Solution

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The absolute intensities of the infrared absorption bands in the 600—250 cm⁻¹ part of the spectrum have been measured for tris-oxinato complexes of aluminium, iron(III) and cobalt(III) in chloroform solution. Some bands assigned as corresponding to metal-oxygen vibrations have such intensities that the degree of covalent contribution to the M—O bonds is supposed to decrease in the order Co > Fe > Al. The same sequence of covalency is also suggested from the absolute intensities of the C—O stretching bond of the oxinato ligand at about 1100 cm⁻¹.

The infrared absorption of metal complexes that corresponds to the ligand-metal vibration modes is of great interest, as it can give information about the conditions of bonding between metal and ligand. So far, most investigations have been planned with the aim of determining the force constants of these vibrations. However, even if the force constants are more or less directly related to the bonding strength of the bonds in question, they cannot differentiate between bonds of large polarity (*i.e.* a low degree of "covalency") and bonds of low polarity, where the neutralization of charges is great.

The infrared intensity, however, being related to the change of the dipole moment of the molecule during the vibration that corresponds to the absorption frequency observed, could in principle give information about the polarity of a certain bond. The assumptions that must be made are, firstly, that the vibration mode is an almost pure vibration of the A—B bond, which can be clearly distinguished from vibrations of the rest of the molecule, and, secondly, that the factor determining the change of the dipole moment of that bond (A—B) is the variation of distance between the residual charges (q_A and q_B) on the atoms A and B. This latter assumption has been shown to be invalid in many cases, but should it be valid at all, it will be so for the metal-ligand bond in a coordination complex, where the electrostatic nature of the bond is certainly great.

In spite of the wellknown theoretical difficulties in obtaining absolute infrared intensities, it thus seems to the present authors that measurements

of the absorption intensities of the metal-ligand vibrations for a series of related complexes should give at least qualitative information about the polarity of the metal-ligand bonds.

As an introductory exercise in this field we have investigated some tris-oxinate complexes in chloroform solution in the frequency range 600—250 cm^{-1}. In order to relate the metal-ligand bonding to changes in the vibration of the ligand, we have also measured the intensity and the frequency of the absorption peak at about 1100 cm^{-1}, ascribed by previous investigators[1,2] to a C—O stretching mode. No other part of the complicated spectrum in the NaCl range was measured, as there does not seem to be any normal coordinate analysis of oxinate complexes reported in the literature.

EXPERIMENTAL TECHNIQUES AND RESULTS

Oxinato complexes of Al(III), Fe(III), and Co(III) were prepared from standard analytical prescriptions. They were recrystallized and analysed for H, C, and N.

Al(oxinate)$_3$ (Found: C 69.1; H 4.12; N 9.07. Calc. C 70.58; H 3.95; N 9.15).
Co(oxinate)$_3$ (Found: C 63.9; H 3.80; N 8.36. Calc. C 65.99; H 3.69; N 8.55).
Fe(oxinate)$_3$ (Found: C 66.3; H 3.61; N 8.64. Calc. C 66.41; H 3.72; N 8.61.

The spectra were measured with a Perkin Elmer PE 521 spectrophotometer. During the measurements in the low frequency region the instrument was carefully flushed with dried air. The slit program of the instrument[3] was set so that a spectral slit width (S) of 2 cm^{-1} or less was obtained (Table 1), $i.e.$ slit program 700 for the low frequency range

Table 1. Spectral width $\Delta\nu$ at an instrument slit program of 700. S = mechanical slit width.

