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INFRARED SPECTRA OF THE ALUMINUM, GALLIUM AND INDIUM DIBENZOYLMETHANATES

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Recorded are infrared spectra of Al, Ga and In dibenzoylmethanates (1,3-diphenyl-1,3-propanedionato chelates) and of the partly deuterated Al chelate. An attempt is made to assign, as completely as possible, the observed infrared bands using the available information about the spectra of various acetylacetonates (1,3-dimethyl-1,3-propanedionates) and of monosubstituted benzenes as a guide. Deuteration (estimated to be approximately 70% complete) on the γ hydrogen of the chelate ring is helpful in assigning the δ(CCH) and, especially, γ(CCH) modes. The infrared spectra of the investigated chelates can be treated sattisfactorily in the 1:1 metal-to-ligand approximation, the coupling between the vibrations of the three chelate rings (particularly those localized mainly in the Ph-C-CH-C-Ph part of the molecule) being relatively weak. The phenyl groups can be treated as approximately independent units with vibrational frequencies (most noteworthy — those of the non-„X-sensitive“ *ring* modes) falling in the usually quoted ranges. In variance with the case of acetylacetonates, there is no appreciable mixing of the in-plane deformation C-C-H vibration and the antisymmetric C⩵O stretching vibration, whereas some δ(CCH) character is found in the case of the vibration which is mainly antisymetric C⩵C⩵C stretching in character. Several vibrations, interpreted as M—O stretchings or chelate ring deformations have appreciably *higher* frequencies in the spectra of the dibenzoylmethanates than in those of the corresponding acetylacetonates, in line with the increased stability of the former type of compounds.

INTRODUCTION

The spectra of the acetylacetonates of various metals have been investigated by numerous authors, starting with the early work of Lecomte and his colaborators [1—3], up to some quite recent papers [4—8]. The assignments of the bands in the spectra of the acetylacetonates have been made both empirically and by using normal-coordinate calculations with various degrees of sophistication, the majority of workers still basing their intepretations on the assignments of Nakamoto and his colaborators [9—11]. The experimental results of Pinchas *et al.* [4] who used ^{18}O enriched acetylacetonates and of Junge and Musso [7] who investigated ^{18}O, ^{13}C and ^{2}H substituted acetylactonates showed that the assignment of some of the absorption bands, as proposed originally by Nakamoto, requires revision in order to account for the observed isotopic shifts. Nakamoto and his co-workers, recently [5] revised some of the previously favored assignments, but questioned [8] the validity of the arguments advanced by Pinchas *et al.* [4] concerning the interpretation of some of the low-frequency bands. In any case, the data presently accumulated permit a reasonably certain interpretation of the spectra of acetylacetonates and assignment of almost all bands, both those associated with vibrations of the methyl groups and those which are predominantly chelate-ring vibrations in character.

On the other hand, the spectra of the dibenzoylmethanates (1,3-diphenyl-1,3-propanedionato chelates), $M(DBM)_n$ have not, to the best of our knowledge, been completely analyzed. This is, probably, at least partly due to the great confidence of the investigators in the Nakamoto's early assignment of the spectra of acetylacetonates which, however, makes the complete interpretation of the spectra of dibenzoylmethanates at best very difficult. Thus, in reporting on the spectra of dibenzoylmethanates, many authors simply list (completely or partially) the absorption frequencies, attempting, occasionally, an interpretation along the lines suggested by Nakamoto [9—11] for the assignment of the spectra of acetylacetonates or make use of the conclusions reached by Nakamoto *et al.* [12] as a result of a perturbation treatment of the same assignment. This, however, has sometimes led to absurd situations, such as assigning [13] certain bands in the spectra of dibenzoylmethanates to CH_3 vibrations! It is worthwhile mentioning that Durie *et al.* [14], reporting recently on their analysis of the spectra of dibenzoylmethane and its copper chelate (both enriched with ^{18}O), concluded that all vibrations belong to the molecule as a whole and no vibration is localized mainly in the *O*-containing groups (i. e. C— O and M—O). Our preliminary investigation of the spectra of a number of dibenzylomethanates of various tervalent metals [15], showed that this certainly is not quite the case, since a number of bands were clearly metal-sensitive (and, consequently, presumably due to vibrations localized mainly in the -CO-M-CO- parts of the molecule), while the rest were not. All this, together with our interest in the chemistry and infrared spectra of β-diketone chelates [16], led us to attempt to make an as complete as possible assignment of the spectra of some dibenzoylmethanates. Of a much larger group of compounds, the synthesis of which (by ligand-substitution reaction) we have reported [16*b*], for examination we chose the chelates of the aluminum group of metals (Al, Ga and In), leaving the dibenzoylmethanates of the transition metals for a later study. The compounds were so chosen because we wanted to avoid, as much as possible, the complicating factors related to the differences in the electronic configurations of the transition metals. One would, namely, expect a similar type of bonding throughout the three selected chelates with only quantitative differences due to variations in the ionic radii, the total number of electrons etc. The remarkable similarity of the spectra of these three compounds (except for the metal-sensitive bands) fully supported these expectations. The spectrum of Al $(DBM)_3$ was, partly, reported by Singh and Sahai [17] and their assignment agrees, in general, with ours which, however, is more complete.

EXPERIMENTAL

The aluminum, gallium and indium dibenzoylmethanates were prepared [16*b*] from the corresponding acetylacetonates by action of excess of dibenzoylmethane. The liberated acetylacetone was distilled off under reduced pressure, together with the xylene which was also added to the reaction mixture and served as a solvent. The chelates were then recrystallized from a suitable solvent and their composition was checked by elemental analysis.

The aluminum chelate was partly deuterated (only the active γ-hydrogen was exchanged) by standing several months at 120°C in a sealed tube half-filled with D_2O. From the recorded spectra the degree of deuteration of the γ-hydrogen was estimated as being close to 70%.

