

On the Infrared Spectra of Some Tris-acetylacetonato Metal(III) Complexes and Some Bromo- and Nitro-analogues in Chloroform Solution

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The intensities have been measured for the infrared absorption bands of the complexes $M(\text{acac})_3$ where $M = \text{Al}, \text{Cr(III)}, \text{Fe(III)}$, and Co(III) in the spectral ranges $1600-1300 \text{ cm}^{-1}$ and $600-250 \text{ cm}^{-1}$. Also, the spectra of $M(\text{acac-X})_3$, where $M = \text{Cr(III)}$ or Co(III) , and X is NO_2 or Br , have been recorded. From the magnitude of the $M-O$ vibration absorption intensities the following sequence of increasing covalency of the $M-O$ bonds was found: $\text{Al} < \text{Cr} < \text{Fe} < \text{Co}$.

The intensities of the absorption bands of the ligands are discussed in relation to this sequence by using a valence bond resonance model. Similar comparisons are made for the spectra of the substituted complexes. Inductive effects seem to be more important than mesomeric ones. It is also suggested that a metal-ligand electron donation occurs, which is most important for the Co(III) complexes. An unusually strong absorption band in the spectrum of $\text{Fe}(\text{acac})_3$ is tentatively ascribed to an electronic transition.

The metal complexes of β -diketones and especially those of acetylacetonato are well known and have been extensively studied.¹ For this reason they present an interesting field for the testing of the proposition made in an earlier work² that the infrared absorption intensity of metal-ligand vibration modes can be used as a measure of the polarity of the metal-ligand bond. This proposition rests upon the assumption that the residual charges on metal and ligand atoms do not change during the vibration. This will hold strictly only for a purely ionic bond and the conditions are thus never completely fulfilled. This assumption may not be valid for complexes, where the metal-ligand bonds have large components of both σ - and π -type of covalent bonding. The acetylacetonato complexes are probably of this kind,³ so deviations from the behaviour of purely ionic compounds may be expected.

Nevertheless, we have considered it interesting to investigate how far the model of fixed charges can be used to explain qualitatively the infrared absorption intensities of the metal-ligand vibrations.

We have therefore measured the absorption intensities in the range 600–250 cm^{-1} of the acetylacetonato complexes of Al(III), Cr(III), Fe(III), and Co(III) in chloroform solution. In order to correlate the metal-ligand charge distribution to that of the ligands we have also made intensity measurements of some intense absorption bands in the 1250–1600 cm^{-1} range, thought to correspond to C=C and C=O vibrations.

Furthermore, it has been considered relevant to investigate the effect upon the metal-ligand vibrations of a substitution of the γ -proton by groups

Table 1. Spectral data of the unsubstituted complexes.

Al(acac) ₃				Cr(acac) ₃			
$\nu(\text{cm}^{-1})$	$\epsilon(\text{M}^{-1}\text{cm}^{-1})$	$\Delta\nu_{1/2}(\text{cm}^{-1})$	$A(\text{M}^{-1}\text{cm}^{-2})$	$\nu(\text{cm}^{-1})$	$\epsilon(\text{M}^{-1}\text{cm}^{-1})$	$\Delta\nu_{1/2}(\text{cm}^{-1})$	$A(\text{M}^{-1}\text{cm}^{-2})$
1589	2050	18.5	37930	1573	2200	15.0	33000
1575	495	13.0	6435	1555	850	22.0	18700
1532	2835	17.8	50460	1519	2980	13.0	38740
1457	930	27.2	25300	1425	480	30	14400
1411	1090	30	32700	1380	1950	28.0	54600
1385	1160	25.5	29580	1277	577	9.5	5482
1288	573	6.5	3725	596	200	8.0	1600
579	133	20.0	2660	559	11	16.0	176
562	51	13.2	673	460	570	10.9	6210
490	401	19.6	7860	417	88	10.8	950
430	78	8.0	624	352	135	9.8	1294
419	256	8.0	2050				
394	106	10.6	1328				
Fe(acac) ₃				Co(acac) ₃			
$\nu(\text{cm}^{-1})$	$\epsilon(\text{M}^{-1}\text{cm}^{-1})$	$\Delta\nu_{1/2}(\text{cm}^{-1})$	$A(\text{M}^{-1}\text{cm}^{-2})$	$\nu(\text{cm}^{-1})$	$\epsilon(\text{M}^{-1}\text{cm}^{-1})$	$\Delta\nu_{1/2}(\text{cm}^{-1})$	$A(\text{M}^{-1}\text{cm}^{-2})$
1572	1927	18.2	35070	1573	2200	18.0	39600
1553	710	18.0	12780	1556	600	14.0	8400
1522	3250	12.3	39980	1517	2370	12.5	29630
1428	457	44	20110	1425	330	30	9900
1383	1400	20.2	28280	1380	1580	21.0	33180
1360	980	20.7	20290	1278	316	7.5	2370
1273	700	8.8	6160	465	308	8.4	2590
569	56.2	9.6	540	435	35	18	630
556	40.0	15.4	616	381	55	14	770
545	80.5	10.4	837	369	13	7.5	56
437	264	17.7	4673	360	29	14.2	412
413	86	5.4	464				
406	85	5.5	468				
297	204	23.6	4814				
274	61.5	14.8	910				

Table 2. Spectral data of the substituted complexes.