ν (cm^{-1})	600	500	400	300	250
S (μm)	372	459	965	1290	1303
$\Delta\nu$ (cm^{-1})	1.82	1.54	1.91	1.34	0.88

and 1000 at $\nu \approx 1100$ cm^{-1}. Spectra for six different concentrations were run and the values of the transmission, T_0, of the zero line (adjusted from a run with pure solvent in both sample and reference cells) and of the transmission, T, were read at every whole wave-number. These readings were transformed to molar extinction coefficients by an electronic computer, giving also the mean of the molar extinction coefficients and the standard deviation. These extinction coefficients were then plotted against wavenumber (Fig. 1) and the apparent spectral characteristics $\varepsilon^{(a)}$ and $\nu_{\frac{1}{2}}^{(a)}$ were estimated from these plots for each peak (Table 2, Fig. 2). For the 1100 cm^{-1} peak, the absorption at the peak maximum was calculated and from this the halfwidth for every concentration. This peak was also measured for an aqueous solution of oxine in an excess of sodium hydroxide. Even with the rather high resolution of the spectrophotometer, the spectral slit widths are in many cases comparable to the halfwidth of the absorption peaks recorded. Hence, some type of correction has to be introduced. Following Ramsay[4] we have multiplied the product of the apparent extinction coefficient and the apparent half-width with a coefficient K, which has the value that can be found in Table III of Ref. 4. That is, lim $K = \pi/2$, when $\Delta\nu/\Delta\nu_{\frac{1}{2}}^{(a)} \to 0$.
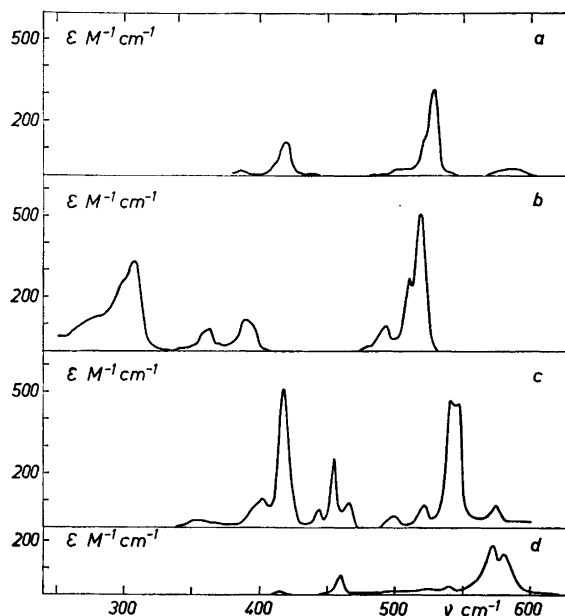
Fig. 1. The observed spectra in the 250—600 cm⁻¹ range of the a) Co(III), b) Fe(III), and c) Al(III) oxinato complexes in chloroform and d) of oxine in paraffin oil.

As our values of $\varepsilon^{(a)}$ are the means of readings at various optical densities and the correction factor K depends [4] upon the optical density, we have adopted some kind of mean value for this factor. Thus for ε in the ranges of 100—500, 100—50, and 50—10 M^{-1} cm⁻¹ the rows of $\ln(T_0/T) = 0.6$, 0.4, and 0.2 were used. The error in taking a not quite correct optical density row will be appreciable only when $\Delta\nu/\Delta\nu_{\frac{1}{2}}^{(a)} > 0.5$, a case that is seldomly or never encountered (Table 2).
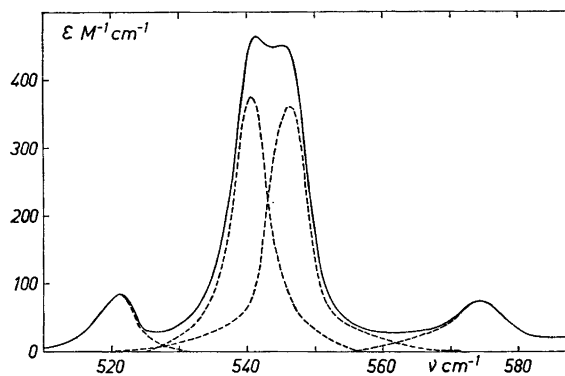

Fig. 2. Illustration of the estimation of the spectral data of composite peaks. The actual spectrum is that of the Al(oxinate)₃ complex between 500 and 600 cm⁻¹.

