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INFRARED SPECTRA OF METAL β-KETOENOLATES AND RELATED COMPLEXES

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CONTENTS

A. SCOPE OF THE REVIEW

Metal β-ketoenolates, in particular the complexes of acetylacetone, probably have a more extensively examined chemistry than any other chelate system. The ligands have been known for almost a century and metal acetylacetonates were, not surprisingly, among the first metal complexes to be studied by IR spectroscopy just 50 years ago (ref. 1 and references cited therein.)

The versatility with which acetylacetone and related ligands coordinate with metal ions yields numerous classes of chelated and open-chain complexes in which the ligand occurs variously as

(1) a monoanionic bidentate oxygen donor in the enol form,
(2) a neutral bidentate oxygen donor in the keto form,
(3) a monoanionic ligand coordinating through the methine carbon atom,
(4) a π-allylic donor,
(5) a monoanionic monodentate oxygen donor in the enol form,
(6) a bridging ligand of various types.

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These are the more common species of complexes; a total of at least 18 classes has been recognized. The vast majority of complexes which have been synthesized and studied by various physical techniques are derived from the first of these ligand categories. So far at least 90% of published studies refer to the complexes of type (1). For this reason, the scope of this review has been confined to these complexes only.

There has been much interest over the past 20 years in the complexes of β-ketoenolate analogues in which one or both of the oxygen donors has been replaced by other groups or atoms such as NH (β-ketoimines), S (mono- and dithio-β-ketoenols) or Se (diseleno-β-ketoenols). In these complexes, the ligands serve as monoanionic bidentate ligands resembling the class (1) β-ketoenolates and they have therefore been included in this review.

It is anticipated that the major application of this review will be (hopefully) to assist readers who have problems with band assignments in related molecules under investigation or who wish to derive bonding or structural information from IR data. These areas, which are also of principal interest to the author, have therefore been emphasized. There have been few applications of Raman spectroscopy to these complexes, insufficient to justify replacing the word 'infrared' in the title by 'vibrational'. Those papers which have appeared are included in this review.

B. THE ASSIGNMENT PROBLEM

The earliest work on the IR spectra of metal acetylacetonates was carried out by Lecomte and coworkers [1–3] who recognized 12 principal regions of absorption within the range 1700–400 cm^{-1} which are common to the spectra of most metal acetylacetonates. There are also three bands which are practically unaffected by the metal ion [4] near 3090 cm^{-1} (ν(C–H) of the methine group), 2970 and 2870 cm^{-1} (the antisymmetric and symmetric ν(C–H) of the CH_3 groups). These latter three bands, present in all β-ketoenolate spectra, will not be referred to again in this review. For the remaining bands, we shall adopt a band numbering system based on the spectrum of iron(III) tris(acetylacetonate) (Fig. 1) taken on a modern instrument. This numbering system will suffice for most acetylacetonates in view of the approximate band-for-band correspondence of the spectra and will avoid complications from the various band numbering systems used by different authors.

Lecomte and coworkers [1–3] regarded bands 1–11 and 15–17 to be independent of the metal ion. A four-stage semiempirical approach to the assignment problem was adopted by considering the following in turn:

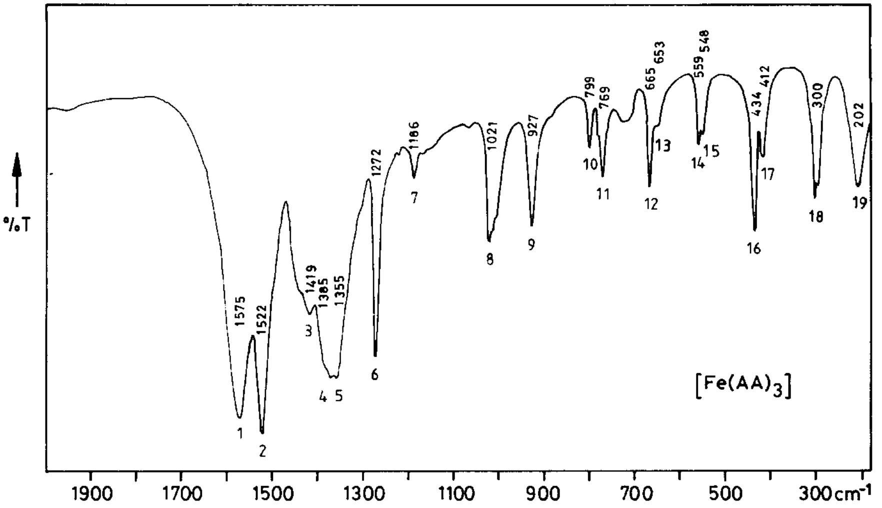


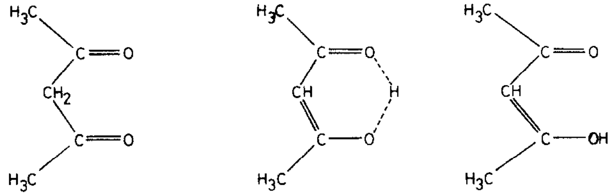
Fig. 1. IR spectrum (2000–200 cm^{-1}) of iron(III) acetylacetonate with band numbers and frequencies (cm^{-1}).

(a) The skeletal vibrations of acetylacetone. These bands were assumed to be derived from the in-phase and out-of-phase coupling of two acetone molecules linked by a common methylene group. This accounted for bands 6 and 7 (seen originally as one band), 10 and 11 (seen as one band) and 15–17 with frequencies near those of the acetone vibrations from which they are derived.

(b) The characteristic vibrations of the C–H bonds assigned by comparison with the corresponding bands of acetone. Bands 3, 5, 8 and 9 were accounted for in this way.

(c) The carbonyl vibrations. Absence of absorption in the 1700 cm^{-1} region was construed as evidence that coordination occurs through the enol tautomer. Band 1 was assigned to the stretching frequency of a C=O bond of reduced double bond order and band 4 to a C–O bond of increased single bond order. Band 2 remained for assignment to a perturbed C=C bond. Absence of absorption in the ν(O – H) region in the spectrum of acetylacetone was considered as evidence that the free ligand is a proton chelate and therefore exists largely in the chelated enol form (Fig. 2) while the low frequency of the carbonyl vibration and absence of a band which could be ascribed to olefinic C=C absorption were consistent with a cyclic structure for the metal complexes with coordination through both carbonyl groups even in the complexes of monovalent metal ions.

(d) Characteristic bands due to the metal ion. Besides the bands common to all the complexes and accounted for above, between one and four

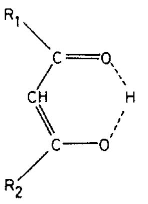


(a) (b) (c)

Fig. 2. Tautomeric forms of acetylacetone: (a) keto form, (b) chelated enol form, (c) open enol form.

additional bands were observed in the 600–700 cm^{-1} region (bands 12–14 in the iron(III) complex), the number and their position varying with the coordinated metal ion. Lecomte commented that the frequencies were not related in any obvious manner to the mass of the metal ion, complexes of heavy ions such as thorium(IV) giving bands in the same region as those of much lighter ions such as beryllium(II).

In 1954, Bellamy and Beecher [5] reported a detailed IR study of keto–enol tautomers including acetylacetone. Since $\nu(O{-}H)$ is considerably weakened and broadened by intramolecular hydrogen bonding, the dependence of $\nu(C{=}O)$ on the strength of the hydrogen bond was studied. Enol tautomers were found to produce a considerable reduction in $\nu(C{=}O)$ when compared with analogous compounds in which hydrogen bonding is not possible. Thus, chelated enolic acetylacetone (Fig. 2(b), $\nu(C{=}O) = 1608\ cm^{-1}$) shows a decrease of 90 cm^{-1} when compared with acetylacetonyl acetate, which is a diketone ($\nu(C{=}O) = 1698\ cm^{-1}$). Acetylacetone and benzoylacetone (Fig. 3) gave bands at 1724 cm^{-1} (keto forms) and 1608–1600 cm^{-1} (enol forms) respectively. Extending this work to metal complexes, Bellamy and Branch [6] found that no relationship exists between the stabilities of the copper(II) complexes of acetylacetone, benzoylacetone and dibenzoylmethane and the frequency of the first band in the spectrum below 1600 cm^{-1} which was assigned (correctly, as it later transpired) to the carbonyl stretching frequency. It is interesting to note that Bellamy and Branch [6] commented that the carbonyl frequencies for the



$R_1 = R_2 = CH_3$ acetylacetone (HAA)
$R_1 = CH_3$, $R_2 = C_6H_5$ benzoylacetone (HBA)
$R_1 = R_2 = C_6H_5$ dibenzoylmethane (HDBM)
$R_1 = R_2 = C(CH_3)_3$ dipivaloylmethane (HDPM)
$R_1 = CH_3$, $R_2 = C(CH_3)_3$ pivaloylacetone (HPA)
$R_1 = CH_3$, $R_2 = CF_3$ trifluoroacetylacetone (HTFA)
$R_1 = R_2 = CF_3$ hexafluoroacetylacetone (HHFA)
$R_1 = \alpha$-thienyl, $R_2 = CF_3$ thenoyltrifluoroacetone (HTTA)

Fig. 3. Formulae of some common β-ketoenols.

acetylacetonates are essentially similar for the complexes with cobalt, nickel, copper and zinc. These are quoted as cobalt, 1586; nickel, 1605; copper, 1580; and zinc, 1577 cm^{-1}. In fact, the shifts follow the order of crystal field stabilization energies: cobalt < nickel > copper > zinc, a point which will be referred to later.

The first paper to describe the influence of the metal ion and the ligand substituent on the IR spectra of metal β-ketoenolates was the report by Holtzclaw and Collman in 1957 [7] in which the spectra of the acetylacetonates of 11 metals were discussed. These authors considered the frequency of the carbonyl band to be largely dependent on three factors: (a) the masses of the groups bound to the CO moiety; (b) interaction of the carbonyl with neighbouring π or d orbitals; and (c) the relative electron density of the σ bonds, the latter being, for the most part, controlled by the electronegativity of the 1,3-ligand substituents.

The mass effect was considered to play only a very minor role in determining the metal–O bonding for complexes of the same ligand with different metals. It was considered that an increase in the conjugation between the metal ion and the carbonyl group would result in a stronger metal–O bond, less double bond character in the carbonyl group and a lowering of the frequency of the perturbed carbonyl band. This supposition was probably based on the bonding in metal carbonyls which exhibit an inverse relationship between the metal–C and C–O bond orders, i.e. any influence such as substitution of a carbonyl group by a trialkylphosphine, raises one bond order at the expense of the other and there remains constancy of bond order summation about the carbon atom. It will be shown later that this assumption does not apply in general and specifically is valid for the metal β-ketoenolates only so far as the effect of the metal ion is concerned but not the ligand substituent. In fact, later work shows that an increase in the conjugation between the metal ion and the carbonyl group raises the frequencies of both the M–O and C=O bonds. In contrast to Bellamy and Branch [6], Holtzclaw and Collman [7] found a relationship between $\nu(C=O)$ and the stability order reported by Fernelius and coworkers [8] (nickel was anomalous). There was, however, considerable disagreement between the values of $\nu(C=O)$ from the two groups of workers. Holtzclaw and Collman's values are in good agreement with more recent values. They suggested that Bellamy and Branch may have assigned the more intense of the two bands in the carbonyl region to $\nu(C=O)$ but the second band has a far lower frequency than those reported. A more likely reason for the discrepancies is that some complexes may have been the anhydrous polynuclear β-ketoenolates, others the hydrated molecules. Such structural differences have a considerable effect on $\nu(C=O)$.

In discussing the spectra of the copper(II) complexes, that of 2-furoylperfluorobutyrylmethane was observed to yield three bands near 1600 cm^{-1} (1615, 1598 and 1580 cm^{-1}). Almost certainly correctly, the middle band was assigned to a furan vibration. Later it was found that phenyl- and heterocyclic-substituted β-ketoenolates always give rise to this band which has occasionally been wrongly assigned to ν(C=O) or ν(C=C). Although no relationship between ν(C=O) and the stabilities of the copper(II) β-ketoenolates was established, it was noted that copper(II) benzoylacetonate gave a ν(C=O) value (1561 cm^{-1}) considerably lower than that of the acetylacetonate (1580 cm^{-1}), a factor attributed to quinonoid resonance of the phenyl group with the chelate ring. Strongly electronegative substituents such as the CF_3 groups in copper(II) hexafluoroacetylacetonate were found to raise ν(C=O). Among the copper(II) complexes of nine γ-substituted acetylacetonates it was noted that there was a roughly inverse relationship between the masses of the substituents and ν(C=O).

The band near 1425 cm^{-1} was found to be present only in the spectra of β-ketoenolates with methyl substituents. This band, suggested by Lecomte and coworkers [1–3] as originating in the CH_3 groups, was assigned to a methyl deformation. Later work confirmed this assignment. It was proposed that the band near 800 cm^{-1}, assigned by Lecomte and coworkers to a skeletal C–C vibration, is in fact an out-of-plane C–H deformation π(C–H). This assignment has also been confirmed as correct. However, bands in the 700 cm^{-1} region are observed in the spectra of many γ-substituted metal β-ketoenolates where this assignment is invalid. The spectra were measured only to 650 cm^{-1}, some of the bands in the 700–650 cm^{-1} range being tentatively assigned to ν(Cu–O).

Belford et al. [9], in a comprehensive study of trifluoro-substituted β-ketoenols and their copper(II) complexes, noted that the perturbed carbonyl band in the IR spectra of the copper(II) chelates increased in the order $Cu(AA)_2 < Cu(TFA)_2 < Cu(HFA)_2$, the values being 1582 (1582), 1615 (1616) and 1643 (1655) cm^{-1} (more recent frequencies in parentheses). Thus the frequency increases as the stability of the complex decreases. The ν(C=C) values exhibited a slight decrease in the same order. A more recent detailed study of substituent effects confirmed these relationships [10] (Section E).

West and Riley, in 1958 [11], determined the spectra (down to 650 cm^{-1}) of 18 metal acetylacetonates. They noted that serious discrepancies existed in the published frequencies previously reported and were the first to realize the importance of establishing the identity and purity of the complexes studied by microanalysis. This is particularly essential for those complexes which, by different synthetic methods, may be obtained either as the anhydrous or solvated products. They were also the first workers to include a range of complexes of monovalent metals (lithium, sodium, potassium, caesium, thallium, silver). The reluctance of the large and weakly polarizing alkali metal ions to act as electron acceptors implies that covalent M–O bonding in metal β-ketoenolates should be at a minimum in the chelates of these ions. Although, in common with the experience of others, successful combustion analyses of the alkali metal(I) β-ketoenolates could not be obtained, careful synthesis in anhydrous solvents ensured that the products were the anhydrous complexes rather than the more normally isolated dihydrates. The most salient feature of the spectra commented upon by West and Riley was their striking similarity even for such stoichiometrically diverse species as M(AA), $M(AA)_2$ and $M(AA)_3$. However, they differed from Bellamy and Branch in finding some significant shifts in ν(C=O) which were related to the ionization potentials of the metals. Although they were unable to scan their spectra below 650 cm^{-1}, they correctly attributed some of the bands in certain of the spectra to ν(M–O), notably the 822 cm^{-1} band in $Be(AA)_2$ with its exceptionally high frequency.

Although the spectra of a large number of metal acetylacetonates were recorded and discussed during the period 1950–1960, these were mostly confined to the sodium chloride region and the assignments of Lecomte and coworkers were used without any significant changes. In 1960 Nakamoto and Martell [12] carried out a normal coordinate treatment of copper(II) acetylacetonate employing a simplified 1:1 complex model in which the methyl groups were considered as separate atoms. The interatomic distances were taken from the crystallographic study of iron(III) acetylacetonate because the different bond lengths which had been reported for the two C=O and C=C bonds in each ring of $Cu(AA)_2$ were considered to arise from incomplete refinement of the structure of the copper(II) chelate. Allowance was made in the calculation for the effects of vibrational coupling. The most significant results of this treatment were (a) reversal of the ν(C=O) and ν(C=C) assignments previously proposed by Lecomte and coworkers, (b) assignment of band 3 near 1425 cm^{-1} to a second carbonyl band, coupled with a C–H bending mode, (c) assignment of Lecomte and coworkers second carbonyl band (band 4) to a C–H deformation mode of the methyl group, and (d) assignment of two bands at 680 and 654 cm^{-1} (previously noted by Lecomte and coworkers as sensitive to the coordinated ion) to variously coupled ν(Cu–O). The calculation showed the least-coupled Cu–O stretching mode to be represented by the band at 455 cm^{-1}.

The force constant of the Cu–O bond is intermediate between those of the Ni–C bond in $Ni(CO)_4$ and the Fe–C bond in the $[Fe(CN)_6]^{4-}$ ion. Since the metal–C bonds in these compounds have partial double-bond character, the Cu–O bond in $Cu(AA)_2$ was also assumed to have bond multiplicity exceeding unity in accordance with benzenoid resonance of the type shown in Fig. 4.

In an independent paper published simultaneously with that of Nakamoto

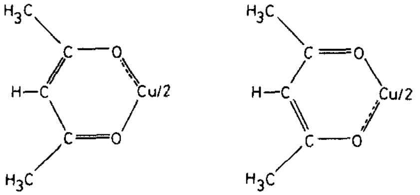


Fig. 4. Benzenoid resonance in copper(II) acetylacetonate.

and Martell [12], Lawson [13] reported the mull spectra of 30 metal acetylacetonates, including those of monovalent, divalent, trivalent and tetravalent metals and vanadyl acetylacetonate, down to 290 cm^{-1}. Since Nakamoto and Martell had taken their spectra to 400 cm^{-1} but their calculations yielded a *predicted* M—O band near 300 cm^{-1}, it is of interest to observe that neither Lawson nor subsequent workers observed bands near those predicted for the majority of acetylacetonates. Lawson noted that ν(C=C) (incorrectly assigned as ν(C=O)) shifts to higher frequency as the ionization potential of the metal ion increases. Furthermore, the order of ν(C=C) was claimed to parallel that of the stabilities.