Co(acac-Br)₃ (Solvent CHCl₃)

$\nu(\text{cm}^{-1})$	$\epsilon(\text{M}^{-1}\text{cm}^{-1})$	$\Delta\nu_{1/2}(\text{cm}^{-1})$	$A(\text{M}^{-1}\text{cm}^{-2})$
1548	2837	18.4	52200
1446	900	17.4	15660
1420	935	12.1	11310
1415	370	21.0	7770
1359	1060	11.6	12300
1340	1720	14.8	25460
474	365	9.8	3577
456	68	15.5	1054

Co(acac-Br)₃ (Solvent CH₂Cl₂)

$\nu(\text{cm}^{-1})$	$\epsilon(\text{M}^{-1}\text{cm}^{-2})$	$\Delta\nu_{1/2}(\text{cm}^{-1})$	$A(\text{M}^{-1}\text{cm}^{-2})$
475	389	9.7	3773
456	73	16.5	1205
381	34	7.0	238
367	22	7.8	172
361	19.5	7.0	137

Co(acac-NO₂)₃

$\nu(\text{cm}^{-1})$	$\epsilon(\text{M}^{-1}\text{cm}^{-1})$	$\Delta\nu_{1/2}(\text{cm}^{-1})$	$A(\text{M}^{-1}\text{cm}^{-2})$
1569	1000	6	6000
1562	2960	12	35500
1555	1470	5	7500
555	45.5	9.0	410
542	24.5	13.6	330
468	302	12.8	3870
429	24.0	25	600
380	19.5	7.0	137
370	52.5	11.1	583
361	54.5	7.6	414

Cr(acac-Br)₃ (Solvent CHCl₃)

$\nu(\text{cm}^{-1})$	$\epsilon(\text{M}^{-1}\text{cm}^{-1})$	$\Delta\nu_{1/2}(\text{cm}^{-1})$	$A(\text{M}^{-1}\text{cm}^{-2})$
1549	3320	17.8	59100
1451	1550	12.5	19380
1422	1220	18.2	22200
1413	320	12.0	3840
1358	1900	13.0	30400
1341	2500	16.0	40000
467	750	11.5	8630
440	100	17.0	1700

Table 2. Continued.

Cr(acac-Br)₃ (Solvent CH₂Cl₂)

$\nu(\text{cm}^{-1})$	$\epsilon(\text{M}^{-1}\text{cm}^{-2})$	$\Delta\nu_{1/2}(\text{cm}^{-1})$	$A(\text{M}^{-1}\text{cm}^{-2})$
467	834	11.4	9508
441	75	11	825
352	95	13.0	1235
375	13	7.0	91
381	22	5.5	121

Cr(acac-NO₂)₃

$\nu(\text{cm}^{-1})$	$\epsilon(\text{M}^{-1}\text{cm}^{-1})$	$\Delta\nu_{1/2}(\text{cm}^{-1})$	$A(\text{M}^{-1}\text{cm}^{-2})$
1578	750	7	5300
1568	3100	17	53000
1555	1200	8	9600
553	33.8	14.2	480
464	537	11.9	6390
418	54.0	21.1	1140
369	14.0	8.5	119
353	97.5	11.6	1120
345	10	4.8	48

such as —NO₂ or —Br, affecting the electron distribution within the ligand. These latter groups are easily introduced^{4,5} in the γ -position because of the semi-aromatic structure of the acetylacetonato complexes. Consequently, analogous intensity measurements have been made of the complexes Co(acac—Br)₃, Co(acac—NO₂)₃, Cr(acac—Br)₃ and Cr(acac—NO₂)₃. Here acac—X means an acetylacetonato ion with the γ -proton substituted by the group X.

EXPERIMENTAL TECHNIQUES AND RESULTS

The M(acac)₃ complexes were prepared by standard methods⁶ and the Br- and NO₂-compounds by the methods described by Collman and coworkers.^{4,5}

All complexes were purified by recrystallization until analysis for hydrogen and carbon gave satisfactory results.