The infrared spectra were recorded, as KBr pressed disks, on a Perkin-Elmer Model 521 Infrared Spectrophotometer. Pellets with different sample content were used so that both strong and weak bands could be recorded with sufficient precission.

RESULTS AND DISCUSSION

The spectra of the three investigated chelates are reproduced in Fig. 1 and the frequencies of the absorption bands are listed, together with qualitative estimation of their intensity, in Table I.

Each molecule $M(C_{15}H_{11}O_2)_3$, containing 85 atoms, should have 249 normal vibrational modes, the degeneracy and activity of which would depend on the overall symmetry of the molecule and of its site in the unit cell. If more than one molecule exists in the Bravais cell, a possible coupling between the vibrations of different molecules would, then, further increase this number by the so-called correlation-filed splitting. Such an enormous number of frequencies would be, of course, virtually impossible to handle. Fortunately, the spectra, although rather rich in bands, are far from showing all the bands which could be predicted on theoretical grounds. This can be due to the fact that the molecule (and/or its site) has high symmetry or, even more likely, to the fact that the vibrations in the identical parts of a given molecule (especially those localized in the Ph-C-CH-C-Ph parts) are only weakly coupled and, thus, accidentally degenerate.

It seems that the 1:1 metal-to-ligand approximation can be used almost throughout in the assignment of the chelate-ring vibrations and that

TABLE I

*Infrared spectra (1600—300 cm^{-1}) of the dibenzoylmethanates of Al, Ga and In**

Al(DBM)$_3$		Ga(DMB)$_3$		In(DBM)$_3$		Approximate description **
1600	sh	1599	sh	1598	sh	*k* and *l* (νC—C)
1595	s	1594	s	1590	ms	
1549	vs	1543	vs	1535	vs	ν_sC$=$O
1526	vs	1526	vs	1524	vs	ν_{as}C$=$C$=$C$+\delta$C—C—H
1481	s	1481	s	1480	s	*m* (νC—C)
1461	s	1461	m	1453	m	*n* (νC—C) (F.R.)
1443	vw	1443	w	1442	w	2 *f* (2×724)
1417	s	1404	s	1397	s	ν_{as}C$=$C and 2υ (F.R.)
1384	s	1371	s	1364	s	
1326	s	1320	s	1310	s	ν_sC$=$C$=$C
1305	m	1305	ms	1305	sh	*o* (νC—C)
1293	sh	—		1291	ms	*e* (δC—H)
1226	m	1228	m	1228	ms	δC—C—H
1181	w	1181	w	1181	w	*a* (δC—H)
1157	w	1157	w	1156	w	*c* (δC—H)
1127	vw	1128	w	1128	w	Combination?
1095	sh	1097	w	1094	w	Combination?
1077	m	1074	m	1058	m	*q* (X-sens.)
1068	m	1068	m	1068	m	*d* (δC—H)
1026	m	1025	m	1024	ms	*b* (δC—H)
1000	w	1000	w	1000	w	*p* (ring breathing)
987	vw	987	vw	988	vw	*j* (γC—H)
973	vw	973	vw	972	vw	*h* (γC—H)
949	m	944	m	937	m	Complicated chelate vibration

930	vw	928	vw	927	vw	*i* (γC—H)
844	vw	843	vw	842	vw	*g* (γC—H)
813	vw	814	vw	815	vw	*r* (X-sens.)
793 787	sh mw	792 787	sh m	792 786	vw mw	*f* (γC—H)
754	s	757	s	762	s	γ C—C—H
724	s	722	s	721 712	s sh	γ C=C=C
699	s	696	s	692	s	Chelate ring deform.
687	s	686	s	686	s	ν (φC—C)
638 633	sh ms	634	ms	628	ms	Chelate ring deform.
616	vvw	616	sh	616	sh	*s* (αC—C—C)
589	m	562	m	542	sh	ν M—O***
558	m	546	m	535	m	*x* (X-sens.)***
530	m	526	m	522	m	ν M—O***
461	w	455	w	452	w	*t* (X-sens.)? (see text)
418 415	sh m	445	sh	440	w	opp Chelate ring deformation
402	w	398	sh	?		*w* (φ C—C)
370	w	(390)?		(380) ?		*u* (X-sens.)
302	vw	—		—		?

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* The frequencies in the Al(DBM)$_3$ spectrum which are sensitive on deuteration are italicized. The relative intensities are denoted in the usual way, w meaning weak, m—medium, s — strong, v — very, sh — shoulder.

** The letter designation and the description of the phenyl modes according to Whiffen [18] where ν denotes stretching, δ — in-plane (ip) and γ — out-of-plane (oop) C—H bending and α and φ denote, respectively, ip and oop ring deformations. In describing the chelate vibrations ν means stretching, δ — ip bending and γ — oop deformation vibration. F. R. means Fermi resonance.

*** Assignments for Ga and In chelate interchangeable (see text).

the phenyl groups can be treated as approximately independent units, the vibrations of which are very little affected by the rest of the molecule. The assignment of the bands originating from vibrations in the phenyl groups is, in general, easier than of those which are due to vibrations located mainly in the chelate rings and is, consequently, discussed first (except for the bands expected to appear below 650 cm^{-1} which will be discussed separately, together with the chelate-ring vibrations falling in the same region). Only the bands below 1650 cm^{-1} will be considered, since the only fundamental modes expected in the high-frequency region are the C-H stretching ones (observed as a complex feature near 3060 cm^{-1}) and they are of no particular interest.