As for Lecomte and coworkers, they found that the number and frequencies of bands in the range 800–600 cm^{-1} were dependent on the metal but no clearly defined pattern for the variation seemed obvious. The different band patterns were also observed to be highly metal sensitive. The chelates of ions with inert gas configurations were considered separately from those of the transition metal ions, the former being free from resonance effects associated with inner orbital splitting. Since the metal–ligand bond strength is directly related to the metal–ligand stretching force constant (diatomic molecule approximation) it is expected that ν(M—O) will follow the order aluminium, gallium, indium > alkali earth > alkali metal. Within each of these three groups, higher ν(M—O) values are expected for the ions of smaller radii. The observed frequencies between 500 and 600 cm^{-1} were, in general, considered to be consistent with these expectations. The frequencies of two bands within the region 600–290 cm^{-1} were observed to follow this order: (?)Pd > 621(Cu) > 592(Ni) > 580(Co) > 565(Zn) and 465(Pd) > 459, 435(Cu) > 427(Ni) > 425(Co) > 426, 393(Zn) and hence were assigned ν(M—O) character. Later work supported the majority of these assignments and the correspondence of the bands listed. A third metal(III)-sensitive band which shifts as expected from crystal field theory was observed: 360(Cr) > 339(Mn) > 301(Fe).

Coinciding with Lawson's paper a discussion of the IR spectra below 700 cm^{-1} of 18 M(I), M(II) and M(III) acetylacetonates was reported by Bailar and coworkers [14]. The spectrum of the acetylacetonate ion was considered to be provided by K(AA). Three strong bands at 654, 520 and 410 cm^{-1} were recognized as being associated with the anionic ligand. Coordination by less-electropositive metal ions was observed to split these vibrations into several new bands. The first of these three bands exhibited an upward frequency shift which did not appear to be connected with any physical property of the coordinated ion. Rare earth acetylacetonates, however, caused little shift of this band and this was attributed to the electrovalent character of the metal–ligand bonding in these complexes. The second band of the acetylacetonate anion at 520 cm^{-1} also exhibited an upward frequency shift on substitution of a less-electropositive ion for K^+. The shift of this band was found to be directly related to the stability constants of the complexes. The importance of this finding is that later work established this band as the least-coupled ν(M—O) mode (a feature not recognized in the normal coordinate treatment of Nakamoto and Martell) and therefore the band most likely to be related to the metal complex stabilities. The third band (at 410 cm^{-1}) of the potassium complex was found to be that most split by the coordination of other metal ions. In the complexes of 3*d* metal(II) ions, manganese(II), iron(II), cobalt(II), nickel(II), copper(II), this band was also found to be related to stabilities as previously proposed by Nakamoto and Martell but the relationship did not hold outside this transition series.

By applying perturbation methods to the normal coordinate treatment of copper(II) acetylacetonate, Nakamoto et al. [15] calculated the vibrational frequencies for the acetylacetonates of a number of divalent and trivalent metal ions. The bis(acetylacetonates) of the metal(II) ions and the tris(acetylacetonates) of the metal(III) ions have very nearly a band-for-band correspondence and the assignments yielded by the perturbation method correspond, in general, to those obtained for the copper(II) complex. The metal–O force constants of the tris complexes are, except for the iron(III) complex, larger than those for the copper(II) complex. The exception was considered to indicate weak Fe—O bonding which is consistent with magnetic and NMR evidence indicating that there is some ionic character in the Fe—O bonds [16]. The calculated force constants of the metal(II) complexes were found to be in qualitative agreement with the order of ΔH_{ML} where this parameter is the enthalpy of the reaction

$$[M^{2+}]_g + 2[L]_{aq} \equiv [M^{2+}L_2]_{aq} + \Delta H_{ML} \qquad (1)$$

Seven years after Nakamoto and Martell's normal coordinate study of copper(II) acetylacetonate, a second treatment of this molecule and the iron(III), chromium(III) and palladium(II) complexes was published by Mikami et al. [17] with the refinement that the complete 29- and 43-body problems for the bis(acetylacetonates) and tris(acetylacetonates) were worked out. This procedure led to assignments basically similar to those proposed by Nakamoto and Martell [12]. One significant exception was that the band at 455 cm^{-1} in the spectrum of $Cu(AA)_2$ assigned by Nakamoto to an almost pure ν(Cu—O) mode was shown by Mikami et al.'s treatment to be less vibrationally pure than a second band near 300 cm^{-1}. The fact that this band is more sensitive to substitution of the metal ion than that at 455 cm^{-1} was considered consistent with its higher vibrational purity. For the iron(III), chromium(III) and cobalt(III) chelates, for which the ions have similar mass, ν(M—O) gives directly the relative strengths of the M—O bonds; otherwise the force constants provide a better measure of relative strengths. The ν(M—O) and force constant values, Rh(III) > Co(III) > Cr(III) > Fe(III) and Pt(II) > Pd(II) > Cu(II) > Mn(II), were in the expected stability order. The complexity of the spectrum of $Mn(AA)_3$ was apparently the reason for not fitting this metal(III) ion into the frequency order (see Section C).

Practically simultaneously with this treatment, Pinchas et al. [18] published an ^{18}O-labelling study of chromium(III) and manganese(III) acetylacetonates which established some assignments significantly different from those of Nakamoto, particularly with respect to ν(C=O) which now became assigned to band 1 since it is shifted by 13 cm^{-1} towards lower frequency on ^{18}O substitution whereas band 2 is not shifted at all. Pinchas et al. attributed the different assignments as possibly due to Nakamoto's assumption of a Urey–Bradley force field which they considered to lead often to very erroneous results, even for simple molecules. Further discrepancy exists with respect to band 3 assigned by Nakamoto to about 50% coupled ν(C=O) + δ(C—H) but found to shift hardly at all on ^{18}O labelling and hence assigned now to nearly pure $\delta(CH_3)$, usually found near 1450 cm^{-1} but shifted towards lower frequency as a result of the unsaturation of the neighbouring carbon atom.

In the spectra below 700 cm^{-1} further significant disagreement with the assignments based on theoretical treatments exists. Band 15 (at 592 cm^{-1} in the chromium(III) complex) exhibits the largest ^{18}O-induced shift of any band in the spectrum and on this basis was assigned to the least-coupled ν(Cr—O) band, whereas the normal coordinate analysis placed this band as an out-of-plane deformation of the chelate ring. Conversely, band 16 (assigned to the vibrationally purest ν(Cr—O) band by the theoretical treatment) exhibits a much smaller ^{18}O-induced shift than band 15. Pinchas et al. regard this band as more probably Nakamoto's ν_{12} vibration (ν(M—O) + δ(C—CH_3)) since band 13, previously attributed to this mode, shifts only 3 cm^{-1} on ^{18}O substitution. Unfortunately, the ^{18}O-labelling study was not extended to the 300 cm^{-1} region in which Mikami et al. assigned the vibrationally purest ν(M—O) band.

In 1968, Junge and Musso [19] carried out an ^{18}O-labelling study of copper(II) acetylacetonate. Measurements were extended only to 400 cm^{-1}. Bands at 614 (^{18}O shift, 16 cm^{-1}), 455 (^{18}O shift, 7 cm^{-1}) and 431 cm^{-1} (^{18}O shift, 9 cm^{-1}) were all assigned to ν(Cu–O). In the same year (1967) Behnke and Nakamoto [20] carried out a further normal coordinate analysis of two platinum(II) acetylacetonates: K[Pt(AA)Cl$_2$] and [Pt(AA)$_2$]. In this study, a modified Urey–Bradley force field was adopted and the effects of deuteration on the spectra were investigated. The calculation led to revised assignments for bands 1 and 2 compared with those obtained in the earlier theoretical treatment of Cu(AA)$_2$, and Behnke and Nakamoto propose that these revised assignments should be applied to other metal acetylacetonates also. Band 1 now becomes assigned to practically pure ν(C=O) while band 2 is ν(C=C) + δ(C–H). Band 2 exhibits a dramatic shift of about 40 cm^{-1} on deuteration of the complexes at the γ-carbon atom since coupling from δ(C–D) is now removed. Bands 3 and 5 disappear in the d_6 and d_7 K[Pt(AA)Cl$_2$] complex and are therefore assigned to δ(CH$_3$) while band 4 (assigned to ν(C=O) + δ(C–H)) is lowered 10 cm^{-1} on γ-carbon deuteration due to loss of coupling by δ(C–D). In accordance with the ^{18}O-labelling study (and by contrast with the normal coordinate treatment of the copper chelate) band 15 now becomes ν(M–O).

In 1970, Nakamoto et al. [21] prepared pairs of isotopically labelled metal acetylacetonates, among them ^{54}Fe(AA)$_3$ and ^{57}Fe(AA)$_3$, ^{50}Cr(AA)$_3$ and ^{53}Cr(AA)$_3$, ^{63}Cu(AA)$_2$ and ^{65}Cu(AA)$_2$, with isotopic purities exceeding 89 at.%. The spectra of each pair were examined in order to determine the relative isotopically induced shifts and hence the vibrational purity (in ν(M–O)) of the bands below 800 cm^{-1}. Bearing in mind that a frequency error of approximately 0.3 cm^{-1} is claimed, the observed shifts (Table 1) indicate that bands 18 and 16 are the least-coupled ν(M–O) bands but some ν(M–O) character is indicated for certain of the remaining bands also. There is quite a substantial disagreement between the ^{18}O- and metal-labelling studies with respect to bands 15 and 16. Both studies show both bands to comprise ν(M–O) but the two techniques yield opposite orders of vibrational purity. In 1974, the ^{18}O-labelling study was extended [22] to band 18, observed to yield the maximum shift on metal ion labelling. This band shifted by only 2 cm^{-1} on ^{18}O labelling (in the Raman spectrum). Nakamoto et al. [21] suggest that the results of the ^{18}O-labelling method must be viewed with caution since ν(M–O) and the ligand vibrations involving the oxygen atom are affected on introducing the heavier oxygen isotope. However, it must also be conceded that if band 18 contains a contribution from a ring deformation mode, then the latter may also be affected by substitution of a heavier metal isotope in a sense which reinforces the shift in ν(M–O).

In view of the serious discrepancy between the ^{18}O- and metal-ion-

TABLE 1

^{18}O- and metal isotope-induced shifts in vibrational bands of metal acetylacetonates[a]

Band	$[Fe(AA)_3]$		$[Cr(AA)_3]$		
	Frequency	$^{57,54}Fe$ shift	Frequency	$^{53,50}Cr$ shift	^{18}O shift
10	802	0	791	0	0
11	772	0	773	0	0
12	667	0	682	0.5	11
13	655	0.5	660	0	3
14	560	0.5	611	1.0	n.o.[b]
15	550	0.2	595	0.7	19
16	437	1.5	462	3.0	5
17	406	0	415	0	8
18	299	5.0	355	3.9	2[c]
19	202	0			

[a] Frequencies and shifts in cm^{-1}. [b] n.o., not observed. [c] Raman band shift [22].

labelling studies with respect to the assignment of bands 15, 16 and 18 in the spectrum of chromium(III) acetylacetonate (summarized in Table 2), Niven and Thornton [23] in 1980 examined the effects of both ^{18}O and $^{68,64}Zn$-labelling (of 72% and 98% isotopic purity respectively) on the IR spectrum of zinc(II) acetylacetonate monohydrate, $[Zn(AA)_2(H_2O)]$, in order to determine whether mutually contradictory assignments were observed for

TABLE 2

Frequencies (cm^{-1}), isotopically induced shifts ($\Delta\nu$, cm^{-1}) and band assignments for $[Cr(AA)_3]$[a]

Band frequency				Method	Ref.
592 (ν_{15})	463 (ν_{16})	416 (ν_{17})	358 (ν_{18})		
oop ring def	ν(Cr–O)	oop ring def	ν(Cr–O)	nct	24
oop ring def	ν(Cr–O) + δ(C–CH_3)	Ring def	ν(Cr–O)	nct	17
ν(Cr–O) $\Delta\nu = 19$[b]	ν(Cr–O) + δ(C–CH_3) $\Delta\nu = 5$[b]	δ(O–Cr–O) $\Delta\nu = 8$[b]	na	^{18}O labelling	18
oop ring def $\Delta\nu = 0.7$[c]	ν(Cr–O) $\Delta\nu = 3.0$[c]	oop ring def $\Delta\nu = 0$[c]	ν(Cr–O) $\Delta\nu = 3.9$[c]	$^{53,50}Cr$ labelling	21
ν(Cr–O) $\Delta\nu = 19$[b]	ν(Cr–O) + δ(C–CH_3) $\Delta\nu = 10$[d]	ip δ(O–Cr–O) $\Delta\nu = 5$[d]	ip δ(C–C–C) $\Delta\nu = 2$[d]	^{18}O labelling	22

[a] Abbreviations: oop, out-of-plane; def, deformation; nct, normal coordinate treatment; na, not assigned; ip, in-plane. [b] Shift in IR band on ^{18}O labelling. [c] Difference in frequencies between ^{53}Cr- and ^{50}Cr-labelled species. [d] Shift in Raman band on ^{18}O labelling.

TABLE 3

Frequencies, isotopically induced shifts ($\Delta\nu$) and band assignments in the IR spectrum of $[Zn(AA)_2(H_2O)]$

Band number	Frequency (cm^{-1})	$\Delta\nu(cm^{-1})$		Assignment
		^{18}O	$^{68,64}Zn$[a]	
	3300			$\nu(C-H)$
	2966			$\nu(C-H)$
	2927			$\nu(C-H)$
1	1599	2		$\nu(C=O)$
2	1522	1		$\nu(C=C)+\nu(C=O)$
	1513	4		$\nu(C=O)+\delta(C-H)$
3	1453			$\delta(C-H)$
4	1400			$\delta(CH_3)$ deg def
5	1370			$\delta(CH_3)$ sym def
6	1264			$\nu(C-C)+\nu(C-CH_3)$
7	1191			$\delta(C-H)$ in-phase
8	1020			$\delta(CH_3)$ rock
9	933	1		$\delta(C-CH_3)+\nu(C=O)$
10	779			$\delta(C-H)$ out-of-plane
11	772			$\delta(C-H)$ out-of-plane
13	656		1	Ring def
14	570		1	Ring def
15	557	3	2	$\nu(Zn-O)+\delta(C-CH_3)$
	439	1	2	$\nu(Zn-OH_2)$
16	422	1		$\delta(C-C-C)$ in-plane
17	413	5	6	$\nu(Zn-O)$
18	388	1	1	$\delta(O-Zn-O)$ in-plane
19	241	6	5	$\delta(O-Zn-O)$ out-of-plane
20	208			$\delta(C-C-C)$ out-of-plane
21	173	1	3	$\delta(O-Zn-OH_2)$

[a] Difference between frequencies of ^{68}Zn- and ^{64}Zn-labelled compounds.

this complex also. The zinc complex was studied because the availability of the ^{68}Zn and ^{64}Zn isotopes represent an isotopic pair with sufficient mass difference to yield reasonable $^{68,64}Zn$-induced shifts. The frequency and shift data are given in full in Table 3.

In the 4000–560 cm^{-1} region, only four bands exhibit ^{18}O sensitivity, suggesting that each has a component of $\nu(C=O)$. These correspond precisely to those four bands for which $\nu(C=O)$ provides a contribution in the assignments previously obtained on the basis of normal coordinate analysis [12]. The ^{18}O-induced shifts are rather small compared with those observed [18] for $[Cr(AA)_3]$, suggesting a greater degree of vibrational coupling in the zinc(II) complex. The remaining assignments are based on normal coordinate analysis of copper(II) and metal(III) acetylacetonates [17,24].

In the 560–150 cm^{-1} region, two bands (at 413 and 241 cm^{-1}) exhibit maximum ^{18}O sensitivity. Moreover, as would be expected, the same two bands exhibit maximum sensitivity to metal isotope substitution. The band at higher frequency (413 cm^{-1}) is firmly assigned to ν(Zn–O) while that at 241 cm^{-1} is assigned to δ(O–Zn–O).

The C_{4v} localized point symmetry of $[Zn(AA)_2(H_2O)]$, which has been crystallographically shown [25,26] to have approximate square-based pyramidal coordination, implies the existence of six IR-active metal–ligand modes: $2a_1+e$ stretches and a_1+2e bends of which two ν(Zn–O) and one $\nu(Zn–OH_2)$ stretches and two δ(O–Zn–O) and one $\delta(O–Zn–OH_2)$ bends are expected. The band at 557 cm^{-1} is logically assigned, on the grounds of its ^{18}O and $^{68,64}Zn$ sensitivities, to the second ν(Zn–O) stretch, while the 439 cm^{-1} band is probably $\nu(Zn–OH_2)$. The 388 and 173 cm^{-1} bands are assigned to δ(O–Zn–O), one of them involving the water molecule.

Two features of $[Cr(AA)_3]$ suggest that ν(Cr–O) in this complex would be considerably higher than ν(Zn–O) in $[Zn(AA)_2(H_2O)]$. One is the crystal field stabilization energy (CFSE) effect. On this basis, the high CFSE of the chromium(III) complex ($12Dq$) would raise ν(Cr–O) well above ν(Zn–O), since the zinc(II) complex has zero CFSE. The second feature is the oxidation state effect which would again yield $\nu(Cr–O) > \nu(Zn–O)$. However, these effects will be offset to some extent by the lower coordination number of the zinc(II) ion in $[Zn(AA)_2(H_2O)]$. Overall, it seems likely that ν(Cr–O) will exceed ν(Zn–O), favouring the assignment of the 592 cm^{-1} band to ν(Cr–O) rather than the 358 cm^{-1} band.

Although the assignment problem in metal acetylacetonates is not yet settled, some significant conclusions may be drawn from the many studies reported. Firstly, there is very nearly a band-for-band correspondence in the spectra of all metal acetylacetonates, at least so far as the more commonly encountered 1:2 and 1:3 species are concerned. In this connection it is worthwhile remembering that the manganese(II), iron(II), cobalt(II), nickel(II) and zinc(II) complexes definitely and the calcium(II) and chromium(II) complexes probably are not four-coordinate monomers but octahedral polymers in the solid state. They are therefore in a broad sense isostructural with the monomeric octahedral tris(acetylacetonates). The band-for-band correspondence among these complexes is almost certainly a result of this structural equivalence. The definitely square planar 2:1 species such as the complexes of copper(II), palladium(II) and platinum(II) do yield slight differences in band patterns which are attributable to their structural differences.