The intensity measurements were made as described before.² The values of the integrated absorption given in Tables 1 and 2 are defined from the equation

$$A = \epsilon \Delta\nu_{1/2}$$

where

$$\epsilon = \frac{1}{c d} \log \frac{T_0}{T}$$

The concentrations c were obtained by weighing solid samples and dissolving these in appropriate volumes of spectroscopically pure chloroform or, in a few cases, methylene chloride. The cell-thickness, d , was checked now and then during the work by interferometry.

As the deductions, that can be made from the intensities, are of an extremely qualitative nature, no correction was made for the effect of the spectral slit width. The instrument settings were the same as in the previous work² and only small errors arise from this omission. Thus, in order to obtain true integrated absorptions, the values given here should be multiplied by the factor $7 \ln 10 \times \pi/2$.

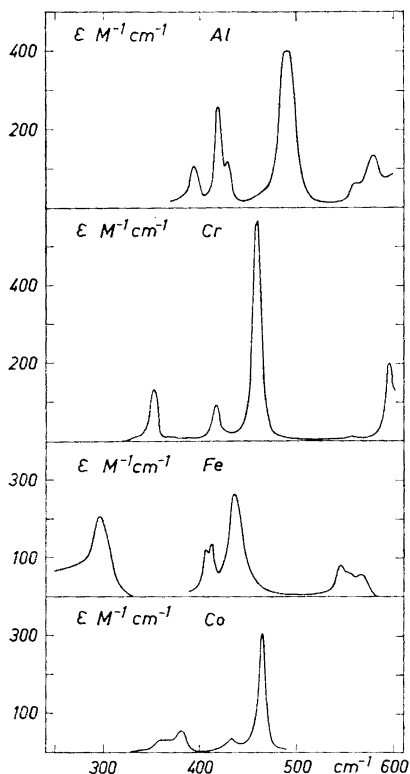


Fig. 1. The spectra of the acetylacetonato complexes in the spectral range of metal-ligand vibrations.

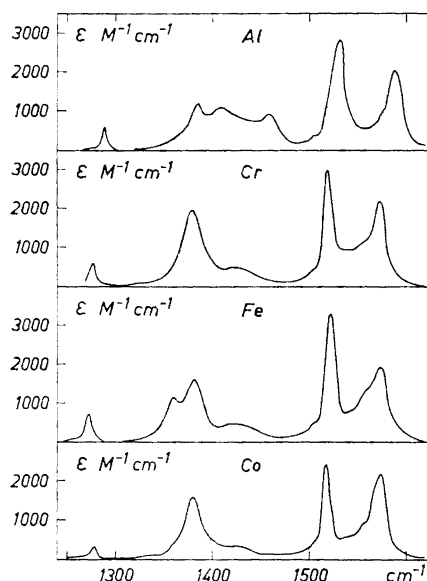


Fig. 2. The spectra of the acetylacetonato complexes in the spectral range of the stretching vibration of the ligands.

The spectra are given in Figs. 1–4. It can be seen that the molar extinction coefficients of the same type of band vary considerably from one complex to another. This emphasizes the wellknown fact (Ref. 8, p. 287) that the mere denotation of a band as strong, medium, or weak is of limited value when comparing spectra of related substances. The detailed spectral properties of the various bands are given in Tables 1 and 2. In order to emphasize the variation of the integrated absorption with the change of M or X in the complex $M(\text{acac-X})_3$ a graphical representation has also been employed (Figs. 5–9). These graphs clearly illustrate that the changes are of such a distinct nature that the small errors introduced by neglecting the slit width factor are of little importance for the qualitative interpretations that can be made.

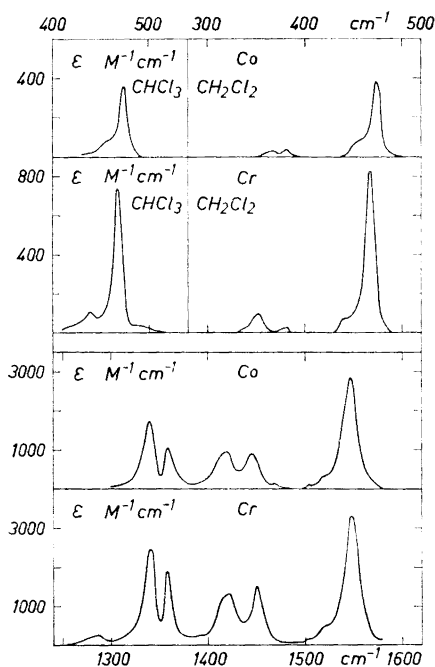


Fig. 3. The spectra of the bromo-substituted complexes of Cr and Co. Upper diagrams, metal-ligand vibration range; lower diagrams ligand vibration range.