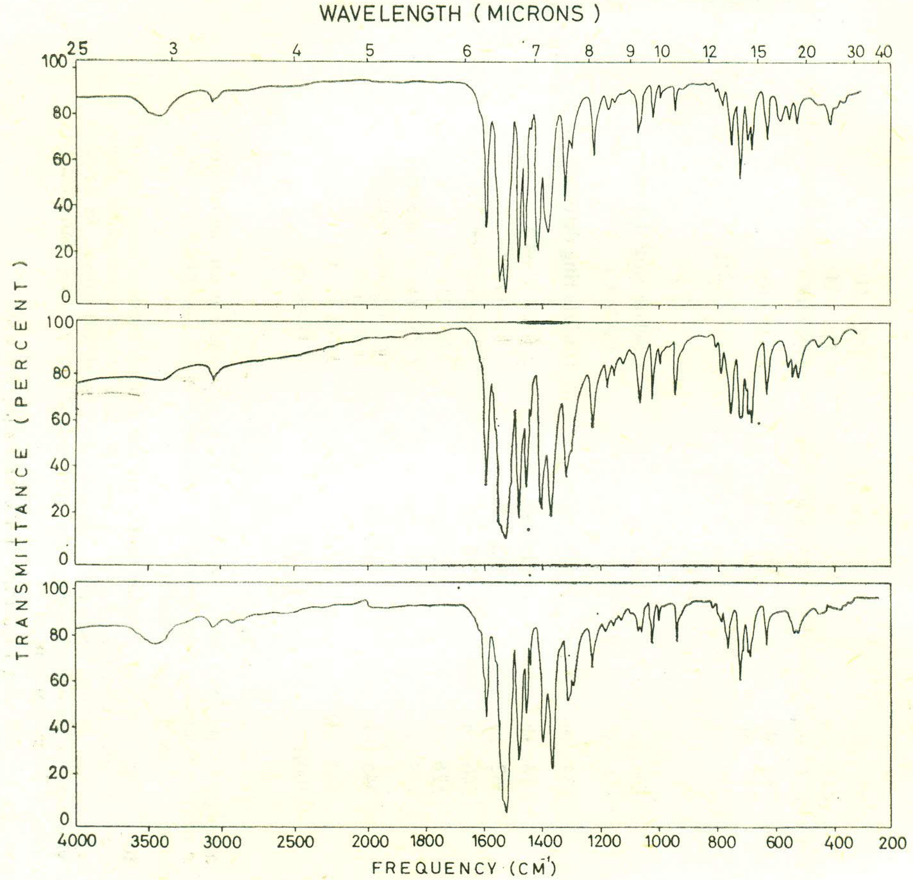

Fig. 1. Infrared spectra of the dibenzoylmethanates of aluminum, gallium and indium

Phenyl vibrations (1650—650 cm^{-1}). — There is, by now, a rather firmly established interpretation of the spectrum of the phenyl group (especially as far as the vibrations above 650 cm^{-1} are concerned), based mainly on the classical work of Whiffen on the monosubstituted benzenes [18]. Using Whiffen's assignment as a guide, the interpretation of the phenyl bands in the above-mentioned region (of which only two are expected to be ,,X-sensitive", i.e. dependent on the nature of the substituent on the benzene ring) is rather straightforward and requires little comment.

The two highest ring stretching vibrations (k and l in the notation of Whiffen [18], which shall be used throughout) appear, except in the case of the In chelate, as a single band exhibiting a shoulder on its high-frequency side and centered around 1595 cm^{-1}. The remaining three ring stretching modes (m, n and o) and the ring breathing mode (p), undoubtedly correspond to the bands observed* at 1481, 1461, 1305 and 1000 cm^{-1} respectively. The C—H in-plane bending modes, with the exception of the d and b vibrations, appear as weak or very weak bands and could be clearly seen only when the sample concentration in the KBr pellet was rather high. Nonetheless, we believe that the assignment of the bands at 1181, 1157, 1068 and 1026 cm^{-1} to the a, c, d and b vibrations rises no doubt. The assignment of the e vibration to the shoulder observed around 1293 cm^{-1} in the spectra of the Al and In (but not Ga) chelates seems also sattisfactory. The bands observed around 973, 930, 844 and 787 cm^{-1} undoubtedly correspond to the out-of-plane C—H deformation vibrations h, i, g and f (notwithstanding Singh and Sahai's [17] assignment of the 930 cm^{-1} band to a C—R stretching mode) and the band around 987 cm^{-1} should, by all means, be assigned to the remaining such mode (j). It should be noted, however, that the only two phenyl modes of the higher-freqeuncy ones which fall slightly outside the regions usually quoted for them [19, 20] are among this class of vibrations: both the i and the f modes are found slightly higher than usually. In fact, in the region where the f mode is most frequently found (760—730 cm^{-1}) there is a rather intense band which could have been assigned to the f mode were it not for the results of the measurment of the spectrum of Al(DBM)$_3$-d_3 which clearly showed that this band is sensitive to deuterium-for-hydrogen substitution and should, therefore, be best described as an out-of-plane deformation CCH mode of the chelate ring (*vide infra*). An identical assignment for this mode has been given by Singh and Sahai [17]. The rather intense band around 721 cm^{-1} almost certainly corresponds to the out-of-plane phenyl ring deformation mode υ although it is found slightly higher than usually [19]. The remaining two non-,,X-sensitive" phenyl bands (denoted s and w) fall below 650 cm^{-1} and will, therefore, be discussed at the appropriate place.