Bands 1 and 2 now seem firmly established as predominantly ν(C=O) and ν(C=C) respectively. Bands 3 and 5 are firmly established as CH_3 bending modes and band 8 as the CH_3 rocking mode. Bands 7, 10 and 11 are the in-plane and out-of-plane bending modes of the C–H bond at the γ-position on the results of all assignment methods. Band 4 may comprise some ν(C=O) but is otherwise predominantly $\delta(CH_3)$. Band 6 is chiefly ν(C=C) and band 9 is mainly $\delta(C{-}CH_3)$. Bands 12–18 may each contain some contribution from ν(M–O), but in the spectrum of $Fe(AA)_3$ band 18 is probably the purest in ν(M–O), followed by 15 and 16, the order of relative purity of the last two bands remaining a subject of controversy. Band 19 is probably a ring deformation mode.

It may be pointed out here that the shift of any of the more metal-sensitive bands may generally be used as a measure of the M–O force constant variation (neglecting mass effects) when a metal β-ketoenolate is substituted either at the metal ion or in the ligand, so that it is not essential in such studies to know which represents the purest ν(M–O) vibration. In practice, band 16 is usually more easily pinpointed in the spectrum in the sense that it lies on the low frequency side of a blank absorption region some 50–150 cm^{-1} wide.

C. METAL(III) β-KETOENOLATES

The spectra of the first transition series metal(III) acetylacetonates within the range 700–250 cm^{-1} are depicted in Fig. 5. The current situation regarding assignments within this range is portrayed in Table 4 [27]. The assignments are referred to the observed frequencies of $[Cr(AA)_3]$ and $[Fe(AA)_3]$ since these two chelates have been the subject of three independent assignment techniques (see previous section).

Theoretically, there are three IR-active M–O stretching modes (one of a_2 and two of e species) in a metal tris(acetylacetonate) of D_3 symmetry. The calculated frequencies [17] for $[Fe(AA)_3]$ are 446 (e), 290 (a_2) and 222 (e) cm^{-1}. The first two of these bands have been observed [17] at 433 and 298 cm^{-1} (438 and 305 cm^{-1} by Fleming and Thornton [27]). Failure to observe a band near 222 cm^{-1} has been ascribed [17] to its being overlaid by a ring deformation band at 202 cm^{-1}. Vibrational coupling complicates the spectrum of any transition metal acetylacetonate and it is generally agreed [17,18,21,24,28,29] that several bands below 700 cm^{-1} may represent ν(M–O) coupled with various ligand vibrations. In fact, reference to Table 4 shows that each of the seven bands listed has previously been assigned on the basis of at least one technique to a metal–ligand vibration.

TABLE 4

Summary of proposed assignment in IR spectra (750–250 cm^{-1}) of metal acetylacetonates $[\mathrm{M(AA)_3}]$[a]

Observation	Source	ν_{12}	ν_{13}	ν_{14}	ν_{15}	ν_{16}	ν_{17}	ν_{18}
Frequency range for $[\mathrm{M(AA)_3}]$[b]	Thornton [27]	666–697	655–661	561–666	543–643	438–472	410–440	289–388
Observed frequency, $[\mathrm{Cr(AA)_3}]$	Thornton [27]	682	661	614	598	463	419	359
Observed frequency, $[\mathrm{Fe(AA)_3}]$	Thornton [27]	668	655	561	552	438	415	305
O-labelled shift, $[\mathrm{Cr(AA)_3}]$[c]	Pinchas et al. [18]	11	3	n.o.	19	5	8	2[l]
M-labelled shift, $[\mathrm{Cr(AA)_3}]$[d]	Nakamoto et al. [21]	0.5	0	1.0	0.7	3.0	0	3.9
M-labelled shift, $[\mathrm{Fe(AA)_3}]$[e]	Nakamoto et al. [21]	0	0.5	0.5	0.2	1.5	0	5.0
$(\nu-\nu_0)$, $[\mathrm{Cr(AA)_3}]$[f]	Thornton [27]	16	1	52	50	23	6	42
Assignments								
Normal coordinate analysis[g]	Nakamoto et al. [24]	ν(M–O) + ring	ν(M–O) + δ(C–CH$_3$)	π?	π?	ν(M–O)	π?	ν(M–O) (n.o.)
Normal coordinate analysis	Mikami et al. [17]	ring	πCH$_3$CCO	ring	ring	ν(M–O) + ν(C–CH$_3$)	ring	ν(M–O)
^{18}O-labelling	Pinchas et al. [18]	ν(M–O)	π	n.o.	ν(M–O)	ν(M–O) + δ(C–CH$_3$)	δ(O–M–O)	(n.o.)
M labelling	Nakamoto et al. [21]	?	ν(M–O) (slight)	ν(M–O) (slight)	π (ring)	ν(M–O) + ν(C–CH$_3$)	π?	ν(M–O)
Other (ν(M–O) only)	See footnotes	ν(M–O)[h,i]	ν(M–O)[h,i]	ν(M–O)[h]	ν(M–O)[j]	ν(M–O)[k]		ν(M–O)[k]
M substitution	Thornton [27]			ν(M–O)	ν(M–O)	ν(M–O) (slight)		ν(M–O)

[a] All numerical data in cm^{-1}. Abbreviations: ν, stretching; δ, in-plane bending; π, out-of-plane bending; ring, ring deformation; n.o., not observed; slight, ligand vibration comprising small contribution from coupled ν(M–O). [b] Observed frequency range for M = Sc, V, Cr, Mn, Fe, Co, Ga. [c] $\nu(^{16}\mathrm{O})-\nu(^{18}\mathrm{O})$. [d] $\nu(^{50}\mathrm{Cr})-\nu(^{53}\mathrm{Cr})$. [e] $\nu(^{54}\mathrm{Fe})-\nu(^{57}\mathrm{Fe})$. [f] See text for significance of $(\nu-\nu_0)$. [g] Application of perturbation theory to normal coordinate analysis of $[\mathrm{Cu(AA)_2}]$. [h] Ref. 7. [i] Ref. 2. [j] Ref. 14. [k] Ref. 30. [l] Raman band shift [22].

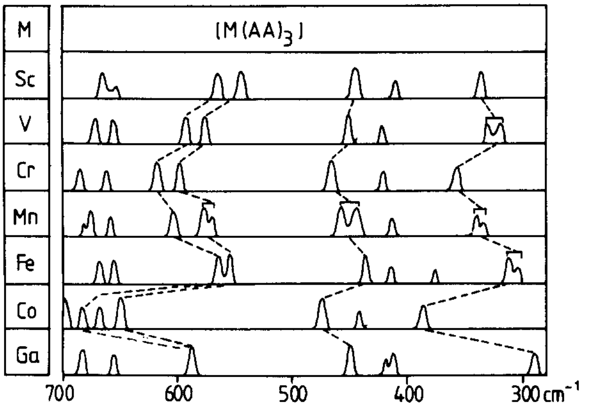


Fig. 5. IR spectra (700–250 cm^{-1}) of metal(III) acetylacetonates.

It seems unanimously agreed (Table 4) that ν_{16} comprises some contribution from ν(M—O). This band was found to be moderately shifted by both metal ion labelling and ^{18}O labelling. Some disagreement between the two labelling studies exists with respect to ν_{15} which was found to be considerably shifted by ^{18}O labelling but very little by metal ion labelling. The band found to be most shifted by metal ion labelling (ν_{18}) was not observed in the ^{18}O study while ν_{14} (moderately sensitive to metal ion labelling) was apparently not resolved from ν_{15} in the ^{18}O study. The combined results of the labelling studies suggest that ν_{14}, ν_{15}, ν_{16} and ν_{18} should be regarded as principal contenders for assignment to variously coupled ν(M—O) bands. Although the inclusion of ν_{15} may be questioned (since none of the normal coordinate analyses assigns this band to ν(M—O)) regard must be paid to the fact that normal coordinate treatments have not been very successful in solving assignment problems in metal chelates with this degree of complexity. Thus agreement between calculated and observed frequencies is often poor, and independent studies [17,24] of the same molecule have produced differing assignments. Furthermore, two independent theoretical treatments [17,24] have led to incorrect assignment of ν(C—O), subsequently corrected by ^{18}O labelling and a third normal coordinate treatment [20].

Hancock and Thornton [28] were the first to recognize that the frequencies of several bands paralleled the variation in CFSE through the transition series [31]. Later, some frequencies were revised by Fleming and Thornton [27] and these are used in this review. Almost invariably, the band exhibiting maximum sensitivity to ^{18}O labelling also exhibits maximum M sensitivity. The CFSEs of the complexes follow the sequence scandium < vanadium < chromium > manganese > iron < cobalt > gallium. The numerical frequency data and values of $(\nu - \nu_0)$ are recorded in Table 5.

TABLE 5

Frequencies and $(\nu-\nu_0)$ values (in parentheses) for metal(III) acetylacetonates (cm^{-1})[a]

Assignment −CFSE[b]	Sc(III) 0	V(III) 14.7*f*	Cr(III) 20.4*f*	Fe(III) 0	Co(III) 45.6*f*	Ga(III) 0
ν_{14}	565	590 (27)	614 (52)	561	666 (100)	584
ν_{15}	543	575 (29)	598 (50)	552	643 (84)	(584)
ν_{16}	442	449 (9)	463 (23)	438	472 (32)	449
ν_{17}	410	419 (7)	419 (6)	415	440 (25)	413
ν_{18}	334	328 (5)	359 (42)	305	388 (88)	289

[a] Frequencies for manganese(III) complex: 604, 574, 562, 459, 442, 412, 339, 330 cm^{-1}.
[b] Calculated as described in refs. 28 and 29 (*f* is a constant for complexes with a common ligand).

If the points for the d^0, high spin d^5 and d^{10} complexes in a plot of ν(M–O) against *d*-orbital population are joined, they yield an interpolation line representing the frequencies which would have been realized in the absence of crystal field stabilization. The differences between the observed and interpolated frequencies $(\nu-\nu_0)$ then give a measure of the effect of CFSE on the frequencies. In the metal(III) tris(acetylacetonates), ν_{14}, ν_{15} and ν_{18} have approximately equivalent $(\nu-\nu_0)$ values, suggesting that they are ν(M–O) bands of similar vibrational purity. Furthermore, these three bands correspond to those which have been shown [18,22] to exhibit maximum sensitivity to ^{18}O labelling and some sensitivity to metal ion labelling in the iron(III) and chromium(III) acetylacetonates.

Manganese(III) is unique among the ions investigated with respect to the expectation of Jahn–Teller distortion associated with its high spin d^4 configuration. Diffraction studies [32] and the complexity of the far-IR spectrum [33] have been cited as evidence of tetragonal structure. Hancock and Thornton [28] found that additional bands in the M–O stretching region occur in the spectra of $[Mn(AA)_3]$, $[Mn(DBM)_3]$ and $[Mn(BA)_3]$ but not in those of $[Mn(DPM)_3]$ and $[Mn(TFA)_3]$, suggesting either that these latter complexes are not distorted or that coincidence of the lower frequency band with some other band in the spectrum occurs. For the complexes in which doubling of the band does not occur, the relationship

$$\nu(\mathrm{M{-}O}) = 0.46(\mathrm{CFSE}) + \nu(\mathrm{Sc{-}O}) \tag{2}$$

(where CFSE is expressed in units of *f**) yields calculated M–O stretching

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**f* is the ligand parameter in the relationship $10Dq = fg$. Hence CFSE $= -(0.4n_{t2g} - 0.6n_{eg})fg$. Using the known occupancy of the t_{2g} and e_g orbitals (n_{t2g} and n_{eg} respectively) and the *g* values for the metal ions, the CFSEs can be calculated in units of *f*.

frequencies which exhibit a maximum deviation of 6 cm^{-1} from the observed frequencies, taking $f = 1.2$, the value for tris(acetylacetonates), as being representative of all the β-ketoenolates studied. The relationship (2) is particularly instructive with respect to the cobalt(III) complexes. Calculation of ν(Co–O) using the alternative CFSEs appropriate to the high and low spin d^6 configuration yields the values recorded in Table 6. Reasonable agreement between the observed and calculated values is obtained only for the low spin CFSEs. This is in accordance with the fact that ligands of very low field strength are necessary to produce high spin complexes of cobalt(III) whereas β-diketones have a field strength greater than that of water.

Hancock and Thornton's data [28] reveal that ν(C–O) exhibits a dependence on CFSE that is generally similar to that exhibited by ν(M–O) and the inverse of that shown by ν(C–C). Clearly the effect of the crystal field on the M–O bond (i.e. an electronic effect) is transmitted to the β-ketoenolate ring, causing a simultaneous increase in the M–O and C–O bond orders. This joint stabilization occurs at the expense of the C–C bond strength.

Calculation shows that the normal CFSE order pertaining to a series of complexes in which the d^4 and d^5 ions are high spin, $d^0 < d^1 < d^2 < d^3 > d^4 > d^5 < d^6 > d^{10}$, changes to the order $d^0 < d^1 < d^2 < d^3 < d^4 < d^5 < d^6 > d^{10}$ when these ions have low spin configuration. Therefore a comparison of the variation of ν(M–L) through a series of complexes in which the alternative spin states are realized provides an excellent test for the validity of a crystal field interpretation of the dependence of ν(M–L) on d-orbital population. Such a series is represented by the metal(III) acetylacetonates of the second transition series (Table 7).

Calculation of the pairing energies of the 4d ions is not possible in view of the absence of reliable values for the interelectronic repulsion parameters. In general, the pairing energies of second row ions are considerably smaller

TABLE 6

Calculated and observed Co–O stretching frequencies (cm^{-1}) for high spin and low spin d^6 configurations

Complex	ν(Co–O)		
	Observed	Calculated low spin	Calculated high spin
$Co(AA)_3$	466	464	443
$Co(BA)_3$	479	471	450
$Co(DBM)_3$	486	485	464
$Co(TFA)_3$	445	451	430
$Co(DPM)_3$	505	501	480

TABLE 7

Vibrational frequencies and CFSE data for second transition series metal(III) acetylacetonates

Configuration	Ion	CFSE	ν(M–O) (cm^{-1})	$(\nu-\nu_0)$ (cm^{-1})
d^0	Y(III)	0	536	0
d^3	Mo(III)	$12Dq$	599	52
d^5	Ru(III)	$20Dq-p^a$	621	67
d^6	Rh(III)	$24Dq-p^a$	650	92
d^{10}	In(III)	0	572	0

than those of the first row. Assuming this is so for the acetylacetonates, the CFSE order will be yttrium < molybdenum < ruthenium < rhodium > indium, which is also that observed for ν(M–O) and for $(\nu-\nu_0)$.

D. METAL(II) β-KETOENOLATES

The transition metal(II) β-ketoenolates are not as straightforward structurally as the metal(III) series. The complexes with M = Ca, Mn, Fe, Co, Ni, Cu and Zn are polymeric with general formula $[M(AA)_2]_n$ except for the square planar monomeric copper(II) complex [34]. Apart from the simple metal(II) acetylacetonates, there exists a series of general formula $Na[M(AA)_3]$ ($M \neq Cu$) [35]. Assignments for the complexes $[M(AA)_2]_n$ are simply made [36] by analogy with the metal(III) series yielding the principal ν(M–O) bands at 590 (Cr, $n > 1$), 535 (Ca, $n > 1$), 545 (Mn, $n = 3$), 558 (Fe, $n = 6$), 581 (Co, $n = 4$), 593 (Ni, $n = 3$), 615 (Cu, $n = 1$) and 565 cm^{-1} (Zn, $n = 3$). The relationship with d-orbital population is depicted in Fig. 6, exhibiting a parallel trend between ν(M–O) and CFSE except for the rather high value for ν(Cu–O). The complexes $Na[M(AA)_3]$ have the ν(M–O) values given in Table 8 [27]. The latter spectra are very simple (Fig. 7). Four bands occur within the range depicted. Similarly, four bands within this range have been observed [21] in the spectrum of the polynuclear octahedral nickel(II) acetylacetonate $[Ni(AA)_2]_3$. In the latter complex, labelling of the nickel(II) ion has led [21] to the assignment of bands at 570 and 421 cm^{-1} to coupled ν(Ni–O) modes. In $Na[Ni(AA)_3]$, Fleming and Thornton [27] observed bands at 569, 438 and 413 cm^{-1}. That at 569 cm^{-1} exhibits maximum M sensitivity in the CFSE order calcium ≈ manganese < iron < cobalt < nickel > zinc and is therefore assigned as the principal (least-coupled) ν(M–O) band.

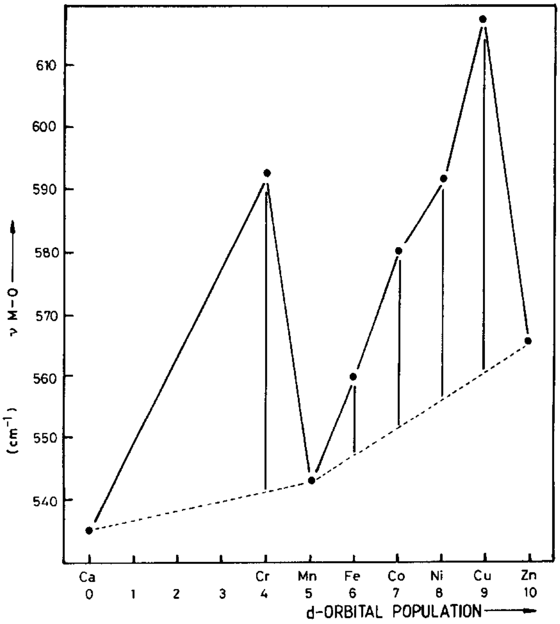


Fig. 6. Relationship between ν(M–O) and d-orbital population for $[M(AA)_2]_n$. The vertical lines represent the values of $(\nu-\nu_0)$.