Table 2. Spectral data of the oxinato complexes in chloroform solution and of oxine in paraffin oil solution. $A = \varepsilon \times \Delta\nu_{\frac{1}{2}} \times K$ (*cf.* the text).

Fe(oxinate)$_3$

ν (cm^{-1})	ε (M^{-1} cm^{-1})	$\Delta\nu_{\frac{1}{2}}$ (cm^{-1})	K	A (M^{-1} cm^{-2})
1107	1735	4.1	1.53	10990
518	510	8.3	1.55	6560
511	256	6.8	1.55	2700
494	86	9.7	1.56	1290
596	30	6.2	1.53	290
390	120	10.7	1.55	1980
364	64	5.5	1.53	530
360	50	7.5	1.55	580
308	333	12.0	1.56	6230
297	184	10.0	1.56	2870

Co(oxinate)$_3$

ν (cm^{-1})	ε (M^{-1} cm^{-1})	$\Delta\nu_{\frac{1}{2}}$ (cm^{-1})	K	A (M^{-1} cm^{-2})
1110	544	9.1	1.56	7630
589	22	10	1.55	340
579	17	8.8	1.55	230
529	318	6.9	1.55	3400
522	110	6.4	1.55	1090
504	18	13	1.56	370
429	8	4	1.47	50
420	121	7.4	1.55	1390
411	35	5.6	1.51	300
385	19	4	1.47	110

Al(oxinate)$_3$

ν (cm^{-1})	ε (M^{-1} cm^{-1})	$\Delta\nu_{\frac{1}{2}}$ (cm^{-1})	K	A (M^{-1} cm^{-2})
1113	1166	7.4	1.55	13400
575	75	10.3	1.55	1200
546	360	6.6	1.55	3680
541	376	6.1	1.55	3560
522	85	7.8	1.55	1030
500	38	11.0	1.56	650
466	91	6.0	1.53	840
455	252	5.4	1.54	2100
444	66	5.2	1.52	520
418	510	8.8	1.55	6960
402	102	8.8	1.55	1390
395	59	5.6	1.54	510
355	27	14	1.56	590

Oxine

ν (cm^{-1})	ε (M^{-1} cm^{-1})	$\Delta\nu_{\frac{1}{2}}$ (cm^{-1})	K	A (M^{-1} cm^{-2})
1083	37	25	1.57	1450
1065	65	15	1.56	1520
636	70	3.9	1.46	400
581	110	10.5	1.56	1800
572	148	10.0	1.56	2310
539	31	6.8	1.54	330
523	19	15	1.56	450
499	9	13	1.56	180
459	68	6.0	1.53	620
415	13	5.3	1.51	100

Cells. In the range 600—250 cm⁻¹ 0.5 mm CsBr cells were used, whereas 0.1 mm NaCl ones were used in the 1100 cm⁻¹ region. All cell thicknesses were checked now and then by interferometric measurements. For the recording of the spectra of the oxinate ion in aqueous solution IRTRAN-2 cells were used with a 25 μ platinum spacer. When recording the spectra of the free oxine it was considered necessary to avoid all contact with metals that might have been slightly corroded and that could then give oxinato complexes, the spectra of which would cover that of the free oxine. Therefore CsBr plates with teflon spacers (0.5 mm) were utilized and a few drops of the solution were placed between the plates. As a consequence of this arrangement paraffin oil was used as a solvent, as it was impossible to avoid leakage when chloroform was the solvent.