BAND ASSIGNMENTS

The assignments of absorption bands of acetylacetonato complexes have been the subject of some controversy. The bands of interest here are those in the range of 1600–1250 cm^{-1} , corresponding—everyone agrees—to vibrations of the O–C–C–C–O skeleton and the ones in the spectral range below 500 cm^{-1} , where, among others, the metal-ligand vibrations are found.

In an early paper, Mecke and Funck⁹ proposed that the strong delocalisation of π -electrons in the ligand made any assignments of bond vibrations impossible. From an analysis of normal coordinates Nakamoto and coworkers,¹⁰ however, gave a detailed description of the character of, among others, the absorption bands at about 1600 cm^{-1} and around 1550 cm^{-1} . The first should be mainly (about 75 %) a C=C stretching band, whereas the latter should correspond mainly to C=O stretchings. Similar deductions were made by Mikami, Nakagawa and Shimanouchi¹¹ from a complete normal coordinate analysis of $\text{Cu}(\text{acac})_2$ and $\text{Fe}(\text{acac})_3$. However, as experimental evidence accumulated, these assignments began to appear unrealistic. Thus, from a normal coordinate analysis of $\text{Pt}(\text{acac})\text{Cl}_2^-$ and some of its deuterated analogues, Behnke and Nakamoto¹² recommended a change of assignments so that the vibration corresponding to the absorption band of the highest frequency should be considered as a C=O stretching one. Similar results were obtained by Musso and Junge¹³ from observations of frequency shifts following on substitution in relevant places with ^{13}C and ^{18}O . From a generalization by

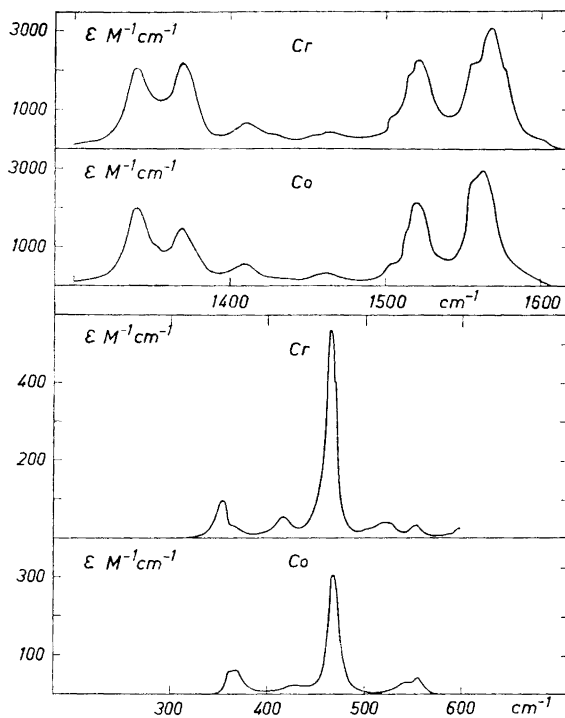


Fig. 4. The spectra of the nitro substituted complexes of Cr and Co. Upper diagrams, ligand vibration range; lower diagrams, metal-ligand vibration range.

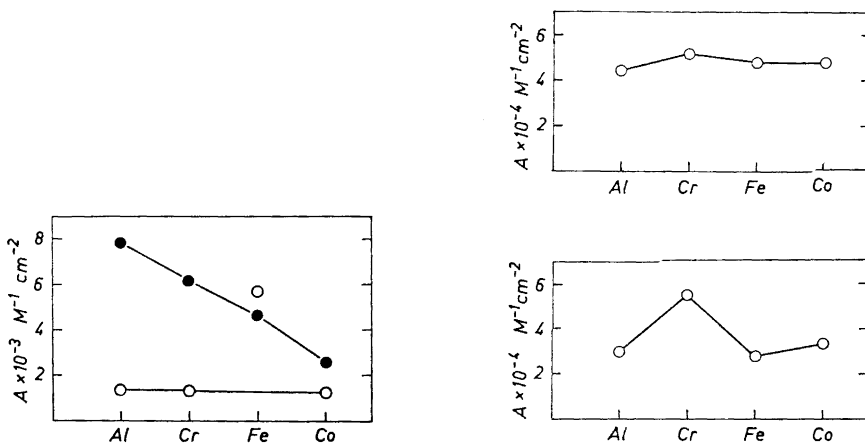


Fig. 5. The intensities of the ν_{30} vibration (●) and of the ν_{32} and ν_{58} vibrations (○) of the unsubstituted complexes.

Fig. 6. The intensities of the C-O vibration (upper diagram) and of the C-O vibration (lower diagram) of the unsubstituted complexes.