TABLE 8

ν(M–O) and $(\nu-\nu_0)$ values (in parentheses) (cm^{-1}) for $Na[M(AA)_3]$

	Ca(II) $3d^0$	Mn(II) $3d^5$	Fe(II) $3d^6$	Co(II) $3d^7$	Ni(II) $3d^8$	Zn(II) $3d^{10}$
−CFSE:	0	0	4.00f	7.44f	10.68f	0
	539	548	554 (6)	561 (13)	569 (20)	549
	420	427	428 (0)	434 (5)	438 (7)	433
	400	404	401 (−4)	410 (4)	413 (5)	410

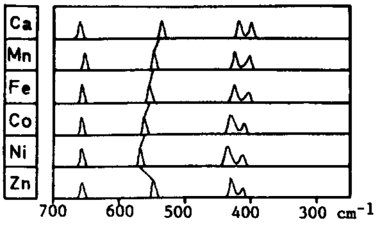


Fig. 7. IR spectra (700–250 cm^{-1}) of $Na[M(AA)_3]$.

The particularly high ν(Cu–O) frequency in [Cu(AA)$_2$] is, of course, due to the change of coordination number from six to four within the series [M(AA)$_2$]$_n$. This may alternatively be described as the result of extreme Jahn–Teller distortion in the copper(II) complex, with sufficient associated stabilization to reverse the CFSE order nickel > copper to nickel < copper. In order to test the validity of this argument, the metal–ligand stretching frequencies of some isostructural pairs of complexes of these ions were determined [36]. Since copper(II) is not found in regular octahedral environments, the examples chosen were necessarily restricted to square planar molecules. Crystal field theory predicts the stability order nickel > copper for square planar complexes since the orbital of highest energy, $d_{x^2-y^2}$, is necessarily occupied in copper(II) complexes but is unoccupied in diamagnetic nickel(II) complexes. Suitable examples for study are afforded by the complexes shown in Fig. 8 (M = Ni, Cu).

Assignment of ν(M–O) was made by comparison of the spectra with that of copper(II) acetylacetonate. A unique band near 600 cm^{-1} in the spectra of the complexes formulated in Figs. 8(b) and 8(c) is assigned to ν(M–N) by virtue of its absence from the spectra of the acetylacetonates (Table 9). In each case the expected frequency order nickel > copper is observed. It is of interest to note that the octahedral dihydrate of Fig. 8(a) (M = Ni) in which the nickel(II) ion is paramagnetic yields a value of ν(Ni–O) 28 cm^{-1} lower than the anhydrous complex. This decrease is undoubtedly due to the combined effects of the higher coordination number and spin state of the dihydrate.

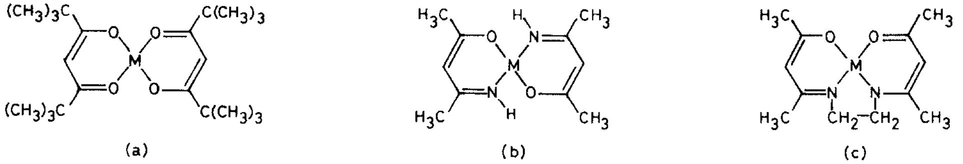


Fig. 8. Formulae of square planar complexes of nickel(II) and copper(II).

TABLE 9

Metal–ligand stretching frequencies (cm^{-1}) of isostructural (square planar) pairs of complexes of nickel(II) and copper(II)

Complex	Fig. 8(a)		Fig. 8(b)		Fig. 8(c)	
	M = Ni	M = Cu	M = Ni	M = Cu	M = Ni	M = Cu
ν(M–O)	664	646	661	620	617	611
	521	518	486	466	484	462
ν(M–N)			630	580	591	572

E. LIGAND SUBSTITUTION IN METAL β-KETOENOLATES

In this section we shall examine firstly the effect of substitution of the methyl groups in a metal acetylacetonate by other groups and secondly substitution of the γ-hydrogen in a metal acetylacetonate by other atoms or groups.

So far as substitution of the methyl groups is concerned, it is appropriate to examine the spectra of the β-ketoenolates of potassium(I), aluminium(III), copper(II), scandium(III), vanadium(III), chromium(III) and iron(III), representing species ranging from complexes with ionic M–O bonds to those with highly covalent M–O bonding. The frequency data are given in Table 10 [10].

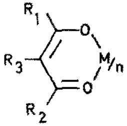
The potassium complexes are representative of those β-ketoenolates in which an electropositive metal ion confers ionic character on the M–O bond, a property which minimizes the mass effect, as is evident from the fact that the M–O stretching frequencies of the sodium(I), potassium(I) and rubidium(I) acetylacetonates are, respectively, 408, 410 and 409 cm^{-1}. By contrast with the potassium(I) complexes, those of aluminium(III) are typical of covalent non-transition metal β-ketoenolates in which ν(M–O) is strongly dependent on the mass of the coordinated ion, being 493, 446 and 434 cm^{-1} [37] for the aluminium(III), gallium(III) and indium(III) acetylacetonates respectively.

The data in Table 10 indicate that, irrespective of the nature of the coordinated ion, alteration of the ligand substituents has a similar effect on the characteristic frequencies. For each ion the combined electron-withdrawing effect of the two trifluoromethyl substituents in the hexafluoroacetylacetone complexes yields the lowest M–O and highest C–O frequencies of the ligands studied. In this respect the effect of hexafluoroacetylacetone relative to the other ligands studied is similar to that of the potassium(I) ion relative to the other ions studied, reflecting considerable ionic character in the M–O bond. The maximum effect is operative in potassium(I) hexafluoroacetylacetonate in which both the ion and substituent effects combined to produce the lowest M–O and highest C–O frequency among all the complexes examined.

The dipivaloylmethanates are directly opposed to the hexafluoroacetylacetonates in having two strongly electron-releasing tertiary butyl groups. These have the effect of yielding the highest M–O frequencies (aluminium excepted), intermediate C–O and the lowest C–C frequencies of the ligands studied. In transition metal dipivaloylmethanates the electron-releasing influence of the two tertiary butyl substituents would have the effect of severely restricting M–O π-bonding so that this ligand may be considered to yield the maximum M–O σ-bond strength which is accompanied by a significant lowering of the C–C bond order.

TABLE 10

M–O, C–O and C–C stretching frequencies (cm^{-1}) of metal β-ketoenolates[a]



Complex[b]	R_1	R_2	R_3	K(I) $n=1$	Al(III) $n=3$	Cu(II) $n=2$	Sc(III) $n=3$	V(III) $n=3$	Cr(III) $n=3$	Fe(III) $n=3$
ν(M–O)										
M(HFA)$_n$	CF_3	CF_3	H	362	424	427[c]		420[d]		421
M(TFA)$_n$	CF_3	CH_3	H	389	464	445	426	429	437	424
M(AA)$_n$	CH_3	CH_3	H	410	493	455	439	449	462	437
M(PA)$_n$	$C(CH_3)_3$	CH_3	H	475[e]		466				
M(DPM)$_n$	$C(CH_3)_3$	$C(CH_3)_3$	H	474	486	496	476	482	485	479
M(BA)$_n$	C_6H_5	CH_3	H	421	472[f]	459	446	451	465	446
M(DBM)$_n$	C_6H_5	C_6H_5	H	443	532[g]	465	460	462	465	455
M(3-MAA)$_n$	CH_3	CH_3	CH_3				450		468	446
M(3-EAA)$_n$	CH_3	CH_3	C_2H_5				452	460	476	446
ν(C–O)										
M(HFA)$_n$	CF_3	CF_3	H	1677	1655	1655[c]		1649[d]		1647
M(TFA)$_n$	CF_3	CH_3	H	1661	1632	1616	1624	1615	1615	1616
M(AA)$_n$	CH_3	CH_3	H	1619	1597	1582	1580	1571	1574	1575
M(PA)$_n$	$C(CH_3)_3$	CH_3	H	1620[e] 1601[e]		1576 1553				
M(DPM)$_n$	$C(CH_3)_3$	$C(CH_3)_3$	H	1592 1581	1582 1560	1571 1555	1561 1556	1563 1549	1566 1549	1563 1550
M(BA)$_n$	C_6H_5	CH_3	H	1571	1569	1562	1553	1547	1555	1551
M(DBM)$_n$	C_6H_5	C_6H_5	H	1569	1556	1549	1540	1530	1540	1533
M(3-MAA)$_n$	CH_3	CH_3	CH_3				1588		1577	1580
M(3-EAA)$_n$	CH_3	CH_3	C_2H_5				1578	1576	1581	1575

ν(C–C)										
M(HFA)$_n$	CF_3	CF_3	H	1555	1630	1618[c]		1612[d]		1623
M(TFA)$_n$	CF_3	CH_3	H	1555	1548	1536	1542	1533	1532	1531
M(AA)$_n$	CH_3	CH_3	H	1508	1535	1536	1529	1526	1522	1530
M(PA)$_n$	$C(CH_3)_3$	CH_3	H	1516[e]		1517				
M(DPM)$_n$	$C(CH_3)_3$	$C(CH_3)_3$	H	1496	1515	1504	1513	1508	1504	1510
M(BA)$_n$	C_6H_5	CH_3	H	1512	1523	1524	1513	1513	1524	1520
M(DBM)$_n$	C_6H_5	C_6H_5	H	1516	1534	1535	1529	1530	1526	1528
M(3-MAA)$_n$	CH_3	CH_3	CH_3				1530		1521	1538
M(3-EAA)$_n$	CH_3	CH_3	C_2H_5				1528	1558	1540	1538

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[a] Data for M(TFA)$_3$, M(AA)$_3$, M(DPM)$_3$ and M(DBM)$_3$ (M = Sc, V, Cr, Fe) from ref. 28. [b] Abbreviations: HFA, hexafluoroacetylacetonate; TFA, trifluoroacetylacetonate; AA, acetylacetonate; PA, pivaloylacetonate; DPM, dipivaloylmethanate; BA, benzoylacetonate; DBM, dibenzoylmethanate; 3-MAA, 3-methylacetylacetonate; 3-EAA, 3-ethylacetylacetonate. [c] Monohydrate. [d] Dihydrate. [e] Na(I) complex. [f] An additional strong band at 437 cm^{-1} may also be attributable to the Al–O stretching frequency. [g] An additional strong band at 453 cm^{-1} may also be attributable to the Al–O stretching frequency.

The transition from complexes of hexafluoroacetylacetone to those of dipivaloylmethane by incorporation of substituents which are progressively more electron-releasing is accompanied by an increase in ν(M–O) in the order hexafluoroacetylacetonates < trifluoroacetylacetonates < acetylacetonates < pivaloylacetonates < dipivaloylmethanates, while the C–O and C–C frequencies generally decrease in this order.

Recently, Swain and Lupton [38] have shown that a substituent effect (σ) may be expressed in the form

$$\sigma = fF + rR \tag{3}$$

where F and R are field (inductive) and resonance (mesomeric) parameters and f and r are coefficients which determine the relative weightings of the field and resonance effects appropriate to the system being examined. In Table 11 the F and R values for the substituents in each ligand are shown. We do not know the weighting factors appropriate to the β-ketoenolates but, except for ligands with phenyl substituents, F and R lie in the same order, with the qualification that R acquires a limiting value of −0.28 for the complexes of acetylacetone, pivaloylacetone and dipivaloylmethane. Clearly, over a wide range of the possible field and resonance contributions from 100% F, 0% R, to 0% F, 100% R the combined field and resonance effects will lie in the same order as either effect separately. Therefore the generally observed order of increasing M–O stretching frequencies given in the previous paragraph for complexes of the various ligands reflects the order of decreasing σ values (Table 11, neglecting compounds with phenyl substituents).

As pointed out by Nakamoto et al. [15] the presence of a phenyl substituent leads to a contribution to the resonance hybrid of the form shown in Fig. 9, representing a mesomeric interaction not possible with the

TABLE 11

Field and resonance contributions of substituents

Complex	R_1	R_2	$F_{R_1+R_2}$	$R_{R_1+R_2}$	f	r	$\sigma = fF + rR$	ν(M–O) $Cu(L)_2$ (cm^{-1})
$M(HFA)_n$	CF_3	CF_3	1.26	0.38	0.75	0.25	0.85	427
$M(TFA)_n$	CF_3	CH_3	0.58	0.05	0.75	0.25	0.45	445
$M(AA)_n$	CH_3	CH_3	−0.10	−0.28	0.75	0.25	−0.15	455
$M(BA)_n$	C_6H_5	CH_3	−0.15	−0.23	0.25	0.75	−0.16	459
$M(DBM)_n$	C_6H_5	C_6H_5	0.28	−0.18	0	1.00	−0.18	465
$M(PA)_n$	$C(CH_3)_3$	CH_3	−0.15	−0.28	0.75	0.25	−0.18	466
$M(DPM)_n$	$C(CH_3)_3$	$C(CH_3)_3$	−0.20	−0.28	0.75	0.25	−0.22	496

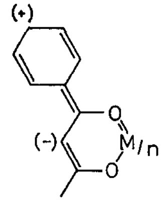

Fig. 9. Quinonoid form of a phenyl-substituted β-ketoenolate.

other substituents. In Table 11, values of σ calculated on the weightings 75% *F* and 25% *R* are given for ligands without phenyl substituents. Use of the same field and resonance contributions for complexes of benzoylacetone and dibenzoylmethane yields σ values which are inconsistent with the position of these complexes in the order of M—O stretching frequencies. In fact, the only possible mode of adjustment which would yield σ values consistent with the M—O frequencies of the phenyl-substituted complexes would be to increase considerably the weighting of the resonance parameter for these complexes. Calculation shows that a weighting of 25% *F* for benzoylacetonates and 0% *F* for dibenzoylmethanates (relative to 75% *F* for other ligands) would yield values of σ which are consistent with the order of M—O frequencies. That the mesomeric interaction represented by the form in Fig. 9 plays a prominent role in the phenyl-substituted complexes is consistent with the low C—O stretching frequencies of the dibenzoylmethanates.

The complexes of 3-methylacetylacetone and 3-ethylacetylacetone have M—O frequencies which are slightly higher than those of acetylacetone with a common ion. This is consistent with the additional field and resonance contributions imposed by the third alkyl substituent.

In 1971, Shephard and Thornton [39] made a detailed study of the IR spectra of α-thenoyltrifluoroacetonate (TTA) complexes (Fig. 10). Three species of complexes were represented: the anhydrous metal(II) species,

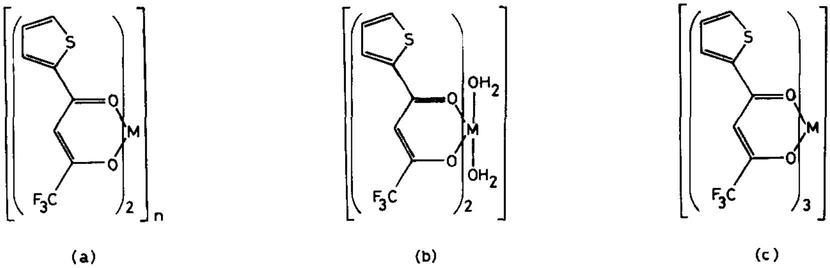

Fig. 10. Formulae of TTA complexes.

$[M(TTA)_2]_n$ (M = Ca, Mn, Co, Ni, Cu, Zn); metal(II) dihydrates, $[M(TTA)_2(H_2O)_2]$ (M = Mn, Fe, Co, Ni, Zn); and the metal(III) chelates, $[M(TTA)_3]$ (M = Sc, V, Cr, Mn, Fe, Ga). For each metal(II) complex, the spectra of the anhydrous and hydrated compounds were practically identical, suggesting that the anhydrous compounds have the polynuclear octahedral structure established for the corresponding acetylacetonates. Magnetic moment determinations reveal that the complexes of the $3d^4$–$3d^7$ ions all have a spin-free configuration. Four or five vibrational bands with frequencies less than 700 cm^{-1} were found to exhibit a frequency variation with *d*-orbital population which is consistent with the order of CFSEs and hence with their assignment as coupled metal–O stretching modes (Fig. 11). Of interest here are the very high $\nu(Cu{-}O)$ values in the copper(II) complexes which result from the transition from polynuclear octahedral structure for the nickel(II) and zinc(II) complexes to the square planar four-coordinate copper(II) complex. Furthermore, it will be seen from Fig. 11 that the spectrum of $[Mn(TTA)_3]$ exhibits doubling of many $\nu(Mn{-}O)$ bands in the range 700–250 cm^{-1}, which is the result of Jahn–Teller distortion in this molecule.

In conclusion, the effects of metal ion type, CFSE and ligand substituent on the frequencies may be summarized as follows.

(a) The effect of the metal ion type is associated with the degree of ionic character in the M–O bond. Ionic complexes have low $\nu(M{-}O)$ and high $\nu(C{-}O)$. Covalent complexes reverse this relationship. The effect is independent of the nature of the ligand substituents.

(b) The effect of CFSE (ipso facto only relevant to transition metal complexes) is associated with the ion configuration and magnitude of Dq. Large CFSEs produce high $\nu(M{-}O)$ and high $\nu(C{-}O)$. The effect is independent of the nature of the ligand substituents.

(c) The effect of the ligand substituent is associated with the field and resonance contributions of the substituents. Strongly electron-withdrawing substituents produce low $\nu(M{-}O)$ and high $\nu(C{-}O)$. Electron-releasing substituents reverse the relationship. The effect is independent of the nature of the coordinated ion.

So far as the effect of 3(γ)-substituents is concerned, apart from the remarks made above, we shall consider the effect of varying R in the series of β-ketoenolates depicted in Fig. 12. The frequency data for the region 700–250 cm^{-1} are given in Table 12.