DISCUSSION

Concentrating first on the C—O ligand-vibration we notice a decrease of the integrated absorption A (M⁻¹ cm⁻²), counted per ligand, in the sequence Al (4500) > Fe (3700) > Co (2500). The corresponding value for the aqueous solution of the oxinate ion was found to be 3600 M⁻¹ cm⁻², but no direct comparison can be made, of course, between the measurements in chloroform and water. The intensity sequence of the chelates, however, can be interpreted in terms of decreasing polarity of the C—O bond. As in the previous study on glycolate complexes,[5] we would like to suggest that this decrease of polarity is caused by a partial neutralization of charge on the oxygen atom, caused by electron donation towards the metal ion. This should mean that the aluminium complex is the most electrostatically bonded complex in this series and that the cobalt ion has achieved a considerable decrease of its charge. This then ought to be reflected in the absorption intensities of the metal-ligand vibrations.

The value of the intensity of the C—O vibration in the oxine molecule is very low, which makes it difficult to make a reliable assignment among the feeble absorption peaks in the region 1200—1000 cm⁻¹ to this vibration mode. Indeed, Charles *et al.*[1] report the 1100 cm⁻¹ peak of the oxinates as characteristic of the salts and not present in the free acid. From measurements in paraffin solutions we suggest that one or both of the two peaks found at 1083 and 1065 cm⁻¹ (Table 2) do correspond to the C—O vibration. As to the latter alternative, splitting may be caused by hydrogen bond interaction between two oxine molecules. Because of the low values of absorption the oxine concentration could not be varied adequately to check this proposition from the mass action law dependence of the postulated species. Probably only one of the peaks recorded, however, corresponds to a C—O vibration and then it is interesting to note that the intensity is lower than even that for the Co(III) oxinate (1500 compared to 2500). This indicates from our postulates that the charge compensation is more effective in the proton complex than in the metal complexes investigated. It is, of course, not possible to make any close comparison between the intensities because of the different solvents that were used.

Turning to the low frequency vibrations we strongly feel the lack of a normal coordinate analysis. However, we consider it plausible that with so heavy and rigid a ligand as the oxinate ion, absorption corresponding to the metal-nitrogen vibration modes must lie far out in the low frequency region of the spectrum. Indeed, investigations of pyridine [6,7] and quinoline [7] com-

plexes of various metal ions — although divalent ones — indicate that the M—N vibrations are to be found in the range 260—200 cm^{-1}. As any absorption below 275 cm^{-1} is difficult to observe with our present equipment, weak M—N bands may possibly be present in the range 275—250 cm^{-1} without having been detected.

There are some fairly strong bands, however, especially for the Fe(III) and Al(III) complexes that do not appear in the spectrum of the free oxine molecule. These are the systems of bands around about 300 cm^{-1} for the Fe(III) complex and the three-band system at 466, 455, and 444 cm^{-1} for the Al(III)-complex. In the latter case the strong peaks at 418 and 402 cm^{-1} are also unaccounted for in the oxine spectrum, $i.e.$ if the assignment of Sawyer et $al.$[8] is followed, which relates the 459 cm^{-1} peak (Table 2) to the C—O bending vibration mode, appearing at higher wavenumbers in the complexes. We suggest, then, that these absorption peaks correspond to metal-oxygen vibrations. The peaks at 396, 390, 364, and 360 cm^{-1} for the Fe(III) complex, 395 and 355 cm^{-1} for the Al(III) complex, and probably the one at 385 cm^{-1} for the Co(III) complex, correspond to out-of-plane or ring deformations of the ligand, as they appear almost in the same position for the three complexes.

In the spectrum of the oxine there is a weak band at 415 cm^{-1} (Table 2) (421 cm^{-1} in KBr [8]) that has been ascribed to a ring deformation mode [8] and as many other ring deformation vibrations give rise to stronger absorption in the complexes than in the acid ($e.g.$ the ones about 500 cm^{-1}) it may be reasonable to assume that some bands of this type, not noticable in the oxine spectrum, may be enhanced upon coordination, the more so, the greater the polar nature of the metal-oxygen bond.