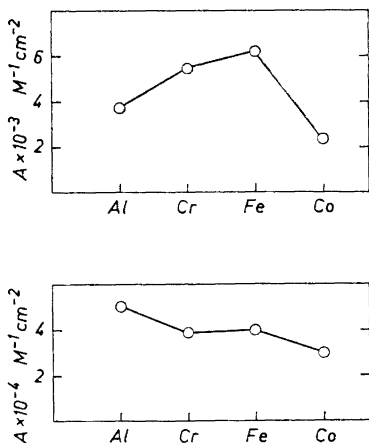


Fig. 7. The intensities of the symmetric C-C-C stretching vibration (upper diagram) and the C-C-C asymmetric stretching vibration (lower diagram) of the unsubstituted complexes.

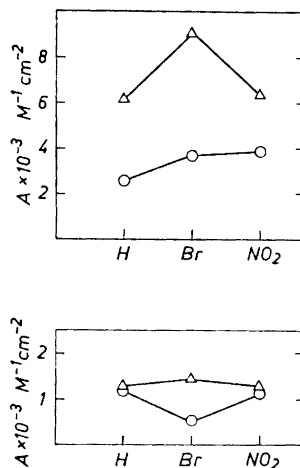


Fig. 8. The intensities of the ν_{36} vibration (upper diagram) and of the $\nu_{32} + \nu_{58}$ vibrations (lower diagram) of the substituted Cr (Δ) and Co (\circ) complexes.

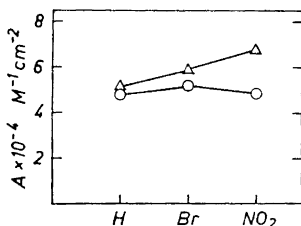


Fig. 9. The intensities of the C-O stretching vibration of the substituted Cr (Δ) and Co (\circ) complexes.

Lüttke,¹⁴ that such shifts are related to the amplitudes of the atoms in a certain vibration mode, it was possible to characterize most of the absorption bands.

It can be mentioned in connection with this that Hancock and Thornton¹⁵ believe they have found empirical support for these new assignments. From studies on complexes of the type $XX'Sn(acac)_2$ Kawasaki, Tanaka and Okawara¹⁶ have obtained empirical assignments that are exactly the same as the revised ones now proposed by Behnke and Nakamoto.¹²

In the present work we will rely upon the empirical results of Musso and Junge.¹³ Thus the following assignments will be used (the frequencies are only indicative of the approximate position of the bands): 1580 cm^{-1} $\nu(C\equiv O)$, 1530 cm^{-1} $\nu_{as}(C\equiv C\equiv C)$, and 1280 cm^{-1} $\nu_s(C\equiv C\equiv C)$.

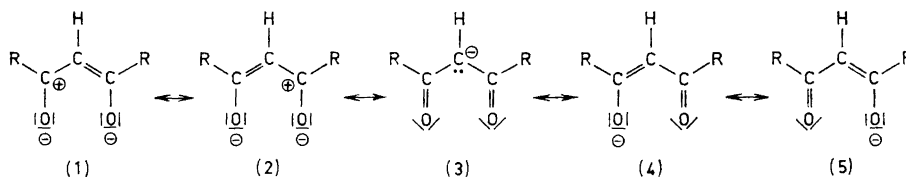
In spite of the pessimistic predictions by Dismukes, Jones and Bailar,¹⁷ it now seems possible to make rather coherent assignments of the MO_6 vibra-

tions. In this work we will use the detailed assignments of Mikami, Nakagawa and Shimanouchi.¹¹ The band at about 450 cm^{-1} is designated by these authors as ν_{30} , a MO_6 stretching vibration of E symmetry. This assignment is in agreement with those given by Gillard, Silver and Wood¹⁸ and by Nakamoto and coworkers.¹⁰

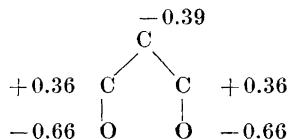
The band appearing in the range $290\text{--}390\text{ cm}^{-1}$ for various complexes is shown¹¹ to be composed of two bands corresponding to two MO_6 stretching vibration modes, one (ν_{32}) of E symmetry and one (ν_{58}) of A_2 symmetry. These deductions, too, agree with those of Gillard, Silver and Wood.¹⁸

DISCUSSION

The acetylacetonato ion can be depicted in simple valence bond resonance structures as:



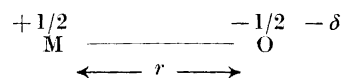
Actually, Hückel MO calculations³ and SCF MO calculations¹⁹ show that the π -electrons are concentrated on the γ -carbon atom and the oxygen atoms. The latter method¹⁹ gives the following charge distribution, where the excess of electron density is given with a negative sign.



This indicates that the resonance forms (1)–(3) are the most important, while small contributions are made by (4) and (5).