The CFSEs of the metal(III) complexes follow the sequence scandium < vanadium < chromium > manganese > iron < cobalt > gallium. Reference to Table 12 shows that for each series of complexes of these ions with common R, the bands corresponding to ν_{14}, ν_{15} and ν_{18} in the unsubstituted

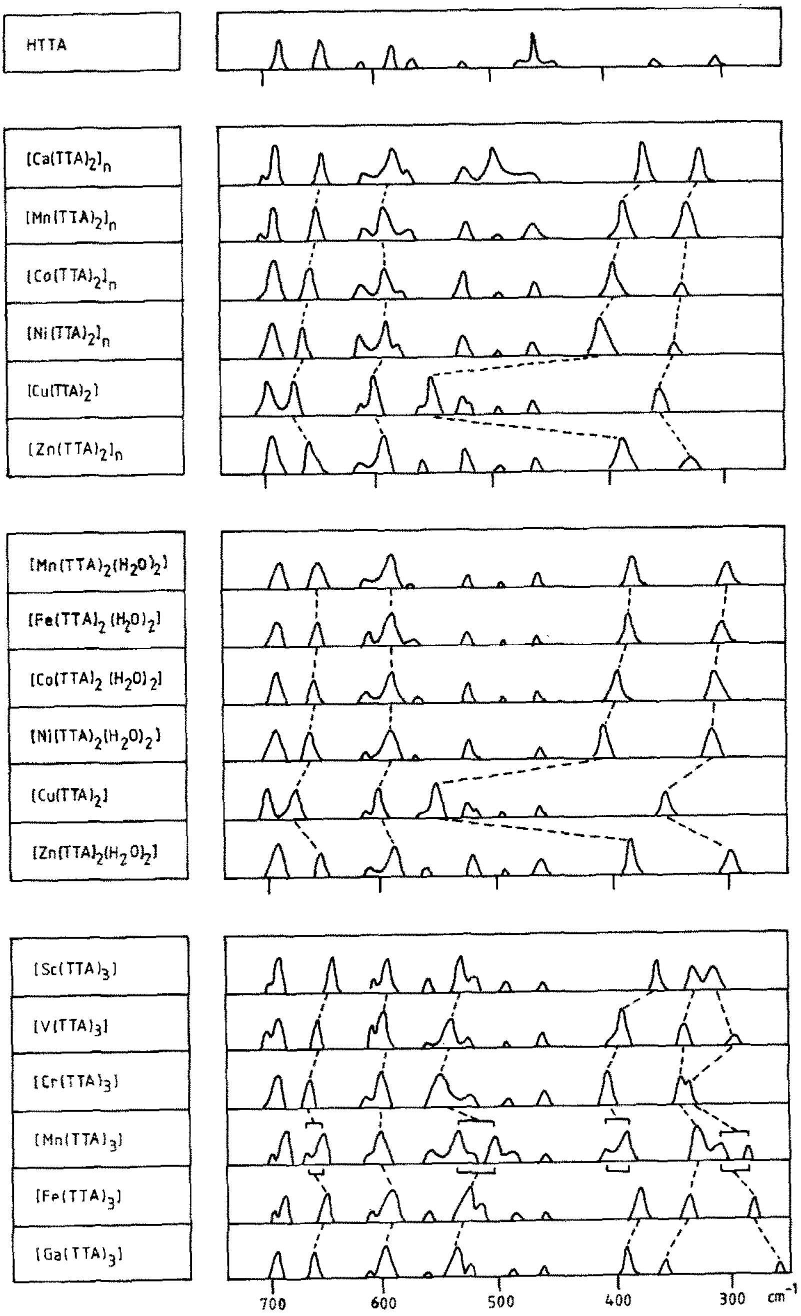

Fig. 11. IR spectra of thenoyltrifluoroacetone complexes, 700–250 cm^{-1}.

TABLE 12

CFSE and IR data (cm^{-1}) for complexes of 3-substituted 2,4-pentanediones[a]

Substituent R	Metal(III) complex $[ML_3]$					
	Sc(III) $3d^0$	V(III) $3d^2$	Cr(III) $3d^3$	Fe(III) $3d^5$	Co(III) $3d^6$	Ga(III) $3d^{10}$
−CFSE[b]:	0	14.7*f*	20.4*f*	0	45.6*f*	0
$R = NO_2$	621		655 (29)	629	678 (51)	620
($\sigma_p = +0.78$)	(621)		639 (20)	618	648 (30)	(620)
	533		530 (−3)		546 (12)	534
	464		470 (12)	454	480 (27)	450
	319		363 (45)	317	390 (72)	319
R = SCN			655	622	651	
($\sigma_p = +0.70$)			634	590	628	
			513	511	523	
			472	459	479	
			361	313	380	
R = CN[c]	617	637 (17)	649 (28)	624		628
($\sigma_p = +0.66$)	567	573 (6)	635 (68)	566		566
	515	539 (21)	551 (31)	523		527
	425	455 (24)	470 (36)	440		446
	321	327 (10)	361 (46)	311		311
R = I			641	583	652	
($\sigma_p = +0.28$)			611	568	640	
			466	454	472	
			417	408	442	
			359	317	389	
R = Br	564	586 (15)	625 (50)	582	670 (72)	600
($\sigma_p = +0.23$)	542	560 (5)	614 (52)	576	655 (60)	(600)
	457	465 (11)	473 (20)	450	481 (30)	457

	412	435 (20)	445 (28)	420	431 (8)	436
	338	337 (9)	359 (36)	314	370 (57)	308
$R = Cl$	566	596 (25)	622 (49)	578	653 (72)	593
$(\sigma_p = +0.23)$	544	582 (31)	602 (48)	561	653 (86)	(593)
	444	454 (10)	468 (23)	445	476 (32)	444
	410	420 (7)	425 (11)	416	438 (20)	426
	338	325 (−2)	361 (39)	313	381 (74)	286
$R = H^d$	565	590 (27)	614 (52)	561	666 (100)	584
$(\sigma_p = 0)$	543	575 (29)	598 (50)	552	643 (84)	(584)
	442	449 (9)	463 (23)	438	472 (32)	449
	410	419 (7)	419 (6)	415	440 (25)	413
	334	328 (5)	359 (42)	305	388 (88)	289
$R = C_6H_5{}^e$	593	617 (21)	636 (39)	601	676 (74)	604
$(\sigma^* = +0.60)$	588	604 (15)	620 (30)	591	651 (59)	594
	462	463 (6)	471 (16)	450	476 (24)	460
	429	440 (9)	443 (10)	436	439 (7)	418
	335	325 (−1)	354 (31)	315	367 (57)	292
$R = CH_2C_6H_5$	577	604 (25)	623 (43)	582	666 (81)	595
$(\sigma^* = +0.22)$	569	593 (23)	509 (38)	572	646 (69)	(595)
	459	463 (10)	473 (23)	445	481 (34)	454
	442	440 (5)	450 (18)	425	471 (40)	(454)
	339	336 (5)	378 (51)	319	394 (81)	290
$R = CH_3$	567	603 (32)	626 (51)	578	666 (85)	593
$(\sigma^* = 0)$	561	590 (26)	611 (46)	568	651 (78)	(593)
	454	458 (6)	471 (20)	449	480 (30)	453
	408	416 (7)	420 (10)	411	470 (59)	412
	343	331 (−1)	363 (36)	317	387 (75)	292
$R = C_2H_5$	563	600 (33)	621 (51)	574	666 (88)	593
$(\sigma^* = -0.10)$	560	585 (22)	608 (43)	568	649 (76)	(593)
	462	456 (−1)	472 (17)	451	480 (28)	454
	411	412 (−6)	439 (17)	429	470 (40)	432
	340	331 (0)	362 (35)	318	380 (67)	293

TABLE 12 (continued)

Substituent R	Metal(III) complex $[ML_3]$					
	Sc(III)	V(III)	Cr(III)	Fe(III)	Co(III)	Ga(III)
	$3d^0$	$3d^2$	$3d^3$	$3d^5$	$3d^6$	$3d^{10}$
−CFSE[b]:	0	14.7*f*	20.4*f*	0	45.6*f*	0
R = *n*-C_3H_7	559	600 (30)	619 (46)	582	656 (72)	590
($\sigma^* = -0.12$)	554	590 (27)	606 (38)	577	652 (23)	(590)
	455	466 (13)	475 (23)	450	480 (29)	455
	409	410 (1)	418 (8)	410	411 (1)	411
	350	332 (−6)	365 (33)	320	380 (65)	295
R = *n*-C_4H_9	561	603 (33)	630 (55)	584	660 (74)	593
($\sigma^* = -0.13$)	552	585 (24)	609 (44)	574	650 (72)	(593)
	461	461 (3)	474 (18)	453	480 (25)	461
	403	404 (1)	405 (2)	403	423 (23)	403
	344	333 (0)	363 (35)	318	380 (67)	295

Substituent R	Metal(II) complex $[ML_3]$ Na$[ML_3]$					
	Ca(II)	Mn(II)	Fe(II)	Co(II)	Ni(II)	Zn(II)
	$3d^0$	$3d^5$	$3d^6$	$3d^7$	$3d^8$	$3d^{10}$
−CFSE[b]:	0	0	4*f*	7.4*f*	10.7*f*	0
R = CN	613	615	618 (2)	621 (5)	625 (8)	618
($\sigma_p = +0.66$)	546	560	561 (0)	565 (3)	570 (7)	565
	520	527	535 (7)	535 (5)	548 (17)	534
	397	408	410 (1)	417 (7)	417 (6)	414
R = H	539,537	548,543	554 (6) 558	561 (13) 561	569 (20) 568	549, 547
($\sigma_p = 0$)	420,415	427,412	428 (0) 415	434 (5) 422	438 (7) 426	433, 415
	400,400	404,401	401 (−4) —	410 (4) 407	413 (5) 408	410, 407

R = C_6H_5	580	586	589 (3)	593 (5)	598 (10)	568
($\sigma^* = +0.60$)	523	530	532 (2)	533 (3)	542 (10	532
	430	450	452 (0)	452 (1)	452 (1)	453
	406	408	420 (9)	423 (8)	425 (1)	425
R = $CH_2H_6H_5$	551	565	578 (11)	585 (16)	593 (23)	574
($\sigma^* = +0.22$)	448	454	452 (−2)	456 (1)	456 (1)	457
R = CH_3	551	565	578 (11)	585 (16)	593 (23)	574
($\sigma^* = 0$)	458	467	461 (−5)	463 (−2)	465 (1)	463
	423	425	427 (2)	428 (3)	430 (3)	427
R = C_2H_5	559	567	573 (6)	579 (12)	587 (18)	569
($\sigma^* = -0.10$)	443	463	465 (1)	469 (4)	469 (3)	468
	419	419	420 (1)	421 (2)	424 (6)	418
R = n-C_3H_7	559	564	572 (7)	579 (13)	585 (18)	569
($\sigma^* = -0.12$)	453	464	467 (1)	571 (3)	571 (1)	475
	425	423	425 (2)	431 (8)	434 (11)	423
R = n-C_4H_9	552	567	572 (5)	580 (12)	588 (19)	569
($\sigma^* = -0.13$)	456	464	470 (5)	470 (5)	472 (6)	467
	425	424	424 (1)	428 (3)	428 (2)	427

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[a] Frequencies of metal(III) complexes are given in the order ν_{14}, ν_{15}, ν_{16}, ν_{17}, ν_{18}. Figures in parentheses represent ($\nu - \nu_0$) [28]. [b] Calculated as described in refs. 28 and 29 (f is a constant for each series of complexes with a common ligand substituent). [c] Frequencies for manganese(III) complex: 632 (ν_{14}); 568, 535 (ν_{15}); 484, 462 (ν_{16}) 442 (ν_{17}); 336 (ν_{18}) cm^{-1}. [d] Frequencies for manganese(III) complex: 604; 574, 562, 459, 442, 412, 339, 330 cm^{-1}. [e] Frequencies for manganese(III) complex: 623, 604, 598, 470, 437, 359, 345, 340 cm^{-1}.

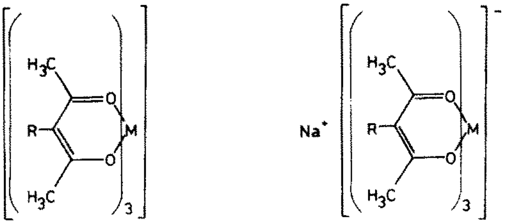

Fig. 12. Formulae of γ-substituted metal(III) and metal(II) acetylacetonates.

acetylacetonates (R = H) are substantially M sensitive and that the shifts are generally in the order of calculated CFSEs. The bands corresponding to ν_{16} and ν_{17} also generally shift in this order but their shifts are substantially smaller. Table 12 also lists the values of $(\nu - \nu_0)$ which are found to be similar in magnitude for bands ν_{14}, ν_{15} and ν_{18}, the most M-sensitive bands and also those bands which are most sensitive to ^{18}O labelling [18]. The M sensitivity of these bands and also the corresponding bands in the metal(II) complexes Na[M(β-dik)$_3$] are shown in Fig. 13.

In previous work [40,41] on the effects of ligand substitution on the IR spectra of transition metal complexes, it has generally been found that the band which is most sensitive to isotopic labelling of the ligand donor atom and to metal ion substitution, is also significantly shifted by substitution in the ligand molecule. This R sensitivity of metal–ligand vibrations is understandable if a mechanism exists whereby the electronic effects of the substituents may be transmitted to the metal–ligand bonds and if the substituents span a sufficiently wide range of electron-releasing and electron-withdrawing species. The substituents presently under consideration may be classified as those which are expected to affect the M–O bonds largely by their inductive effects (R = alkyl group) and those which are expected to exert a significant resonance effect (R = NO_2, SCN, CN, halogen, phenyl). As an index of the relative inductive effects of the alkyl groups, Taft's [42] parameter σ^* is appropriate while σ_p may be considered as a suitable measure [42,43] of combined inductive and resonance effects. (A recent analysis [38] of substituent parameters shows that σ_p comprises an approximately equal weighting of resonance and inductive effects.)

The frequency data in Table 12 indicate that ν_{14} and ν_{15} exhibit the maximum R sensitivity. These two bands shift towards higher frequencies with increased electron-withdrawing capacity of the substituents. The direction of shift is significant since transition metal β-ketoenolates are capable of both donor (metal–ligand) and acceptor (ligand–metal) π-interaction [44]. The observed shifts are consistent with facilitation of metal–ligand π-bonding by electron-withdrawing substituents.

That electron-withdrawing substituents facilitate metal–ligand π-bonding

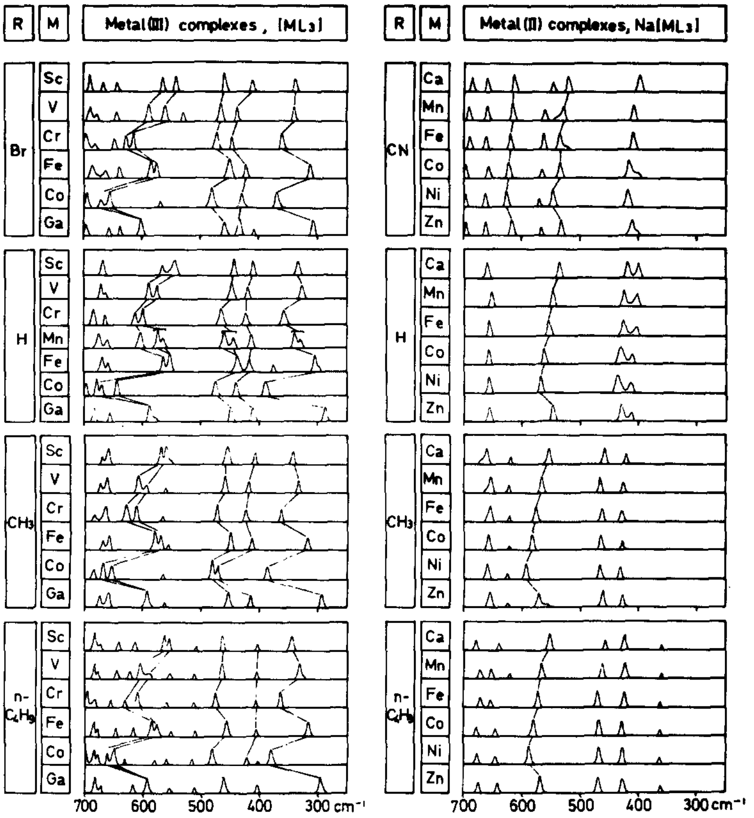

Fig. 13. M sensitivity of bands in IR spectra of 3-substituted 2,4-pentanedione complexes. Linked bands in metal(III) complex spectra are ν_{14}, ν_{15}, ν_{16}, ν_{17} and ν_{18}. Linked bands in metal(II) complex spectra are those with maximum M sensitivity.

cannot apply to the complexes of scandium(III) which have no 3*d* electrons available for entering into such bonding. It is therefore of interest to note that only in the scandium(III) complexes is there any appreciable R sensitivity in ν_{18}. Furthermore, electron-withdrawing substituents shift ν_{18} towards lower frequency as would be expected if the major effect of such substituents is to reduce the donor capacity of the oxygen atoms for the scandium(III) ion.

It has been suggested [44] that π bonding plays a smaller role in the metal(II) acetylacetonates than in the metal(III) derivatives. Under these circumstances there will be less electron delocalization in the chelate rings of the metal(II) complexes and the conditions will be less favourable for vibrational coupling. The fact that the band within the range 500–600 cm^{-1} in the spectra of the complexes Na[ML$_3$] exhibits a considerably greater M and R sensitivity than any other band is consistent with a smaller degree of vibrational coupling in the metal(II) chelates. In these complexes this band is firmly assigned as the principal ν(M–O) band.

F. ADDUCTS OF TRANSITION METAL(II) β-KETOENOLATES

Initially we shall discuss the IR spectra of nickel(II) acetylacetonate with anilines and pyridines as adducting agents [45] since these adducts have received most attention in the literature. The formulae of the adducts are depicted in Fig. 14.

While it is known [46–48] that trimeric anhydrous nickel(II) acetylacetonate reacts with water and nitrogenous bases to form monomeric octahedral bis adducts, displacement of water from the dihydrate by an amine provides a more convenient synthesis. The higher ligand field strength of the amines causes a general colour change from green to blue. A trans octahedral configuration has been established for several base adducts by both X-ray structural [47,49] and spectrophotometric [47] methods, cis complexes being confined largely to chelating bidentate ligands such as 2,2′-bipyridine. The internal similarity of the IR spectra of the adducts within each class of amine suggests that they all have a trans configuration.