Of the two ,,X-sensitive" modes expected in the region above 760 cm^{-1} it is easier to assign the q mode which appears as a medium-intense band around 1077 cm^{-1}, (at the high-frequency side of the band attributed to the mode d in the spectrum of Al(DBM)$_3$) and is shifted to lower frequen-

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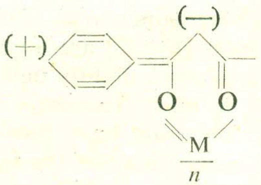
* Unless specified otherwise, the frequenceis which are quoted correspond to the bands in the Al(DBM)$_3$ spectrum.

cies (in agreement with its considerable C-X stretching character) in the spectra of the Ga and In chelates, the corresponding values of their frequencies being 1074 and 1058 cm^{-1} respectively (the former of these values is less certain, since the two bands, belonging to the *q* and *d* modes, are almost completely overlapped. The second of the „X-sensitive" bands, denoted *r* (mostly an in-plane ring deformation) should be found [18—20] in the region 800—650 cm^{-1}. The bands in this region, however, show very little variance on passing from Al$(DBM)_3$ to In$(DBM)_3$ and this makes the correct assignment rather difficult. In fact, the only bands exhibiting a significant shift are found at 754, 757 and 762 cm^{-1} in the spectra of the Al, Ga and In chelates respectively (as could be noted, the shift is to higher frequencies). The deuteration data, however, show unequivocally that this is an out-of-plane CCH bending mode of the chelate ring. The only non-assigned band near the above-mentioned region is the very weak one found around 813 cm^{-1} and it is this band which is, tentatively, ascribed to the *r* mode.

It is noteworthy that practically all phenyl frequencies in the region above 650 cm^{-1}, particularly the non „X-sensitive" *ring* vibrations, fall in the respective regions usually quoted for them [19, 20]. The only exceptions are, as pointed out above, the *i* and *f* modes, both of which are *C—H* deformation modes. Our analysis of the presented here spectra, therefore, does not seem to lend much support to the proposal, first advanced by Nakamoto *et al.* [12] and recently renewed by Hancock and Thornton [21] about the prominent role of mesomeric interactions of the form (I) in the phenyl-substituted β-diketone chelates.



(I)

Ligand vibrations (1650—650 cm^{-1}). — The extensive work on acetylacetonates shows that, exclusive of methyl vibrations, the following ligand vibrational modes are expected to appear in the region 1650—650 cm^{-1} (in order of decreasing frequency)*: $\nu_s(C\overset{\cdots}{-}O)$; $\nu_{as}(C\overset{\cdots}{-}C\overset{\cdots}{-}C)+\delta(C—C—H)$; $\nu_{as}(C\overset{\cdots}{-}O)$; $\nu_s(C\overset{\cdots}{-}C\overset{\cdots}{-}C)$; $\delta(C—C—H)+\nu_{as}(C\overset{\cdots}{-}O)$; a complicated mode (near 940 cm^{-1}) which is difficult to describe in terms of the simple group-frequency concept; $\gamma(C—C—H)$; a ring deformation mode with some C—R stretching character (R denoting the side groups: methyl or, in our case, phenyl) and, finally, a $\gamma(C\overset{\cdots}{-}C\overset{\cdots}{-}C)$ mode. The remaining chelate-ring vibrations are expected to appear in the region below 650 cm^{-1} and will be discussed in the following paragraph.

Although the description of the vibrational modes which was derived for acetylacetonates may not be completely adequate for dibenzoylme-

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* The description of the modes follows that of Junge and Musso [7].

thanates (or, for that matter, other β-diketonates), it is to be expected that, at least qualitatively, the character of the vibrations will be similar for the two classes of compounds.

The comparison of the spectra of ordinary and deuterated Al $(DBM)_3$ permits a clear-cut assignment of the modes involving motion of the γ-hydrogen. On the basis of their shift on deuteration the bands around 1226 cm^{-1} (shifted to around 932 cm^{-1}; $R=\nu_H/\nu_D=1.32$) and 754 cm^{-1} (shifted to about 553 cm^{-1}; $R=1.36$) are unequivocally assigned to the in-plane and out-of-plane C—C—H deformations respectively. The fact that the former of these two bands has practically the same frequency in the spectra of all three chelates indicates that here, in variance with the case of acetylacetonates [7], there is little or no coupling with the antisymmetric C═O vibration. On the other hand, the appreciable shift (≈ 60 cm^{-1}) of the 1526 cm^{-1} band suggests that here, as well as in the case of the acetylacetonates, the C═C═C antisymmetric stretching mode is mixed with the C—C—H bending one. The shift on deuteration of the 949 cm^{-1} band (found at ≈895 cm^{-1} in the spectrum of Al $(DBM)_3$-d_3) shows that it belongs to a mode also having some C—H character, whereas its decreasing frequency on passing from the Al to the In chelate suggests (see below) some C═O character in it as well. In the 700—650 cm^{-1} region of the spectrum of Al $(acac)_3$ there are two bands : one around 687 cm^{-1} (attributed to a ring deformation mode) and a sharp and not very intense band around 660 cm^{-1} which, according to Junge and Musso [7], is better described as γ (C═C═C) mode than as a δ (C—R) + ν (M—O), as was originally suggested by Nakamoto [11] (the isotopic-shift data of Nakamoto *et al.* [8] support such a conclusion). Of the two intense bands found between 700 and 650 cm^{-1} in our spectra, the higher-frequency one (located around 699 cm^{-1} in the spectrum of Al $(DBM)_3$ and slightly shifted downwards in the other two cheates) corresponds probably to the chelate-ring deformation, whereas the other one (in all three chelates found at almost the same frequency, around 686 cm^{-1}) most probably corresponds to a predominantly γ (C═C═C) mode. Singh and Sahai [17] have assigned the corresponding band in their $Al(DBM)_3$ spectrum to a mode involving M—O stretching, ring deformation and C—R stretching, but if the shifts of the corresponding bands in the $Al(acac)_3$ spectrum on 1,3,5-$^{13}C_3$ substitution [7] and the in the Fe $(acac)_3$ spectrum on ^{59}Fe- ^{57}Fe substitution [8] are taken into account, it does not seem probable that the mode in question should have an appreciable M—O stretching character.