Taking the band systems at about and above 500 cm^{-1} as corresponding to in-plane C—O bonding and ring vibration modes as suggested by Tackett and Sawyer,[8] the assignments made above leave us with the 420 cm^{-1} and 411 cm^{-1} peaks of the Co(III) complex unaccounted for. We tentatively propose that they correspond to Co—O vibration modes. If this is correct, the sum of the integrated absorptions of the metal-oxygen peaks of the three complexes falls in the sequence Al (11 800) > Fe (9100) > Co (1690). This is the order that is expected from the trend of charge compensation of the oxygen atom.

So far, we have neither offered assignments nor an explanation for the various positions of the M—O absorption bands proposed. For one thing, we will suggest that the difference in metal ion mass of the Al and Fe(III) complexes is governing the shift of the Fe(III)—O absorption towards the low-frequency part of the spectrum. The force constants of these two complexes with not very differing polarity of the M—O bond should be about the same, so that the vibration frequency is determined by the effective reduced mass. However, the smaller size of the Al^{3+} ion compared to the Fe^{3+} ion will probably make the Al—O force constant a little greater than that of the Fe—O bond in spite of the increased degree of covalency in this case, thus shifting the absorption more towards the high frequency side should be expected from the reduced mass relation only.

If the 420 and 411 cm^{-1} peaks of the Co(III) complex are really corresponding to Co—O vibrations, the change of frequency compared to the Fe(III)

case must be related to an increase of the force constant of the Co—O bond compared to that of the Fe—O one resulting from the much higher degree of covalent bonding that is suggested from the low intensity of the C—O and the (supposed) M—O bands.

Another important aspect is the possible existence of different geometrical isomers. For a tris(bidentate), principally octahedral, complex $M(AB)_3$ there exist two such isomers.

In analogy with the tris-glycinato Co(III) complexes we call the 1,2,3-isomer β and the 1,2,6-isomer α (Ref. 9, Chapt. 3). The β form is then, considering the MO_3N_3 unit only, of C_{3v} symmetry, and the α-form of C_{2v} symmetry.

It then seems reasonable that the β-isomer of higher symmetry should have a simpler M—O vibration spectrum than the α-isomer has.

Indeed, if we, in consequence with what has been said earlier on the relatively large separation of M—N and M—O vibration frequencies, take only the MO_3 units into consideration, the β form will be of a pyramidal XY_3 type and the α form of a planar ZXY_2 type. These units, of course, still retain their respective symmetries, C_{3v} and C_{2v}. As to stretching vibrations, the only ones of importance here, the XY_3 unit will have two vibrations of E and A_1 symmetry (Ref. 10, p. 85), whereas the ZXY_2 unit will have three (Ref. 10, p. 95), one XY sym. (A_1), one XY asym. (B_2) and one XZ (A_1) stretching vibration. Of the latter, the A_1 should really be IR-inactive for a strictly linear shape of the Y—X—Y bonding. However, a slight deformation will probably be present in the oxinate complexes and hence there will appear in the spectra three lines related to the α-form. In Table 3 we have collected the different absorptions and the suggested assignments. By doing this we have followed the frequency order of the A_{1xy} B_{2xy} and A_{1xz} vibrations of ClF_3 (Ref. 10, p. 95) and that of the E and A_1 ones from the examples given in Table II-19 of Ref. 10.

Table 3. Assignments of the metal-oxygen vibrations (cm⁻¹) for the tris-oxinato complexes.

	A_{1xy}		
Al (α)	466 A_{1xy}	455 B_{2xy}	444 A_{1xz}
Al (β)	418 E	402 A_1	
Fe (α)	Possibly around 360		
Fe (β)	308 E	297 A_1	
Co (β)	420 E	411 A_1	

Hence we suggest that the labile aluminium system contains comparable amounts of both isomers and that the absorption peaks at 418 and 402 cm^{-1} correspond to the β-isomer, whereas the three peaks around 455 cm^{-1} are related to the α-isomer.