Thus it is evident that in the free anion, the oxygen atoms have a considerable negative charge originating from the π -electron cloud. Further contributions to the oxygen charge will emerge from the C–O σ -bond charge distribution, which is, however, difficult to estimate. Then, if no covalent metal-ligand bonding was present in a $\text{M}(\text{acac})_3$ complex, one should expect a strong infrared intensity of the M–O stretching modes. On the other hand, if by some means (σ - or π -bonding) part of the excess charge of the oxygen atoms was transferred to the metal ion, the polarity of the M–O bond would decrease and—on a fixed charge model—the infrared intensities of the M–O stretching vibration modes would also decrease.

It should be observed that we, when making this proposition, consider the dipole moment of the M—O bond to be determined by the charge on the metal atom. As it is reasonable—as a first approximation—to divide the charge of the metal atom equally among the six M—O bonds and as we know from the SCF MO calculations¹⁹ that the negative charge of the oxygen is *at least* 0.66 units (*i.e.* we have to add the σ -bond polarity of the C—O bonds to the π -bond polarity) one obtains the following picture if no charge neutralization of the metal ion takes place.



Here δ is at least 0.16 units. To the best of our understanding, it is the derivative of the bond dipole moment $\mu = r \times 0.5 \times 4.8 \times 10^{-10}$ esu that determines the infrared intensities of the M—O vibration modes, not the total charge of any of the atoms involved.

That a decrease of intensity is actually observed is illustrated in Fig. 5 for the ν_{30} mode.¹¹ Indeed, the intensities of the transition metal complexes fall in the order Cr > Fe > Co.

Consequently, we can propose that the order of covalency in these complexes is Co > Fe > Cr, which is the order of these metals in the nephelauxetic series,²⁰ supposed to indicate the tendency towards covalent bonding. It may be pointed out in this context that the intensities thus reveal the order of expected covalency better than do the force constants estimated by Shimanouchi and coworkers.¹¹

The intensities of the other M—O vibration modes (ν_{32} and ν_{38}) seem to be more insensitive to the nature of the metal, although for the metals Al, Cr, and Co the same trend can be traced (Fig. 5). The possible origin of the deviation found for Fe will be discussed later in this paper.

Then, turning our attention to the effects of coordination on the infrared absorption bands of the ligands, and especially to the intensities of these bands, for a qualitative discussion one may refer to the resonance structures (1)—(5) given above. As in the case of the thiocyanato ligand previously treated,²¹ one can probably assume that those resonance structures that carry the highest formal charge on the donor atom (atoms) will be more important in determining the wave function of the ligand, when the ligand is coordinated, than when it is free. Thus structures (1) and (2) will be more important than (3) and probably structures (4) and (5) will contribute to a greater extent than in the free ion.

It is then to be expected that the polarity of the C—C bonds will increase as should that of the C—O bonds. In the latter case one has, however, also to add the effect discussed above of the charge decrease of the oxygen atom from covalent bonding to the metal. Fig. 6 shows the expected increase of the C—O stretching intensity from Al to Cr, but this trend is then reversed, possibly by the operation of increased charge neutralization by the covalent O→M bonding.

It is interesting that the absorption band around 1390 cm^{-1} also exhibits the same pattern (Fig. 6). This band is assigned by Behnke and Nakamoto,¹²

as a C—O stretching vibration coupled with CH₃ deformation vibrations, whereas Musso and Junge¹³ hesitate to give it any bond vibration character, although they state that, if anything, it should correspond mainly a C—O stretching. The similarity found between intensity changes for the 1580 cm⁻¹ and 1390 cm⁻¹ bands seems to support the idea that the latter band can really be characterized as a C—O stretching band. The results of the C—C—C vibrations present a more difficult problem. The symmetric stretching vibration¹³ (Fig. 7) shows the expected increase (Al < Cr < Fe) in the order of increasing covalency as judged by the M—O polarity (*cf.* above). The extremely low value for the Co complex is somewhat puzzling.

The asymmetric stretching¹³ of the C—C—C moiety will probably not allow the use of anything similar to a fixed charge model. Rather, the asymmetric stretching will cause (*cf.* Ref. 22) a predominance of structures (1) and (4) in one phase of the vibration and of structures (2) and (5) in the other phase, thereby creating a flow of charge across the C—C—C bonds during one vibration period, giving rise to a much higher intensity than what is found for the symmetric vibration (Fig. 7). Hence, it is no wonder that the nature of the metal in the complexes is of little importance in determining the intensities of these bands and that no easily interpreted trends are found.

If we now turn our attention to the substituted acetylacetonato complexes, it is reasonable to attribute the observed differences between spectra of substituted and unsubstituted complexes to a combination of the "inductive" and "mesomeric" effects of the substituent groups (Ref. 23, chapt. 3).