The bands which show frequencies with a pronounced metal-sensitivity must be, in one way or another, connected with vibrations localized mainly in the -CO-M-CO- part of the chelate ring and, for the bands in the presently discussed region, should be best described as C═O (pure or mixed) stretching vibrations. Of these, probably the most easily noticable shift is exhibited by the high-frequency component of the doublet at 1549/1526 cm^{-1} in the spectrum of Al $(DBM)_3$. While in this case the doublet is clearly resolved, in the spectra of the Ga and In chelates only a shoulder (at 1543 and 1535 cm^{-1} respectively) is visible on the high-frequency side of the band at around 1526 cm^{-1} which, itself, remains at virtually the same frequency in all three investigated compounds. The assignment of the latter band to a C—C—C antisymmetric stretching mode with some C—C—H bending character in it (*vide supra*) seems, therefore, quite certain and the assignment of the high-frequency component of the doublet to the symmetric C—O stretching mode is, then, also straightforward. Further support for this latter assignment (similar intepretation was recently offered by Singh and Sahai [17] and by Hancock and Thornton [21], although their frequencies do not quite agree with ours) is found by analyzing the published [15] spectra of copper dibenzoylmethanate with various degrees of ^{18}O enrichment. Namely, in the spectrum of the ^{16}O chelate there are two distinct bands in the correponding region (quite similar, in appearence, to those found in our Al (DBM)$_3$ spectrum), whereas by increasing the ^{18}O content the high-frequency component is gradually shifted towards lower frequencies to become, in the spectrum of the chelate enriched to more than 46% with ^{18}O, a hardly noticable shoulder.

The band around 1400 cm^{-1} and the high-frequency component of the 945/932 cm^{-1} doublet in Durie's spectra [15] also show changes in form, position and intensity on ^{18}O enrichment and are, thus, characterized as arising from vibrations involving the C—O part of the molecule, the former of the above-mentioned bands being due, undoubtedly, to the antisymmetric C—O stretching vibration. The assignment of this vibration in the spectra of the investigated by us compounds requires, perhaps, some additional comment. Namely, whereas in the spectra of some tris dibenzoylmethanates [15] there is only a single band of considerable intensity in the 1400 cm^{-1} region, in the spectra of the three discussed here chelates there are two bands of comparable intensity. The high-frequency band is stronger in the spectrum of Al (DBM)$_3$, the two bands are almost equally intense in the spectrum of the gallium compound, whereas in the spectrum of In(DBM)$_3$ the low-frequency component is the one that has higher intensity. Since the only chelate-ring band expected in this region is the one due to ν_{as}(C—O) and no phenyl fundamental should be found there either, at first [22] we thought that the two bands were components of the degenerate (by symmetry or accidentally) mode of the molecule as a whole. The separation between the bands ($\approx$ 33 cm^{-1}), however, is much larger than that found in almost all other bands (particularly those in the high-frequency region) which does not, ordinarily, exceed a couple of cm^{-1}, so other possibilities were also investigated. The most plausible one seemed the interpretation of the two bands as due to Fermi resonance between the ν_{as} (C—O) fundamental and an overtone or combination. With this assumption in mind we calculated the approximate unperturbed frequencies of the two bands, using the formulae given by Overand [23]. The values thus obtained were 1402 and 1398; 1388 and 1387, and 1381 and 1380 cm^{-1} for the Al, Ga and In chelate respectively. If we take the more intense band as the perturbed fundamental, the approximate unperturbed frequencies of the ν_{as} (C—O) would be 1402, 1387 and 1380 cm^{-1} for Al(DBM)$_3$, Ga(DBM)$_3$ and In(DBM)$_3$ respectively. The gradual shift towards lower frequency (when passing from the Al to the In chelate) of this, as well as of the other bands associated with vibrations involving the C=O group, suggests a progressive weakening of the corresponding bond in the same order. The reason for this must be the gradual increase in the covalent character of the M—O bond on passing from Al to In, a trend observed also in other complexes of the same metals [24]. As for the other component of the doublet, the frequency of the 1398 cm^{-1} band in the spectrum of Al(DBM)$_3$ is almost exactly double that of the chelate-ring deformation mode of 699 cm^{-1} and the 1388 and 1381 cm^{-1} bands in the other two chelates can also be interpreted as overtones of the same phenyl vibration.

Singh and Sahai [17] assigned to this C=O stretching mode (coupled, according to their assignment, with the C—H bending one) a strong band reportedly found at 1365 cm^{-1} in the Al (DBM)$_3$ spectrum. Despite the fact that the agreement between their and our frequencies is, in general, only qualitative, we were able to find, in all cases except for this one, the counterparts of their bands in our spectra. In this case, however, the reported frequency falls in the absorption *minimum* between the strong bands at 1384 and 1326 cm^{-1}, so that it is difficult to decide which one Singh and Sahai [17] have actually assigned to the mode in question. None of the bands in the corresponding region of our Al (DBM)$_3$ spectrum shows a dependence on deuteration, however, and, therefore, the conclusion that the C=O stretching mode is coupled with the C—H in-plane bending mode does not seem to be justified.

650—[illegible]00 cm^{-1} region. — The intepretation of the bands in the region below 650 cm^{-1} is rather complicated and uncertain. In this region, namely, besides two phenyl modes which are not ,,X-sensitive" (denoted *s* and *w* by Whiffen [18]) and at least some of the four ,,X-sensitive" modes, *t*, *u*, *y* and *x* (which could also fall in the above-mentioned region), several chelate-ring vibrations are expected to appear between 650 and 300 cm^{-1}, most of which have, at least some, M—O character. Of these only the *s* and *w* phenyl modes are comparatively easy to assign: the former to the very weak band which is clearly resolved in the spectrum of Al (DBM)$_3$ around 616 cm^{-1} and appears as a shoulder at the same frequency in the spectra of the other two chelates and the latter to a component of the complex feature around 400 cm^{-1}. The identification (and, in the case of the chelate-ring vibrations, the correct description) of the other bands can, at best, be made only tentatively. The reasons for this are manifold. Thus, the regions usually quoted [19, 20] for the ,,X-sensitive" phenyl bands extend, sometimes, to several hundreds reciprocal centimeters and, moreover, there is an apparent disagreement in the assignment of two ,,X-sensitive" bands, those denoted *y* (B_2) and *x* (B_2) by Whiffen [18], between this and other authors (e. g. [20, 25]) on the one hand and, for example, Scott *et al.* [26] and authors, which have used this assignment as a guide, on the other [27, 28]. Furthermore, there does not seem to exist, as yet, a complete consent about the correct description of the vibrational modes of the chelate ring, despite the fact that isotopic-shift studies and theoretical calculations have yielded valuable results, at least for the case of acetylacetonates.