The many bands around 390 add 360 cm^{-1} of the iron(III) system, some of which have a surprisingly high intensity, may possibly indicate the presence of the α-isomer, if the 308 and 297 cm^{-1} peaks are then thought to represent the β-form. As stated above, these bonds may, however, also be related to internal ligand vibrations.

The two single peaks of the Co(III) complex suggest that in this case only the β-isomer is present. This complex is certainly rather inert and should not undergo any rearrangements in solution. It is worth remarking that in the β-isomer all the more or less negatively charged oxygen atoms lie close on one octahedral face and most probably repel one another slightly. Hence the M—O distance should be somewhat greater than is the case for the α isomer and, from Badgers rule, the force constant should be smaller for the β than for the α-isomer. This fits in with our assignment of the absorption peak of lowest frequency as corresponding to the β-form.

Then turning to the bands around and above 500 cm^{-1}, the ones of remarkable intensity at 541 and 546 (Al(III)), at 511 and 518 (Fe(III)) and 522 and 529 cm^{-1} (Co(III)) following Sawyer [8] represent ring deformations. They are then related to the 572 and 581 cm^{-1} bands of the oxine acid. Still following Sawyer we suggest then that the bands, somewhat lower than the just mentioned ones, correspond to the C—O bending mode.

Some interesting observations can be made. For the Al(III) system there are two bands at 500 cm^{-1} and 522 cm^{-1}. These may then be thought to correspond to the two isomers, the existence of which was suggested from the M—O vibration pattern. For the Co(III) and Fe(III) systems we find only one band, at 504 cm^{-1} and 494 cm^{-1}, respectively. The intensities of these bands (Table 2) follow the sequence Al (1680) > Fe (1290 > Co (370). These values should be divided by three to be comparable with the C—O bending intensity for the oxine acid and we then find the sequence oxine (620) > Al (560) > Fe (430) > Co (120). For the complexes this is the intensity sequence that may be anticipated from the decrease of the C—O bond polarity, but the value for oxine falls out of the pattern. Of course, some part of this effect may arise from the different solvents used. For meaningful comparisons, moreover, the bond dipole moments should actually be calculated, but this lies outside the scope of this qualitative investigation.

Another possibility is that one of Sawyer's assignments [8] is not correct: either is the C—O bending mode of oxine not represented by the 459 cm^{-1} band or are the ones related to the complexes represented by some of the bands described above as ring deformations. In the latter case one could choose two peaks for the Al system and one for each of the other two and try to obtain as similar a pattern in the three cases as possible. Then for the peaks 546, 541 cm^{-1} (Al), 518 (Fe(III)), and 529 (Co(III)), one obtains the sequence Al (2400) > Fe (2200) > Co (1150) > oxine (620). But for the agreement between this intensity sequence and that of the C—O stretching modes for this, admittedly rather subjective, choice, one can find arguments to

strengthen it from the work of Saywer *et al.*[8] too, as they report as C—O bending absorptions the strong peaks of Mn(II) (492 cm^{-1}), Co(II) 503 cm^{-1}, Cu(II) 520 cm^{-1}. Extrapolating this sequence towards what may be encountered for three-valent ion complexes, the peaks, reported as strong and appearing at 546 cm^{-1} (Al) and 522 cm^{-1} (Fe(III)) by these authors, may give an indication of the bands, described by us as C—O bending modes, being really of that type.

Thus for similarly built complexes it seems possible to use infrared intensity measurements to obtain a qualitative knowledge about the polarity of the metal-ligand bonds and also to correlate the changes of this polarity with corresponding quantities for well defined single bonds in the ligand.

More specifically, the result of this investigation is that we suggest that the order of "covalency" in the three oxinate complexes decrease in the order Co > Fe > Al. For the two transition metal ions, this order is the one that follows from the nephelauxetic series proposed by Jørgensen.[11]

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