That the Ni–N bonding is weak is indicated by the non-formation of adducts with anilines bearing strongly electron-withdrawing substituents (substituted pyridines are somewhat more versatile) and by the absence of any band above 200 cm^{-1} which may be ascribed to ν(Ni–N). Since even the comparatively strongly bound pyridine in $[NiCl_2py_2]$ yields [50] a frequency of 239 cm^{-1} for ν(Ni–N), this vibration was considered to lie almost certainly below 200 cm^{-1} in the adducts. Despite the weak bonding of the amines, bis adducts of nickel(II) are always obtained. By contrast,

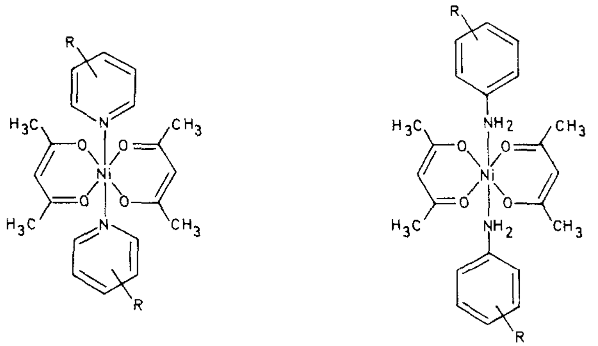

Fig. 14. Formulae of substituted pyridine (left) and substituted aniline (right) adducts of nickel(II) acetylacetonate.

five-coordination is common for adducts of zinc(II) acetylacetonate [51]. This difference is undoubtedly associated with the fact that the first transition series metal(II) ions acquire a maximum CFSE for octahedrally coordinated nickel(II) whereas the zero CFSE of zinc(II) implies that no one stereochemistry is favoured relative to another on the basis of CF effects.

The assignment of ν(Ni–O) in the IR spectrum of nickel(II) acetylacetonate has been subject to some confusion. On the basis of Nakamoto and Martell's normal coordinate treatment [12] of copper(II) acetylacetonate and its subsequent extension [52] to the corresponding nickel(II) complex, a band at 452 cm^{-1} was assigned to ν(Ni–O). This assignment seems doubtful since the theoretical treatment assumed square planar stereochemistry while subsequent work [53] showed that the complex has trinuclear octahedral structure. Furthermore, the composition of the compound was not specified in earlier reports. Thus one report [54] lists the higher frequency ν(Ni–O) band at 569 cm^{-1}, another [13] as a doublet of mean frequency 592 cm^{-1}. Thornton and coworkers [45] have found that the analytically pure dihydrate absorbs at 570 cm^{-1} and the anhydrous complex at 593 cm^{-1}. It seems clear that the earlier reports refer to these alternative species. The most convincing assignments arise from ^{18}O-labelling studies [18] which show that two specific bands in the far-IR region are appreciably shifted by ^{18}O labelling and are therefore likely to represent reasonably pure M–O stretching modes*. When a comparison of the spectra of the adducts with those of the acetylacetonates of nickel(II) and other metal ions is made, these two bands are readily identified. Furthermore, only these two bands are sensitive to substitution in the amine adducts in the 600–200 cm^{-1} region.

The gross effect of amine adduct formation is to lower the value of ν(Ni–O) in the parent anhydrous acetylacetonate. The decrease is evidently associated largely with change of composition rather than of coordination number since the anhydrous acetylacetonate, the dihydrate and the bis(amine) adducts all have octahedral structure.

That the combined shift of both Ni–O stretching frequencies is greater on amine adduct formation than on hydration may be attributed to the higher ligand field strengths of amines. A further increase in ligand field strength is expected to accompany the introduction of electron-releasing substituents in the coordinated amines. This would arise from enhancement of the donor capacity of the amino group and hence increased metal–amine interaction (thus anilines with strongly electron-withdrawing groups, e.g. NO_2, fail to form adducts). As an index of the electronic effects of the substituents, the Hammett substituent parameter (σ) may be employed. This represents [43]

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*One ν(Ni–O) and one ν(Ni–OH_2) band is required for the D_{4h} symmetry of *trans*-[Ni(AA)$_2$(H_2O)$_2$]. Hence at least one of the two ν(Ni–O) bands in the spectrum is a ligand mode coupled with ν(Ni–O).

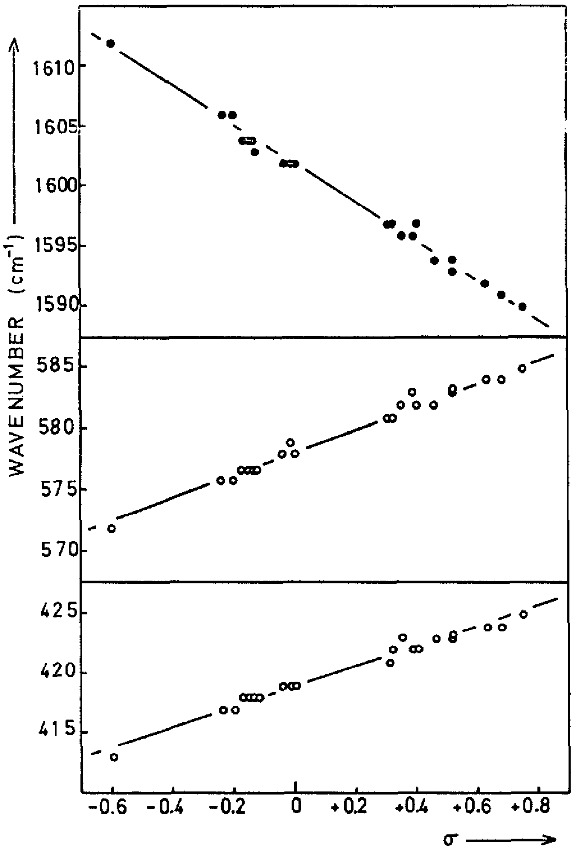


Fig. 15. Relationship between ν(Ni–O) (open circles) and ν(C–O) (solid circles) and Hammett substituent parameter (σ) for substituted pyridine adducts of nickel(II) acetylacetonate.

the resultant of their field and resonance contributions. These have been shown [55] to apply with satisfactory precision to pyridine substituents also. The IR spectra show (Fig. 15) that increased metal–amine interaction occurs at the expense of the Ni–O bonding since amines with electron-releasing substituents shift ν(Ni–O) to lower frequencies. This is not an obvious result of introducing electron-releasing substituents because if the electronic effect were transmitted to the Ni–O bonds by substituent-aided metal–ligand π-bonding, an increase in ν(Ni–O) would be expected. The latter mechanism is apparently not significant in determining the Ni–O bonding.

A secondary effect of varying the amine substituents is the increase in ν(C–O) accompanying the introduction of electron-releasing pyridine substituents. The correlation is shown in Fig. 15. The N–H stretching frequencies of the aniline adducts are sharply defined in the spectra but the correlation with σ is less decisive than that exhibited by ν(Ni–O). This is probably because proximity of the substituents to the amino group causes the mass effect on ν(N–H) to assume importance. A trend to higher frequencies for electron-releasing substituents suggests that the N–H bonds are stabilized by such substituents.

The effect of amine substitution on ν(Ni–O) and ν(C–O) is the precise opposite of the effect [10] of direct substitution in the β-ketoenolate ring (Section E). The difference is evidently due to the fact that the shift in ν(Ni–O) resulting from electron-releasing amine substituents is an indirect result of increased metal–amine interaction whereas the effect of ring substitution does not require to be transmitted through the metal ion.

In the work described above, the IR facilities were restricted to a low frequency limit of 250 cm^{-1}; ν(Ni–N) was not observed. Subsequently [56], upgraded facilities enabled the spectra of the adducts depicted in Fig. 16 to be extended from 250 to 150 cm^{-1} where ν(Ni–N) is expected to occur. These spectra are interesting for several reasons. Firstly, deuteration of pyridine enabled unambiguous identification of the ν(Ni–N) and pyridine ligand vibrations to be made. Secondly, substitution of nickel(II) by cobalt(II) and zinc(II) was used to corroborate the assignments based on the deuteration study. Thirdly, the effects of varying the pyridine substituents enabled the hypothesis [45] that electron-withdrawing groups will shift ν(Ni–O) and ν(Ni–N) in opposite directions to be tested. Finally, assignments resulting from a metal ion labelling study [21] of the pyridine complex (Fig. 16, R = H) could be examined in the light of these results.

The far-IR spectra of the pyridine and pyridine-d_5 adducts of cobalt(II), nickel(II) and zinc(II) bis(acetylacetonate) complexes are shown in Fig. 17. The zinc(II) complex is uniquely five-coordinate and probably has square pyramidal structure by analogy [26] with [Zn(AA)$_2$(H$_2$O)]. In the following discussion, bands shifted by metal ion labelling are termed ^{i}M-sensitive bands; those affected by deuteration of the pyridine ring are referred to as *d*-

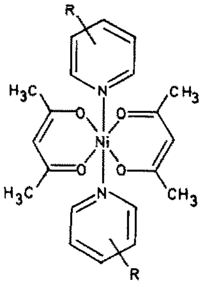


Fig. 16. Formula of substituted pyridine adducts of nickel(II) acetylacetonate.

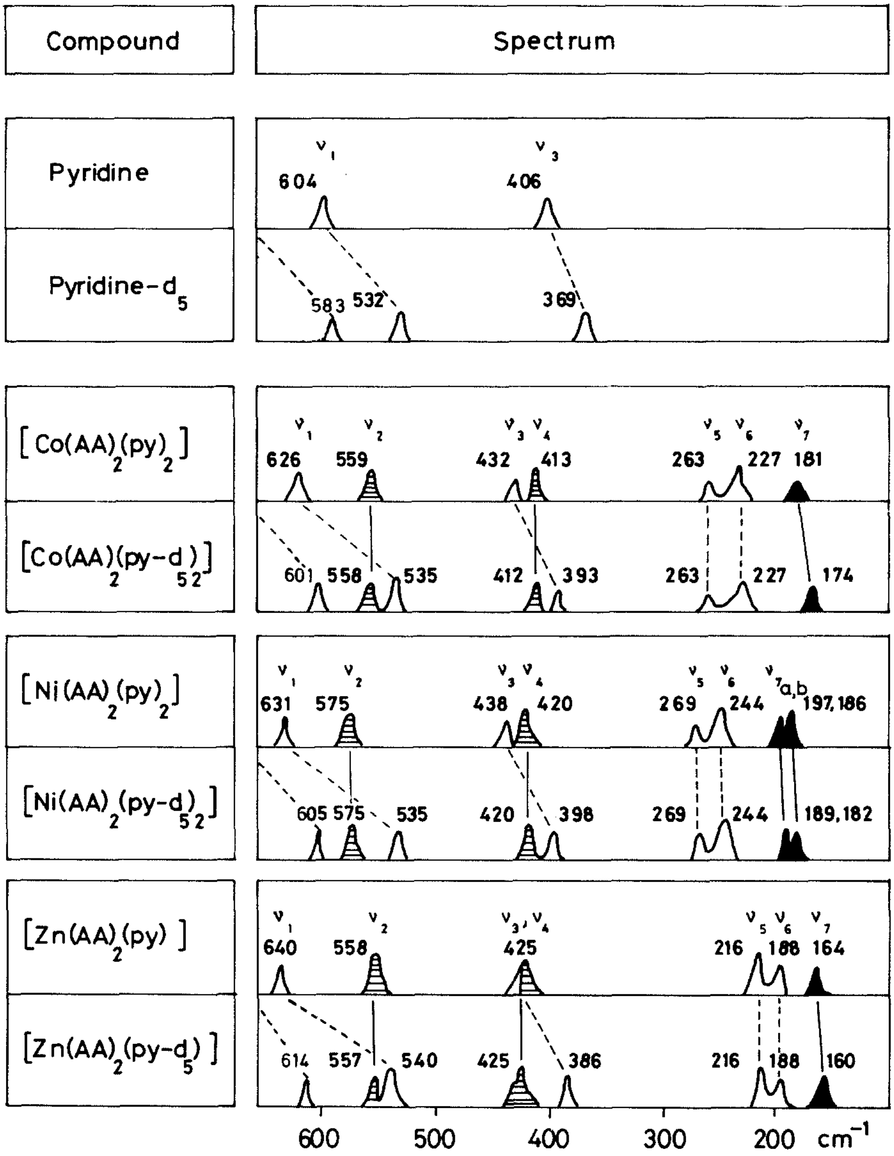


Fig. 17. IR spectra (650–150) cm^{-1} of pyridine and pyridine-d_5 adducts of cobalt(II), nickel(II) and zinc(II) bis(acetylacetonates). ν_1 and ν_3 are pyridine bands; ν_2 and ν_4 (shaded) are coupled ν(M–O) bands; ν_5 and ν_6 are pure ν(M–O) bands; ν_7 (solid) is the ν(M–N) band.

sensitive bands and those which move on varying the pyridine substituents are termed R-sensitive bands.

The ^{i}M, M and *d* sensitivities of the bands in the spectrum of [Ni(AA)$_2$(py)$_2$] are compared in Table 13. On the basis of the results of normal

TABLE 13

Frequencies (cm^{-1}) of far-IR bands in [Ni(AA)$_2$(py)$_2$] and their ^{i}M, *d* and M sensitivities (cm^{-1}) [56]

Band no.	Frequency	^{i}M sensitivity [21][a]	*d* Sensitivity[b]	M sensitivity[c]		Earlier assignment [21]	Revised assignment [56]
				Co	Zn		
ν_1	631	0.5	96	5	−9	$\pi((CH_3)CCO)$	ν(py)[d]
ν_2	575	0.8	0	16	17	ν(Ni–O) + ring[e]	Coupled ν(Ni–O)
ν_3	438	0.8	40	6	13	ν(Ni–O) + ν(C–CH_3)	ν(py)[f]
ν_4	420	0.4	0	7	−5	Ring[g]	Coupled ν(Ni–O)
ν_5	269	5.4	0	6	53	ν(Ni–O)	ν(Ni–O)
ν_6	244	3.8	0	17	56	ν(Ni–N)	ν(Ni–O)
ν_{7a}	197[h]	n.o.[i]	8	11[j]	28[j]	n.o.[i]	ν(Ni–N)
ν_{7b}	186	n.r.[k]	4	11[j]	28[j]	Ring	ν(Ni–N)

[a] ^{i}M sensitivity = frequency for [^{58}Ni (AA)$_2$(py)$_2$] − frequency for [^{62}Ni(AA)$_2$(py)$_2$]. [b] *d* sensitivity = frequency for [Ni(AA)$_2$(py)$_2$] − frequency for [Ni(AA)$_2$(py-d_5)$_2$]. [c] M sensitivity(Co) = frequency for [Ni(AA)$_2$(py)$_2$] − frequency for [Co(AA)$_2$(py)$_2$]. M-sensitivity (Zn) = frequency for [Ni(AA)$_2$(py)$_2$] − frequency for [Zn(AA)$_2$(py)]. [d] A_1 mode, δ(ring) [57]. [e] Independently assigned to ν(Ni–O) [45]. [f] B_2 mode, γ(ring) [58]. [g] Independently assigned to ν(Ni–O) [45]. [h] Shoulder. [i] n.o., shoulder not observed [21]. [j] ν(Ni–N) taken as mean of 197 and 186 cm^{-1} bands. [k] n.r., shift not reported [21].

coordinate analyses of metal acetylacetonates and in view of its small ^{i}M sensitivity, ν_1 has been assigned [21] to the π[(CH$_3$)CCO] vibration. This assignment may be discounted by its high *d*-sensitivity ($\Delta\nu = 96$ cm^{-1}) which is similar in magnitude to that exhibited (Fig. 17) by the 604 cm^{-1} ligand band in pyridine ($\Delta\nu = 72$ cm^{-1}) and by the 635 cm^{-1} band [57] in [Ni(py)$_2$Cl$_2$] ($\Delta\nu = 99$ cm^{-1}). Under these circumstances, ν_1 is firmly assigned to the pyridine vibration. ν_2 has a significantly greater ^{i}M sensitivity than ν_1. This has led [21] to its assignment to a coupled ν(Ni–O) band. Its R sensitivity has also been cited [45] as support for this assignment. Reference to Fig. 17 shows that ν_2 is significantly M sensitive and completely unaffected by pyridine deuteration. The combined evidence supports its assignment to a ν(Ni–O) band.

That ν_3 has an ^{i}M sensitivity comparable with ν_2 has led [21] to its assignment as a second coupled ν(Ni–O) band. This assignment is discounted by the spectra in Fig. 17 since the substantial *d* sensitivity of ν_3 ($\Delta\nu = 40$ cm^{-1}) is similar to the *d* sensitivity ($\Delta\nu = 37$ cm^{-1}) of the 406 cm^{-1} ligand band in the spectrum of pyridine, and its position (438 cm^{-1}) is practically identical with that [57] of the pyridine vibration (440 cm^{-1}) in [Ni(py)$_2$Cl$_2$]. Hence ν_3 is firmly assigned as the pyridine γ-ring vibration of lowest frequency.

The weak ^{i}M sensitivity of ν_4 has led [21] to its assignment to an (unspecified) chelate ring vibration. It has also been assigned [45] to ν(Ni–O) on the grounds of its R sensitivity and the fact that its position (420 cm^{-1}) is close to that of a strong band at 429 cm^{-1}, assigned to ν(Ni–O) in the spectrum of [Ni(AA)$_2$(H$_2$O)$_2$]. The observation [56] that the band is moderately M sensitive but completely insensitive to pyridine deuteration is consistent with its assignment to ν(Ni–O).

Although ^{18}O labelling has not been applied to the compound [Ni(AA)$_2$(py)$_2$], this technique has been used [18] to assign ν(M–O) in certain simple metal acetylacetonates such as [Cr(AA)$_3$] (Section C). In these compounds, the significant ^{18}O sensitivity of bands near 590 and 420 cm^{-1} has led to their assignment to ν(M–O). That the positions of these bands are very similar to those of ν_2 and ν_4 in the spectrum of [Ni(AA)$_2$(py)$_2$] supports the assignment of these bands to ν(Ni–O). However, these bands are unlikely to originate in pure (uncoupled) ν(Ni–O) modes because of their small ^{i}M, M and R sensitivities relative to ν_5 and ν_6 (see below).