The situation can be further complicated by the splitting of the bands in this region which is often (e.g. [16]) observed in the spectra of acetylacetonates and is due to coupling between the vibrations of different chelate rings bound to the same metal atom. It is reasonable to assume that the extent of such a coupling will depend on the mechanical coupling between the appropriate oscillators on the one hand (so that largest separations are expected for vibrations involving mainly the O—M—O parts of the chelate rings) and on the overall symmetry of the complex, on the other (the decrease in symmetry increasing the separations). Such a coupling, however, if observed, could be used as a criterion by which the chelate-ring vibrations could be distinguished from the phenyl modes, which, as seen in the higher-frequency region, are virtually not coupled. A further such criterion could be the metal-dependence of the bands. It should be expected, namely, that the change of the mass of the central atom (Al — 26.98; Ga — 69.72; In — 114.82) would have more effect on the chelate-ring vibrations (particularly those in which the metal atom is directly involved) than on the phenyl (even „X-sensitive") vibrations in which the increased mass of the metal does not increase so significantly the mass of almost the whole molecule which plays the role of the substituent X for a given phenyl group. The comparison with the corresponding acetylacetonates could also be of help, although it should be made with caution. Namely, as is well known [29, 30], the dibenzoylmethanates are more stable than the corresponding acetylacetonates (that this is indeed so is evidenced by, among other things, the fact that the presently investigated dibenzoylmethanates were prepared from the corresponding acetylacetonates by a ligand-substitution reaction) and it is to be expected that, in agreement with the increased strength of the metal-ligand bonds, the M—O stretching frequencies should be found at higher frequencies in the spectrum of the dibenzoylmethanate than of the acetylacetonate of a given metal. Such may, possibly, also be the case with other chelate modes (e.g. chelate-ring deformations) if the increased stability of the complex causes an increased rigidity of the chelate ring in general. Such a comparison, between the spectra of $Al(acac)_3$ and $Al(DBM)_3$ in the 720—350 cm^{-1} region (the spectra below this frequency are unreliable both because of the use of KBr as a matrix material and because the instrument was not, except in recording the spectrum of $Al(DBM)_3$-d_3, purged of the atmospheric water vapor which completely obscurs the low-frequency end of the instrument range) is shown in Fig. 2. Another point which should be borne in mind is the apparent strengthening of the M—O bond in the order Al, Ga, In which, as recalled, is suggested by the change of the C═O stretching frequencies which are lowered in the same order. However, a parallel increase of the M—O stretching frequencies might not, actually, be observed, since the drastic increase of the mass of the central metal atom (which should shift the M—O frequencies *downwards*) could play a more important role in determining the position of the M—O stretching bands than does the strengthening of the metal-oxygen bond and the associated increase of the corresponding force constants (which should, of course, *increase* the frequencies of these bands).

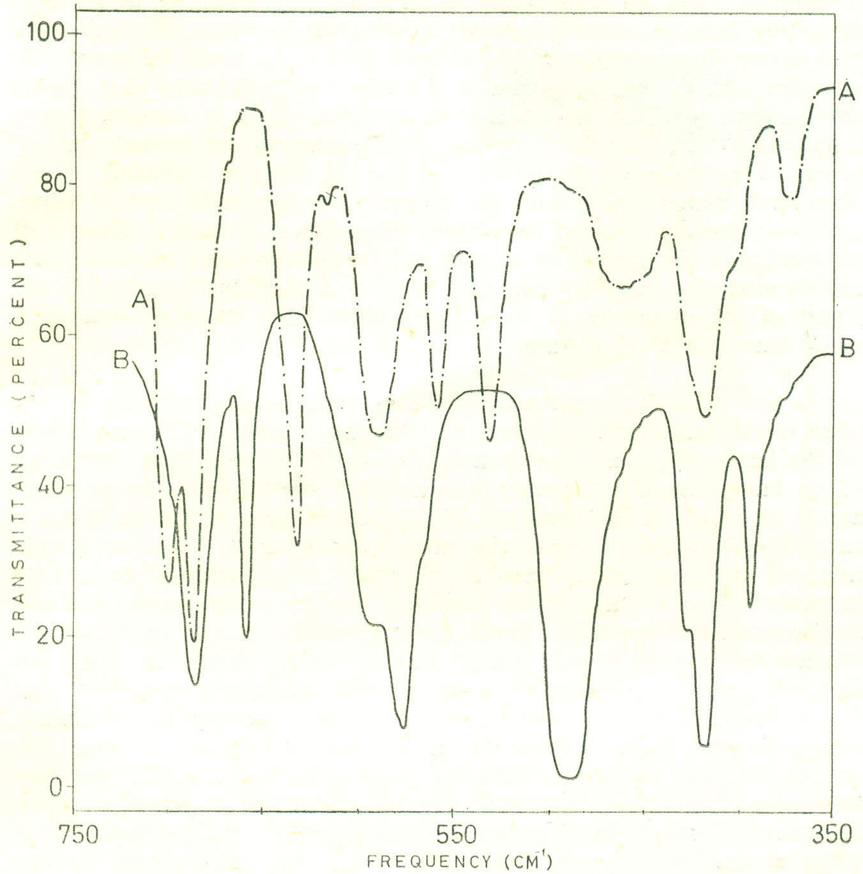

Fig. 2. Comparison of the infrared spectra in the 725—350 cm^{-1} region of aluminum dibenzoylmethanate (A) and acetylacetonate (B).