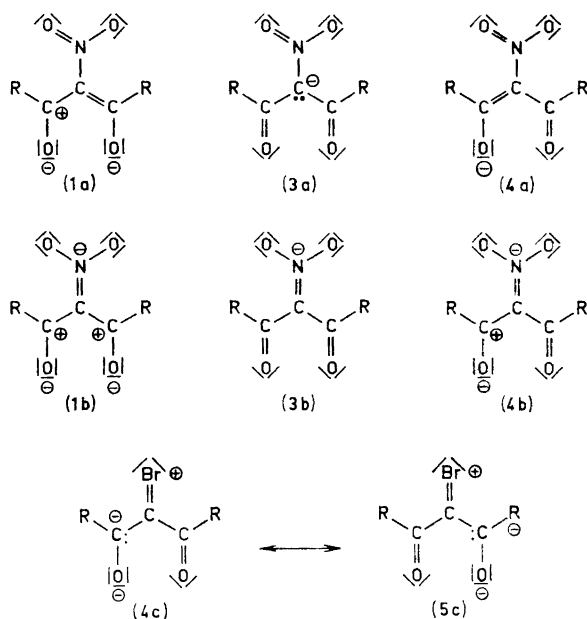
The first of these effects relates to the withdrawal of electrons from the σ -carbon-oxygen structure towards the —Br or —NO₂ groups. This action is known to enhance, *e.g.*, the dissociation constants of carboxylic acids (Ref. 23, chapt. 4). In analogy, one should expect the covalent bonding of the metal oxygen bonds to weaken and that the intensity of the metal-oxygen vibration modes should consequently increase. As the nitro group has a much higher inductive capacity than the bromo group, one should expect the nitro complex to be characterized by a high M—O polarity and infrared intensity. Although the bromo-substituted complexes show this expected rise of M—O intensity it can be seen that the nitro-complexes do not fit into the pattern (Fig. 8).

Thus some other effect—the mesomeric one—must be invoked to explain the relatively low intensity of the nitro complexes.

It appears reasonable that the mesomeric effect causes an increase of the π -electron density on the oxygen atoms. Referring to our resonance structures above, this can be visualized by the addition to structures like (1 a), 3(a), and (4 a) of such structures as (1 b), and (4 b). The structure (3 b) is probably of less importance, as it places the negative charge at the wrong end of the ligand.

Following our previous arguments the thus achieved increase of charge on the oxygen atoms should lead to an increase of the covalency of the M—O bond, and, consequently, a decrease in M—O vibration intensity.

From the bromo-substituted ligands the only meaningful extra resonance structures seem to be (besides the obvious ones, replacing H with Br in (1)–(5) below) of the type (4 c) and (5 c)



All other forms involve very extreme charge redistributions and will probably not be of great importance.

This must mean that the effects observed for the bromo complexes are mainly caused by the inductive change of σ -bond polarities, whereas for the nitro-substituted ligands both effects are operative.

In analogy to what was done for the pure acetylacetonato complexes, the deductions drawn from the intensities of the metal-oxygen vibrations can now be used for predictions about the intensities of internal vibrations of the ligands.

The C—O vibration will be especially considered, as it is easily characterized as corresponding to the absorption band of highest frequency. The other absorption bands are found to be more crowded and not so easily related to the ones of the unsubstituted ligand. Indeed, in the *acac*-NO₂ spectra it is difficult to distinguish the C—O bond clearly, as $\nu_{as}(\text{NO}_2)$ has about the same frequency as $\nu(\text{C}\cdots\text{O})$.

In order to make an assignment of the C \cdots O band we relied upon the relation, put forward by Kross and Fassel,²⁴ between the frequencies of the symmetric and asymmetric stretching vibrations of the nitro group in *p*-substituted nitrobenzenes—a class of compounds comparable, in a way, to the complexes investigated here. From Figs. 2 and 4 it follows that it must be the band at about 1340 cm⁻¹ that corresponds to ν_{sym} of the NO₂ group, as no such band appears in the spectra of the unsubstituted complexes. Hence, following the rule of Kross and Fassel²⁴ the ν_{as} of the NO₂ group should be found somewhere about 1515 cm⁻¹. Consequently, we have regarded the bands in the range 1580—1550 cm⁻¹ reported in Table 2 as corresponding

to the C=O vibration. The splitting is also observed in the spectra of the unsubstituted complexes and is probably caused by a coupling between the vibrations of the three ligands.