That ν_5 (at 269 cm^{-1}) is the most strongly ^{i}M-sensitive band in the spectrum of [Ni(AA)$_2$(py)$_2$] has led [21] to its assignment as a pure ν(Ni–O) band. This assignment is supported by its substantial M and R sensitivity and the complete absence of *d* sensitivity. Furthermore, the spectrum of [Ni(AA)$_2$(H$_2$O)$_2$] exhibits a band at 281 cm^{-1} which undoubtedly has the same origin and excludes the possibility that ν_5 is associated with coordinated pyridine. Entirely similar observations pertain to ν_6 (at 244 cm^{-1}). Its earlier assignment [21] to ν(Ni–N) on the grounds of its substantial ^{i}M sensitivity is definitely discounted by complete absence of *d* sensitivity and the occurrence of a corresponding band at 222 cm^{-1} in the spectrum of $[Ni(AA)_2(H_2O)_2]$. All the available evidence suggests that ν_6 is a second pure ν(Ni–O) band.

Below 200 cm^{-1}, the spectrum of $[Ni(AA)_2(py)_2]$ comprises a shoulder at 197 cm^{-1} (ν_{7_a}) and a peak at 186 cm^{-1} (ν_{7_b}). These are the most strongly M-sensitive bands in the spectrum and are the only bands below 400 cm^{-1} to exhibit any *d* sensitivity. Furthermore, these bands shift on varying the pyridine substituent, R, in the opposite direction to ν(Ni–O) (Fig. 18) and they occur in a region free from absorption in the spectrum of $[Ni(AA)_2(H_2O)_2]$. All these observations support their assignment to ν(Ni–N) modes and an earlier assignment [21] to a chelate ring mode is definitely discounted.

It has been shown [50] that metal–ligand vibrations are in the sequence cobalt < nickel > zinc for a series of octahedral complexes comprising these metal(II) ions bound within the same ligand system. In the pyridine adducts depicted in Fig. 16, the zinc(II) complex is uniquely five-coordinate. Relative to the nickel(II) complex, the lower coordination number of zinc(II) will serve to raise the frequencies of the Zn–ligand vibrations while the zero CFSE of zinc(II) will serve to lower the Zn–ligand frequencies. Thus the observed order of metal–ligand frequencies may be cobalt < nickel > zinc or cobalt < nickel < zinc depending on whether the position of zinc(II) is determined primarily by coordination number or CFSE effects. Figure 17 shows that the sequence cobalt < nickel > zinc obtains for the principal ν(M–O) and ν(M–N) bands. Hence the CFSE effect overrides the coordination number effect in determining the Zn–ligand frequencies.

Figure 18 illustrates the spectra of variously substituted pyridine adducts of nickel(II) acetylacetonate. It had previously been shown [45] that ν_2 and ν_4 (coupled ν(Ni–O) bands) are shifted to higher frequency by electron-withdrawing substituents. Later work [56] confirmed this trend for the pure ν(Ni–O) band, ν_5, and also probably for ν_6, although the appearance of shoulders on ν_6 in the spectra of complexes with electron-releasing substituents introduced difficulties in determining precise frequencies in this region.

So far as the R sensitivity of ν(Ni–N) is concerned, it was found that electron-withdrawing substituents caused a substantial shift of ν_7 towards lower frequency, i.e. the opposite trend shown by ν(Ni–O), thus confirming an earlier prediction [45] that the electronic effects of pyridine substituents would cause ν(Ni–O) and ν(Ni–N) to shift in opposite directions. The effect

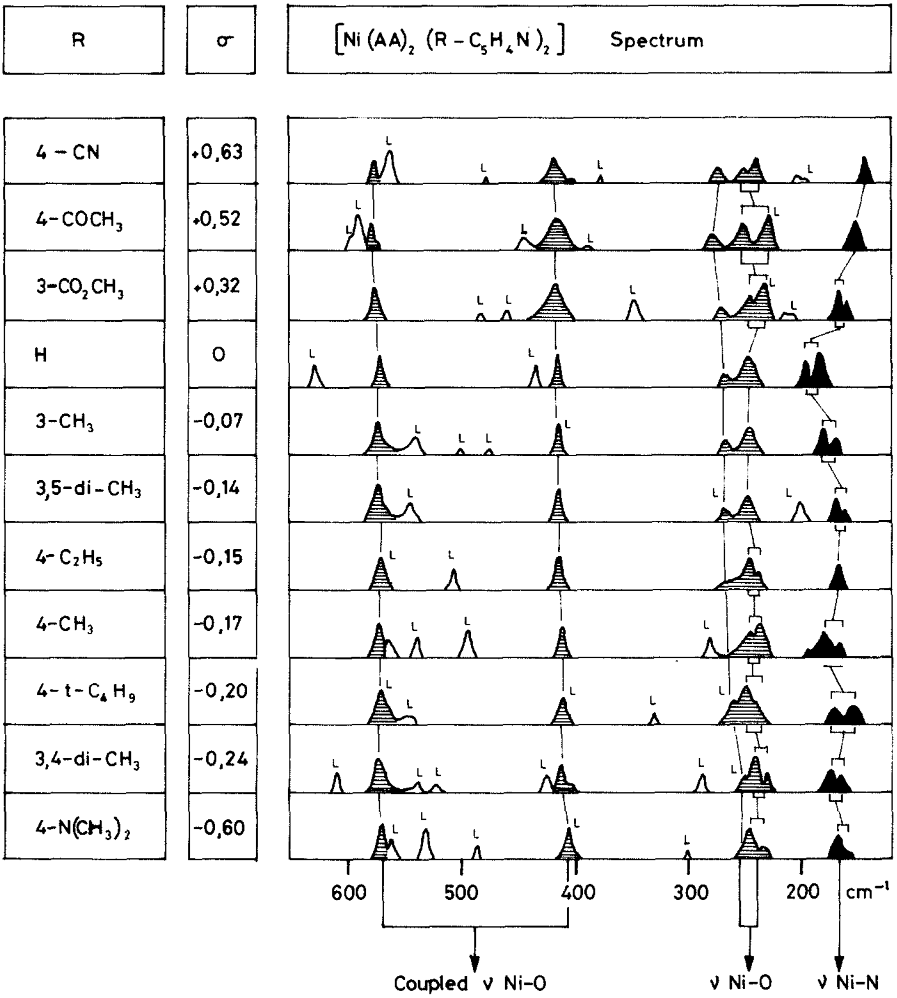


Fig. 18. IR spectra of substituted pyridine adducts: shaded peaks, ν(Ni–O); solid peaks, ν(Ni–N); L, bands occurring at or near regions of absorption in the spectra of the free pyridines.

of electron-releasing substituents is much smaller and ν(Ni–N) remains approximately constant for substituents with negative σ values.

In order to confirm that the shift of ν(Ni–N) towards lower frequency caused by electron-withdrawing substituents does not originate solely in the mass effects of R, allowance was made for the mass effects [59] to yield corrected ν(Ni–N) values, designated ν(Ni–N)$_{\text{corr}}$.

From the ν(Ni–N)$_{\text{corr}}$ values in Table 14, it is clear that the tendency for electron-withdrawing substituents to decrease ν(Ni–N) (which was observed before taking the mass effect into account) retains its direction and signifi-

TABLE 14

Frequencies (cm^{-1}) of principal ν(Ni–O) and ν(Ni–N) bands and ν(Ni–N) corrected for mass effects of R in $[Ni(AA)_2(R-C_5H_4N)_2]$

R	σ	$\nu(NI-N)_{obs}$	$\nu(Ni-N)_{corr}$	ν(Ni–O)
4-CN	+0.63	145	166	275, 244[a]
$4-COCH_3$	+0.52	156	187.5	278, 241[a]
$3-CO_2CH_3$	+0.32	166.5[a]	206	272, 242[a]
H	0	191.5[a]	(191.5)	269, 244
$3-CH_3$	−0.07	175[a]	188	269, 244
$3,5-di-CH_3$	−0.14	166[a]	189	268, 244
$4-C_2H_5$	−0.15	168	191	269, 243[a]
$4-CH_3$	−0.17	172[a]	185	—[b], 243[a]
$4-t-C_4H_9$	−0.20	165.5[a]	204	266, 245[a]
$3,4-di-CH_3$	−0.24	168.5[a]	191.5	264, 240[a]
$4-N(CH_3)_2$	−0.60	164[a]	196	—[b], 241[a]
py-d_5	0	185.5[a]	190.5	269, 244

[a] Mean of doublet. [b] Masked by neighbouring band.

cance after allowing for the mass effects of R. The effect of electron-releasing substituents, on the other hand, is negligible, the $\nu(Ni-N)_{corr}$ values remaining within a relatively narrow range of values above and below the ν(Ni–N) value of the pyridine adduct.

In 1970, Haigh et al. [60] examined the spectra of mono and bis adducts of cobalt(II), nickel(II) and zinc(II) acetylacetonate with amines of general formula RNH_2 where R is a range of alkyl, aryl and aralkyl groups. Two substituent-sensitive bands were found near 550 and 420 cm^{-1}. These were assigned to ν(M–O); ν(M–N) was not observed, occurring beyond the limit of measurement. It was again observed that adduct formation induces a substantial shift of ν(M–O) to lower frequencies and that the shift is greater than that accompanying hydration, because the higher ligand field strength of the amines causes firmer bonding to the metal ion than water and this occurs at the expense of the M–O bonding in the chelate ring. That the magnitude of the ligand field plays a role in determining ν(M–O) is also apparent from the fact that, for a constant substituent, ν(M–O) follows the order cobalt < nickel > zinc, which reflects the CFSE order.

For the purposes of examining the substituent dependence of ν(M–O), the inductive substituent parameter (σ*) was employed. This parameter has been proposed by Taft [42] as an index of the electronic effects of substituents in non-conjugated systems (where the transmission of these effects is by a field mechanism only). In all three series, ν(M–O) exhibits a similar substituent dependence, namely, a shift to lower frequency as the electron-releasing capabilities of the substituents increase. The correlation for the ν(M–O) band of higher frequency is shown in Fig. 19. The implication of this correlation is that electron-releasing substituents increase the donor capacity of the amine for the metal ion, the substituent-induced stabilization of the M–N bond occurring at the expense of the M–O bonding as had been observed for the substituted-pyridine adducts of Ni(AA)$_2$ [56].

The carbonyl stretching frequency of the chelate ring, ν(C–O), which was the subject of the assignment controversy mentioned in Section B, appears as a strong band near 1600 cm^{-1}. Although sharp in the spectra of the parent acetylacetonates, it is overlaid in the adduct spectra by the N–H bending frequency and is therefore too broad for its substituent sensitivity to be determined. The N–H stretching frequencies exhibit no regular correlation with σ^* probably because proximity of the substituents to the N–H bonds enhances the mass effect. This conclusion was supported by the fact that the band of highest frequency has a maximum value for the substituent of lowest mass (R = H) in all three series. The N–H stretching region of the spectrum is useful in that it permits a distinction between five- and six-coordination in the zinc series. Two bands are observed for the former and three for the latter.

In 1971, Percy and Thornton [61] studied the IR spectra of the mixed-ligand complexes [M(N-N)(AA)$_2$] where N-N represents one of the ligands 2,2'-bipyridine (bipy) or 1,10-phenanthroline (phen) and M = Mn, Co, Ni or Zn. These complexes represent a series intermediate between [M(N-N)$_3$]$^{2+}$

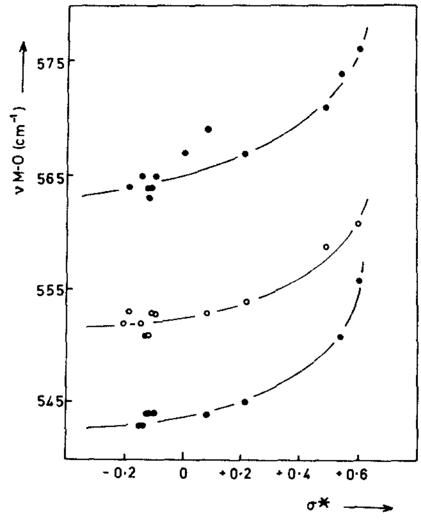


Fig. 19. Correlation of polar substituent constant (σ^*) with M–O stretching frequency for complexes [M(AA)$_2$(RNH$_2$)$_2$]. The ν(M–O) band of lower frequency exhibits a similar relationship.

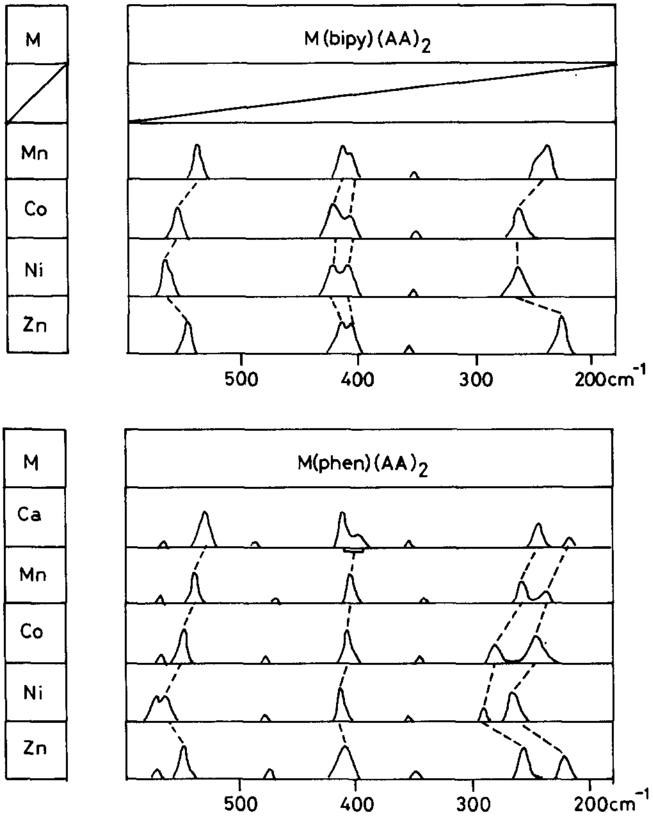


Fig. 20. IR spectra of mixed-ligand complexes, 600–200 cm^{-1}.

and $[M(AA)_3]^-$. Since neither bipy, phen, nor AA can span trans positions, the mononuclear mixed-ligand complexes have cis configuration.

The spectra of $[M(N\text{-}N)(AA)_2]$ (Fig. 20) exhibit one or two metal-sensitive bands below 300 cm^{-1}. Since there is no absorption in the spectra of $K[M(AA)_3]$ in this region, these bands are assigned to $\nu(M{-}N)$ although some coupling with $\nu(M{-}O)$ may occur. Bands near 400 cm^{-1} in the spectra of $[M(N{-}N)(AA)_2]$ are also present in the spectra of $[M(N\text{-}N)_3]^{2+}$ ($\nu(M{-}N)$) and $[M(AA)_3]^-$ ($\nu(M{-}O)$); hence their assignment is uncertain. Bands near 550 cm^{-1} are more reliably assigned to $\nu(M{-}O)$ by analogy with their occurrence in $[M(AA)_3]^-$. All four bands exhibit metal ion sensitivity which conforms with expectations based on the CFSEs. The fact that $\nu(M{-}N)$ and $\nu(M{-}O)$ follow the same trends indicates that stabilization of the M–N bond on replacement of one metal ion by another of higher CFSE is not accomplished at the expense of the M–O bond stability.

For each pair of complexes, $[M(N\text{-}N)_3]^{2+}$ and $[M(N{-}N)(AA)_2]$ (M and

N-N constant), $\nu(\mathrm{M{-}N})$ is higher in the former, and for each pair of complexes $[\mathrm{M(N\text{-}N)(AA)_2}]$ and $[\mathrm{M(AA)_3}]^-$ (M constant), $\nu(\mathrm{M{-}O})$ is higher in the latter. This suggests that the mixed-ligand complexes represent an intermediate series in which the M–N bonds are weaker than in $[\mathrm{M(N\text{-}N)_3}]^{2+}$ and the M–O bonds are weaker than in $[\mathrm{M(AA)_3}]^-$. This is consistent with the calculated f value for the ligand combination $\mathrm{(N\text{-}N)(AA)_2}$ which is derived from

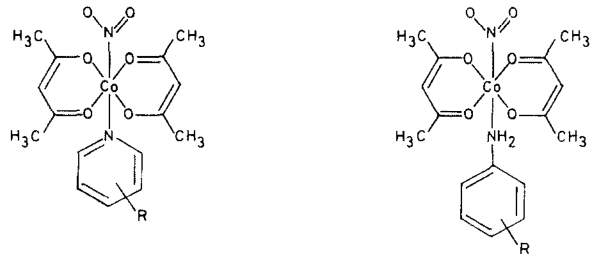
$$f\mathrm{(N\text{-}N)(AA)_2} = 1/3f\mathrm{(N\text{-}N)_3} + 2/3f\mathrm{(AA)_3} \tag{4}$$

This yields an f value of 1.28, intermediate between $f = 1.43$ for $\mathrm{(N\text{-}N)_3}$ and $f = 1.20$ for $\mathrm{(AA)_3}$.

Ammonia and amines are known [62] to displace one of the nitro groups from sodium *trans*-dinitrobis(acetylacetonato)cobaltate(III) to yield a series of monobase adducts of general formula *trans*-$[\mathrm{Co(NO_2)(AA)_2B}]$. Electronic and NMR spectra [62,63] are consistent with a trans octahedral structure (Fig. 21).

The IR spectra [64] of these complexes have been studied and are of interest since the high CFSE associated with the spin-paired t_{2g}^6 configuration of the cobalt(III) ion should yield particularly stable metal–ligand bonds and hence particularly high metal–ligand stretching frequencies. Thus, even amines with strongly electron-withdrawing substituents (such as *p*-nitroaniline) yielded stable adducts whereas these fail to react with nickel(II) β-ketoenolates.