A parallel analysis of the spectra of the acetylacetonates and of the dibenzoylmethanates of Al, Ga and In reveals, first of all, a striking similarity in shape and intensity between the bands found at 590/578, 582 and 571 cm^{-1} in the acetylacetonates of Al, Ga and In respectively and those observed at 638/633, 634 and 628 cm^{-1} in the spectra of the corresponding dibenzoylmethanates. Even the sequence of frequencies (Ga > Al > In if the main maximum of the Al-chelate doublet is taken into account) is the same in both classes of compounds. These bands in the spectra of the acetylacetonates of Al, Ga and In are certainly analogous to the bands in other such chelates (Cr, Cu etc.) found at approximately the same frequencies and variously described as either almost pure M—O stretching [4,7] or a chelate ring deformation mode [11], possibly one in which the oxygen atom is displaced significantly [8]. Its large shift on ^{16}O—^{18}O substitution [4,7] and very insignificant one on substitution of carbon [7] or metal [8] atoms with corresponding isotopes seem to suggest a vibration in which the main contribution comes from motion of the oxygen atoms. As could be noted, the corresponding bands in the spectra of the dibenzoylmethanates have higher frequencies than in those of the acetylacetonates, which is consistent with the expected increase of rigidity of the chelate rings in the former class of compound. The observed, in the case of the Al chelates, splitting is, on the other hand, in agreement with the expectations for bands due to vibrations of mechanically coupled oscillators. The almost complete absence of such a splitting in the spectra of the Ga and In chelates (both acetylacetonates and dibenzoylmethanates) may be a sign of a slighter deviation of the MO_6 part of the molecules of these compounds from its ideal octahedral symmetry than in the Al chelate.

The shift to higher frequencies of the bands associated with the above-described mode makes one to expect an even larger shift in the same direction of the bands which are due to almost pure M—O stretching vibrations. Two such bands, at approximately 463 and 358 cm^{-1}, exist, according to Nakamoto *et al.* [8], in the spectrum of $Cr(acac)_3$. Their counterparts in the $Al(acac)_3$ spectrum are certainly the rather strong bands found at around 490 and 418 cm^{-1}, the weak band at 393 cm^{-1} corresponding, apparently, to the weak 418 cm^{-1} band [8] of $Cr(acac)_3$. In the spectra of the Ga and In acetylacetonates these three bands form complex features in which the maxima are much more closely spaced than in the Al chelate and have frequencies 447 (m), 425 (w) and 411 (ms) in the $Ga(acac)_3$ spectrum and 434 (m), 413 (w) and 404 (m) in the spectrum of the corresponding In chelate. Assuming the weak band to have the same origin throughout (its exact nature is not yet well-understood [7,8]) one expects to find a similar situation in the spectra of the dibenzoylmethanates as well : a pair of bands of considerable intensity (the higher-frequency one being more metal-sensitive than the other, so that on going from Al to In chelate the bands should become more closely spaced) plus a weak band located somewhere around 400 cm^{-1} or slightly higher. It is also to be expected that the frequencies of the two stronger bands should be considerably higher in the spectra of the dibenzoylmethanates than of those of the acetylacetonates, in agreement with the increased stabliity of the former class of compounds. Direct analogy is indeed observed in the 600—500 cm^{-1} region, only instead of *two*, there are *three* bands of comparable intensity (*cf.* Figs. 1 and 2). The separation between the bands is largest in the case of $Al(DBM)_3$, while in the spectra of the other two chelates these bands gradually coalesce, the whole feature being shifted to lower frequencies. The most metal-sensitive is, undoubtedly (*cf.* Fig. 1), the 589 cm^{-1} band in the $Al(DBM)_3$ spectrum whose counterparts in the other two spectra are difficult to single out unequivocally. This band, then, must correspond to the 490 cm^{-1} band of $Al(acac)_3$ and its large ($\approx$100 cm^{-1}) shift to higher frequency in the spectrum of $Al(DBM)_3$ is consistent with its assignment to an M—O stretching frequency. If the other ν(M—O) band is shifted upwards to a similar degree, it is expected around 520 cm^{-1} in the spectrum of $Al(DBM)_3$ and at somewhat lower frequencies in the spectra of the Ga and In chelates. The band which lies most closely to the expected value in the Al dibenzoylmethanate spectrum is located around 530 cm^{-1} and this band is, somewhat arbitrarily, assigned to the other M—O stretching vibration. It is again difficult to pick up the correct counterparts of this band in the spectra of the other two dibenzoylmethanates.

The third band in the above region (600—500 cm^{-1}) must be due to a phenyl vibration, undoubtedly one of the „X-sensitive" modes, *t* (an in-plane deformation of the phenyl ring, being of A_1 symmetry if the C_{2v} point group is assigned to the monosubstituted benzene ring) or one of the two B_2 (in Whiffen's choice of axes) modes, denoted *y* and *x* (both are out-of-plane ring deformations, the former involving a ring-substituent out-of-plane deformation as well). Of these, only the *t* mode is usually (e.g. [20]) quoted to appear as high as 535 cm^{-1}, but some authors (e.g. [27, 28]) place one of the B_2 modes (*x* or *y*) above 500 cm^{-1} and identify the *t* mode with the band appearing around 450 cm^{-1}, i.e. in a region where it could be located in our spectra too. Since our experimental results do not allow us to determine the symmetry or make other unequivocal choice of the proper modes to be assigned to a given band, we tentatively (and, admitedly, rather arbitrarily) assign the band found around 558 cm^{-1} to the *x* mode and that at approximately 460 cm^{-1} to the *t* mode (following King and So [28]), although the reverse assignment, with, possibly, substitution of the *y* mode instead of *x*, could also be in line with the published work on monosubstituted benzenes.