It is realized that if the inductive effect causes an increase of the M—O bond moment, it will certainly increase the C=O bond moment. Thus one should expect an increase of the C=O stretching band intensity. Indeed, one should also expect to find a larger increase for the chromium complex than for the cobalt one, as the electrons are more firmly held by the cobalt ion. That these predictions are actually fulfilled for the bromosubstituted complex — where we have found reason to suppose that mainly inductive effects operate — is clearly seen from Fig. 9.

If mesomeric effects of the kind discussed above for the nitrosubstitution are considered too, it is easily realized that the incorporation of structures such as (1 b) and (4 b) will tend to increase the C—O bond polarity. Thus, in the case of the nitro complexes, both inductive and mesomeric effects are working in the same direction. Consequently, one should expect a prolific increase of the C—O stretching intensity. The possible importance of structures (4 c) and (5 c) would tend to decrease the C—O bond polarity in the bromo-substituted complexes.

All in all, the nitro complexes should show a greater C—O intensity than the bromo ones. It is found, however, (Fig. 9) that this holds only for the chromium complex. One must then conclude that the mesomeric effect discussed here does not seem to be very important for the cobalt complex. This also follows from the smaller decrease in Fig. 8. The results seem rather to indicate that the effects tend to go in the reverse direction to what was expected. One could perhaps suggest that this is due to a "back-donation" from the metal *d*-orbitals to the acetylacetonato ligands, then favouring structure (3 a) and (3 b). In such a case one would think that the cobalt atom was more efficient than the chromium one as it holds the greater number of electrons. If this is so, the same effect may cause the previously observed decrease of the C—C—C vibration intensity in the case of Co(acac)₃ (Fig. 7).

So far we have been able to present a reasonably coherent picture of the variation of the band intensities of the M(acac—X)₃ complexes as M and X are varied. The main deviations between observations and predictions concern the low frequency absorption bands supposed to correspond to the MO₆ vibration modes ν_{32} and ν_{58} . The intensity changes observed for Br and NO₂ substitution are quite unexpected, and we should like to refrain from offering any explanation. One possibility, though, is that the bulky substituents Br and NO₂ interfere more with the CH₃-bending than the small hydrogen atom does. As both the ν_{32} and the ν_{58} vibration modes¹¹ seem to involve CH₃-bending as well as M—O stretching, it may be reasonable to assume that these vibration modes are sterically impossible with large γ -substituents.

Another puzzling effect is the considerable excess of intensity observed for the Fe(acac)₃ band below 300 cm⁻¹ (Fig. 5). Although the low frequency of this band should suggest a rather low force constant compared to the Co and Cr complexes (*cf.* Ref. 11), the intensity sequence of the ν_{30} band does not give any reason to suppose a drastic change in bond polarity. We should like to suggest that the band system of Fe(acac)₃ below 300 cm⁻¹ is really more

composite, than if it consisted of the two ν_{32} and ν_{58} bands only. The extreme broadness of the band system seems to indicate that some other band is present. If so, this must be a band of a half-width rarely encountered for vibration absorptions and with its maximum of absorption at about 280 cm^{-1} . We suggest that this band corresponds to an electronic transition within the complex. As all transitions of the quasi-atomic Fe^{3+} ion system are spin forbidden as in the similar Mn^{2+} ion system,²⁵ it seems reasonable that the absorption band in question is related to a transition between acetylacetonato π -orbitals and orbitals of the Fe^{3+} ion. Inspection of the energy levels calculated by Barnum³ indicates that the most likely one is, in Barnum's notation, a $\pi_3(a_2) \longrightarrow d_\epsilon(a_1)$ transition.

The actual energy separation between these orbitals seems to be of the order of 2000 cm^{-1} for the Fe(III) system and is thus considerably higher than what is found here. However, the precision of calculations cannot be supposed to be so high as to give a reliable estimate. As a matter of fact, the numerical results of the calculations have been questioned by Piper and Carlin²⁶ on the basis of solid state spectral studies on the Cr(acac)_3 complex.

It is obvious that no absorption due to an electronic transition can be found for the Co(acac)_3 complex as the d_ϵ orbitals are filled in Co(III) . For the Cr(acac)_3 complex, however, one should expect an analogous absorption. The reason why this has not been found may be a combination of the findings of Barnum, that the energy separation of the π_3 and d_ϵ orbitals is smaller for the Cr(III) -system than for the Fe(III) one, and that the internal splitting of these energy levels due to metal oxygen π -bonding is also less for the former system than for the latter one.

One should then expect the Cr(acac)_3 electronic transition to appear at a somewhat lower frequency, out of the range of observation with our present equipment. It is disturbing, though, that Gillard and coworkers¹⁸ did not report any absorption in the range $150\text{--}250\text{ cm}^{-1}$ for the Cr(acac)_3 complex. In order to elucidate this problem, measurements ought to be repeated with interferometric techniques to exclude any instrumental errors in the observations.

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