Of the bands in the 600—500 cm^{-1} region, only one is assigned to an Al—O stretching mode by Hancock and Thornton [21], although it is not clear whether their 532 cm^{-1} band corresponds to our 530 cm^{-1} frequency, since no „additional strong band at 453 cm^{-1} . . . also. . . attributable to the Al—O stretching fequency" could be found in our spectra: the 460 cm^{-1} band is, namely, one of the weakest ones in the Al (DBM)$_3$ spectrum. In fact, the only band of considerable intensity near the above value is the one found around 416 cm^{-1} in the spectrum of Al (DBM)$_3$, which is either shifted (leaving only the broad feature corresponding, at least in part, to the phenyl *w* mode) in the spectra of the other two chelates or has there a much lower intensity. The correct assignment of the 416 cm^{-1} band, as well as of the shoulder observed near 400 cm^{-1} and the weak bands around 370 and 320 cm^{-1} (the latter being clearly visible only in the spectrum of the deuterated Al(DBM)$_3$, the only one recorded, as noted earlier, with the instrument purged of atmoshperic water vapor) is not clear. The assignment of one of the bands around 400 cm^{-1} to a mode (probably another out-of-plane chelate-ring deformation in which the oxygen atoms take significant part), identical with the one to which the weak 392 cm^{-1} band in the Al (acac)$_3$ spectrum is due, seems rather convincing : on the one hand the frequency is higher than in the acetylacetonate and, on the other, this could explain the observed doubling of the 450 cm^{-1} band in the spectrum of the Ga and, especially, the In dibenzoylmethanates (as mentioned earlier, the corresponding bands in the spectra of Ga and In acetylacetonates have also frequencies higher than in the Al(acac)$_3$ spectrum).

The 370 cm^{-1} band of Al(DBM)$_3$ (observed near 380 cm^{-1} in the In(DBM)$_3$ spectrum and, apparently, around 390 cm^{-1} in the spectrum of the Ga chelate) could be due to one of the „X-sensitive" phenyl bands, most probably mode *u* (mostly an in-plane Ph-X deformation vibration).

Overtone and combination bands. — Besides the bands included in the foregoing discussion, a number of weak or very weak bands were observed, especially when the sample concentration in the pellet was high. Almost all such bands could be explained as due to overtones or binary combinations of the observed fundamentals and will not be discussed further. We could not, however, find suitable combinations to explain the very weak band around 1127 cm^{-1} and the shoulder at slightly lower frequency (1095 cm^{-1} in the Al(DBM)$_3$ spectrum) so that these bands are apparently due to combinations involving some low-lying fundmental.

It is, probably, also noteworthy that, besides the overtone of the *v* phenyl fundamental (discussed in connection with the assignment of the $\nu_{as}(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$ vibration), another overtone, that of the *f* phenyl mode at 724 cm^{-1}, which appears around 1443 cm^{-1} apparently participates in a Fermi-resonance interaction. This is evidenced by its gradual increase in intensity in going from Al to In dibenzoylmethanate, followed by the weakening of the neighbouring (1461 cm^{-1}) band which is attributed to the *n* phenyl fundamental. This fact indicates that the symmetry of the phenyl group is certainly lower than the ideal C_{2v} in which the *n* mode is of B_1 species, while each overtone has A_1 symmetry. Such a conclusion is, of course, consistent with the appearence of all (even forbidden under C_{2v} symmetry) phenyl fundamentals.

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ИЗВОД

ИНФРАЦРВЕНИ СПЕКТРИ НА ДИБЕНЗОИЛМЕТАНАТИТЕ НА АЛУМИНИУМ, ГАЛИУМ И ИНДИУМ

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Снимени се инфрацрвените спектри на дибензоилметанатите (1,3-дифенил-1,3-пропандионато хелати) на Al, Ga и In, како и спектарот на делумно деутерираниот алуминиумов хелат. Направен е обид да се асигнираат, колку што е можно покомплетно, посматраните инфрацрвени ленти, употребувајќи ги како база постојните информации за спектрите на ацетилацетонатите (1,3-диметил-1.3-пропандионати) и на моносупституираните бензени. Деутерирањето (проценето како 70% целосно) на γ водородот од хелатниот прстен помага при асигнацијата на δ(CCH) и, особено, γ(CCH) модовите. Инфрацрвените спектри на испитуваните хелати задоволително може да се третираат во апроксимацијата метал : лиганд 1 : 1, поради релативно слабата интеракција меѓу вибрациите на трите хелатни прстени (особено оние локализирани главно во Ph-C-CH-C-Ph деловите од молекулата). Фенилните групи може да се третираат како приближно независни единки, со вибрациони фреквенции (пред сè оние на вибрациите на *прстенот* што не се „X-осетливи") што паѓаат во подрачјата кои за секоја од нив обично се наведуват. За разлика од случајот на ацетилацетонатите, изгледа дека тука нема забележително мешање на C-C-H деформацијата во рамнината и антисиметричната C=O валентна вибрација, додека вибрацијата што е предимно антисиметрична C=C=C вибрација има и δ(CCH) карактер. Неколку вибрации, интерпретирани како M—O валентни или деформации на хелатниот прстен имаат значително *повисоки* фреквенции во спектрите на дибензоилметанатите одошто во оние на соодветните ацетилацетонати, во согласност со зголемената стабилност на соединенијата од првиот тип.

ХЕМИСКИ ФАКУЛТЕТ
СКОПЈЕ

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