A range of 17 differently substituted anilines and 14 variously substituted pyridines were employed in order to study the effects of substituents on the frequencies. Assignments for the $\nu(\mathrm{Co{-}O})$, $\nu(\mathrm{Co{-}N})$ and $\nu(\mathrm{Co{-}NO_2})$ bands were made by comparison of the spectra with those of $[\mathrm{Co(AA)_3}]$ and *trans*-$\mathrm{Na[Co(NO_2)_2(AA)_2]}$ and by $^{15}\mathrm{N}$ labelling of the aniline and *p*-toluidine complexes. The spectra are depicted in Figs. 22 and 23 where the complexes are arranged in order of decreasing Hammett σ values. $\nu(\mathrm{Co{-}O})$



(a) (b)

Fig. 21. Structure of complexes of general formula *trans*-$[\mathrm{Co(NO_2)(AA)_2B}]$.

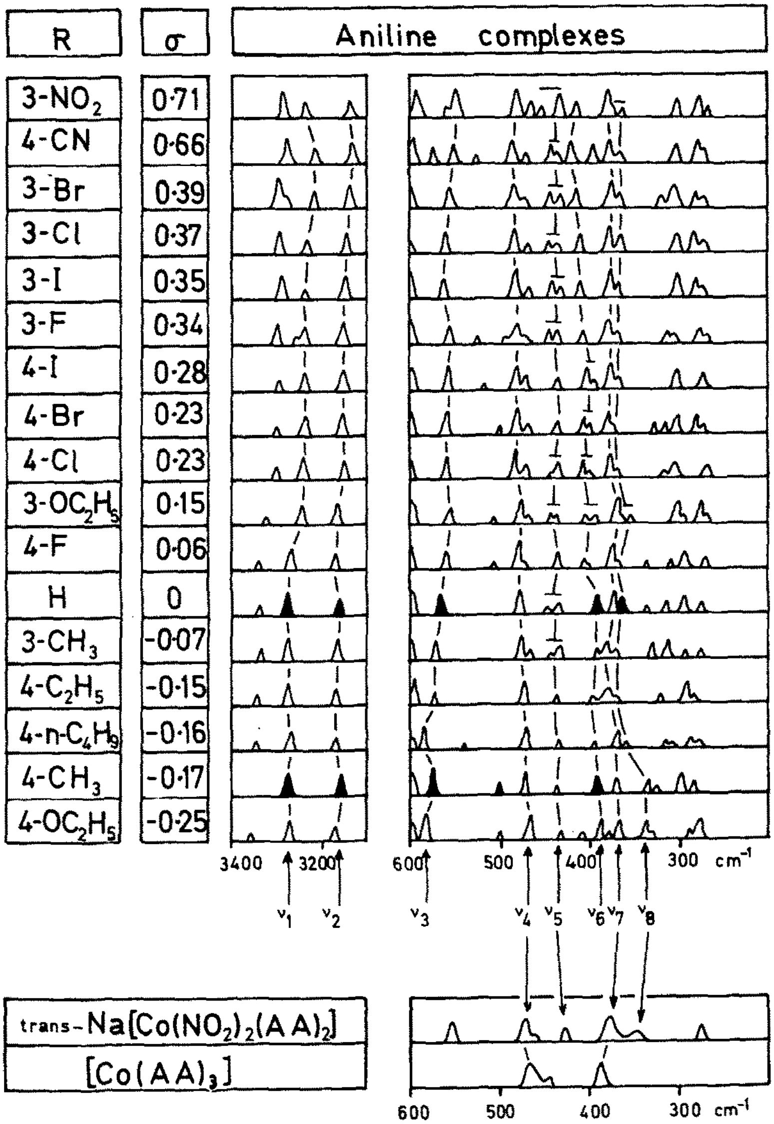


Fig. 22. IR spectra of aniline complexes. Solid bands exhibit ^{15}N shifts greater than 2 cm^{-1}. Assigned bands: ν_1, ν(N–H) antisym; ν_2, ν(N–H) sym; ν_3, ν(Co–N)+NO_2 wag; ν_4, ν(Co–O); ν_5, ν(Co–NO_2); ν_6,ν(Co–N)+ν(Co–O); ν_7, ν(Co–O); ν_8, ν(Co–NO_2).

occurred as two bands near 470 and 370 cm^{-1} while ν(Co–N) was observed near 550 and 390 cm^{-1} for the aniline complexes and 290 cm^{-1} for the pyridine complexes, with a second band of higher frequency being assigned to the NO_2 wagging mode coupled with ν(Co–N). ν(Co–NO_2) appeared as two bands near 430 and 360 cm^{-1} in both series of complexes.

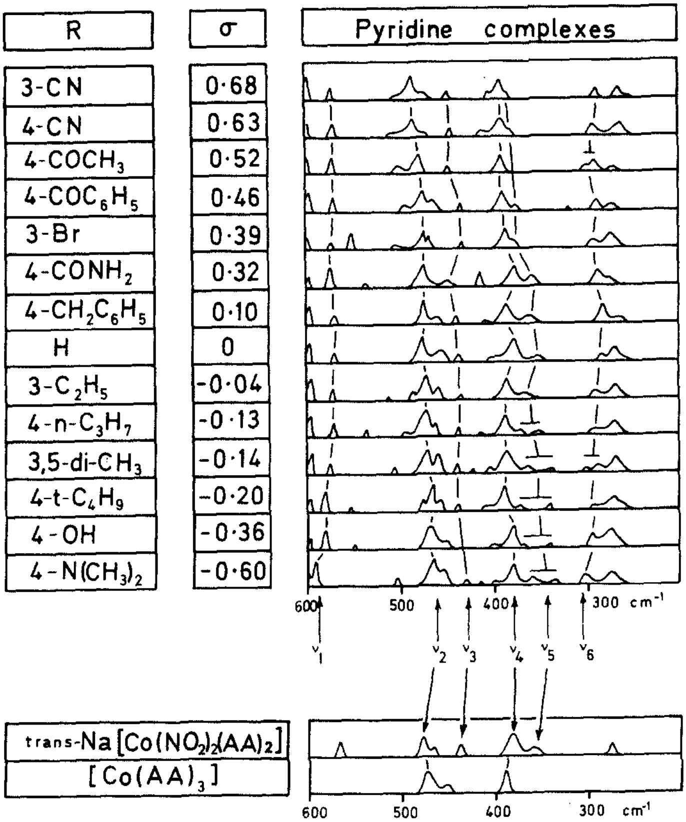


Fig. 23. IR spectra of pyridine complexes. Assigned bands: ν_1 ν(Co—N)+NO$_2$ wag; ν_2, ν(Co—O); ν_3, ν(Co—NO$_2$); ν_4, ν(Co—O); ν_5, ν(Co—NO$_2$); ν_6, ν(Co—N).

Employing the Hammett σ value as an index [43] of the electronic effects of R, ν(Co—N) was found to move to higher frequency with increased electron-releasing capacity of R. Since electron-releasing substituents serve to increase the donor capacity of the nitrogen atom for the metal ion, the observed direction of shift is that expected for a band assigned to ν(Co—N). The ν(Co—O) and ν(Co—NO$_2$) bands are both shifted in the opposite direction to ν(Co—N) by R, thus indicating that substituent-induced increased stability of the Co—N bonds occurs at the expense of both the Co—O and Co—NO$_2$ bonding.

Imidazole (Him) reacts with cobalt(II) and nickel(II) acetylacetonate to form the trans octahedral adducts [M(AA)$_2$(Him)$_2$] whereas bidentate heterocycles such as pyrazine (pz) and pyrimidine (pm) form linear polymers with each of the two nitrogen donors axially bonded to discrete planar M(AA)$_2$ units and formulated as *trans*-[M(AA)$_2$B]$_n$ [65]. The IR spectra [66] of

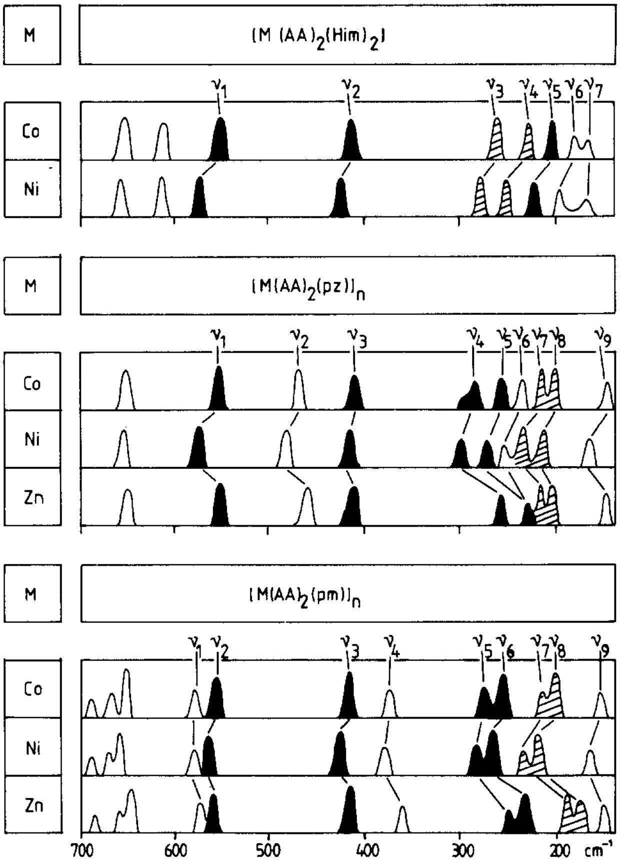


Fig. 24. IR spectra (600–140 cm^{-1}) of base adducts of metal(II) acetylacetonates: solid bands, ν(M–O); shaded bands, ν(M–N).

these adducts are depicted in Fig. 24. For the isotopic labelling technique, only Him and pz were available as their deuterated analogues, Him-d_4 and pz-d_4.

Imidazole has no internal ligand vibrations with a frequency less than 600 cm^{-1}, nor are there any internal vibrations of coordinated acetylacetonate in this region. Hence the seven bands within the 600–140 cm^{-1} range in the spectra of the bis(imidazole) adducts were all assigned to metal–ligand modes. The ν_1 and ν_2 bands were firmly assigned to ν(M–O) for three reasons. Firstly, they are completely insensitive to deuteration of the imidazole ring. Secondly, they are strongly M sensitive in the CFSE sequence cobalt < nickel. Thirdly, their frequencies lie close to those of the ν(M–O) bands in *trans*-$[M(AA)_2B_2]$ (M = Co or Ni; B = H_2O or py). In $[Ni(AA)_2(py)_2]$, the ν(Ni–O) bands are considered [56] to be coupled with the $\delta(C-CH_3)$ mode of the acetylacetonate ring or with a pyridine ligand mode. That ν_1 and ν_2 are coupled $\nu(M-O)$ bands was also proposed for the Him adducts since the M sensitivity of ν_1 and (especially) ν_2 is lower than that of ν_5 (see below).

The ν_3 and ν_4 bands are undoubtedly $\nu(M-N)$ modes since they were found to be significantly *d* and M sensitive. Their frequencies are very close to those reported [67] for $\nu(M-N)$ in the $[M(Him)_6]^{2+}$ complexes in which the assignments were based on the metal-isotope labelling technique. Since ν_5 has a higher M sensitivity than ν_1 or ν_2 but is completely unaffected by deuteration of Him, it was assigned to a vibrationally-pure (uncoupled) $\nu(M-O)$ mode. The alternative assignment to $\delta(O-M-O)$, proposed [22] for a band in this region of the spectrum of $[Cr(AA)_3]$, was considered unlikely since this would place the O−M−O bend at a higher frequency than the M−N stretch. Band ν_6, being both *d* and M sensitive, is either a third $\nu(M-N)$, band or $\delta(O-M-N)$ or $\delta(N-M-N)$. The origin of ν_7 is uncertain since it had no M sensitivity and was too broad for its *d* sensitivity to be determined in the spectrum of the nickel(II) adduct.

Support for the assignments proposed for $\nu(M-O)$ and $\nu(M-N)$ was evinced from a comparison between the frequencies for these vibrations in $[Ni(AA)_2(py)_2]$ [56] and $[Ni(AA)_2(Him)_2]$. As is well known [56], any increase in the strength of the M-base bond on replacing one adducted base by another causes a shift in $\nu(M-O)$ towards lower frequency. Since $\nu(Ni-N)$ in the Him adduct exceeds $\nu(Ni-N)$ in the py adduct, the reverse trend is expected for $\nu(Ni-O)$. This was observed.

So far as the pyrazine adducts are concerned, it was noted that below 600 cm^{-1}, pz exhibits one internal ligand mode, an out-of-plane deformation of the heterocyclic ring at 412 cm^{-1} with a *d* sensitivity of 14 cm^{-1}. This band recurs in the spectra of the pz adducts in the 470 cm^{-1} region (ν_2, Fig. 24). As had been observed for the py adducts [56], coordination of pz led to an increase in the frequency of such internal ligand vibrations. The *d* sensitivity which this band retains in the spectra of the pz-d_4 adducts enables it to be readily distinguished from the *d*-insensitive bands near 560 cm^{-1} (ν_1) and 420 cm^{-1} (ν_3). The latter two bands were assigned to coupled $\nu(M-O)$ on the grounds of their absence of *d* sensitivity and their high M sensitivity in the CFSE sequence cobalt < nickel > zinc.

Of the four (or five) bands within the 300–200 cm^{-1} range, only the two of the lowest frequency (ν_7, ν_8) exhibit significant *d* sensitivity, establishing them firmly as $\nu(M-N)$ bands. Their position near 200 cm^{-1} agrees well with that of the two $\nu(M-N)$ bands in the spectrum of $[Ni(AA)_2(py)_2]$ [56]. The assignment is also supported by the strong M sensitivity of these bands in the sequence cobalt < nickel > zinc. Of the remaining two (or three) bands (ν_4, ν_5, ν_6) within the 300–200 cm^{-1} range, ν_4 and ν_5 were assigned to vibrationally-pure ν(M–O) modes on the grounds of their absence of *d* sensitivity, their significant M sensitivity in the sequence cobalt < nickel > zinc, the occurrence of bands in this region in the spectra of the $[M(AA)_2(H_2O)_2]$ complexes (M = Co or Ni) and $[Zn(AA)_2(H_2O)]$ which undoubtedly have the same origin, and the established [56] existence of two ν(M–O) bands in this region of the spectra of $[M(AA)_2(py)_2]$ and $[Zn(AA)_2(py)]$. The bands below 200 cm^{-1} were considered to originate in metal–ligand bending vibrations.

Pyrimidine has only one ligand band below 600 cm^{-1}, namely at 348 cm^{-1}. The spectra of the adducts yielded four bands within the 600–300 cm^{-1} range. The band of lowest frequency was considered to correspond to the pm ligand band since it is raised 31 cm^{-1} by coordination, a shift characteristic [56] of the shift in the out-of-plane ring vibration on complexation of nitrogen heterocycles. Of the remaining three bands, that near 420 cm^{-1} and the more M sensitive of the two bands near 570 cm^{-1}, were assigned to coupled ν(M–O) modes. Assignment of the two uncoupled ν(M–O) and the two ν(M–N) bands between 300 and 170 cm^{-1} was made by analogy with the assignments of the corresponding py and pz adducts.

Quinoline reacts, either directly or in warm toluene, with transition metal(II) acetylacetonates to yield analytically pure five-coordinate adducts $[M(AA)_2(quin)]$ (M = Cu, Zn) or six-coordinate adducts $[M(AA)_2(quin)_2]$ (M = Mn, Co, Ni). The frequencies of the IR bands of these complexes and the isotopic shifts induced by deuteration of the quinoline ring are shown in Table 15 [68].

The band assignments in the spectra of the quinoline adducts were based on the effects of quinoline dueteration, metal ion substitution and by comparison of their spectra with those of quinoline and the metal acetylacetonates. So far as the *d* sensitivities of the IR bands are concerned, they may be divided into three classes. First, there are the internal quinoline modes which exhibit shifts exceeding 10 cm^{-1} on deuteration. Secondly, there are the ν(M–N) bands which exhibit shifts of between 2 and 7 cm^{-1} and thirdly there are the ν(M–O) and δ(O–M–O) bands which are insensitive to quinoline deuteration. Further confirmation of the assignments proposed was provided by the observation that ν(M–O), ν(M–N) and δ(O–M–O) are M sensitive while the internal ligand modes are not.

Adducts of the β-ketoenolates thenoyltrifluoroacetonate (TTA) and benzoyltrifluoroacetonate (BTA) have been studied by Shephard and Thornton [70]. These have the formulae depicted in Fig. 25 (and the spectra shown in Fig. 26) where they have been grouped into complexes with a common adducting molecule B, comprising TTA^-, H_2O, py, bipy, phen and NH_3. The general formula of these adducts may be written $Na[ML_3]$ or $[ML_2B]$ (L = TTA or BTA). Within each group of complexes with common L and B,

TABLE 15

Frequencies, quinoline-d_7 shifts (cm^{-1}) and assignments for quinoline and the adducts [M(AA)$_2$(quin)$_n$][a]

Band	quin	Mn $n=2$	Co $n=2$	Ni $n=2$	Cu $n=1$	Zn $n=1$	Assignment[b]
ν_1		670 (0)	662 (0)	664 (0)	678 (0)	670 (0)	acac ring def. + ν(M–O)
ν_2		650 (5)	653 (10)	655 (8)	656 (14)	654 (1)	acac ring def. + quin
ν_3	627 (38)	635 (36)	636 (36)	627 (22)	627 (27)	632 (22)	quin δ(ring) (35)
ν_4	610 (42)	621 (41)	622 (41)	(627) (22)	(627) (27)	(632) (22)	quin δ(ring) (21)
ν_5		568 (0)	572 (0)	575 (0)	571 (3)	$\approx$578[c]	acac ring
ν_6		543 (0)	552 (0)	(575) (0)	616 (2)	$\approx$578[c]	ν(M–O)
		(543) (0)	552 (0)	(575) (0)	600 (0)	558 (0)	ν(M–O)
ν_7	521 (17)	526 (17)	525 (16)	527 (16)	525 (16)	528 (16)	quin δ(ring) (9)
ν_8	477 (60)	488 (59)	493 (59)	489 (57)	479 (52)	489 (55)	quin γ(ring) (24)
ν_9	469 (60)	470 (55)	472 (55)	468 (48)	455 (43)	468 (49)	quin δ(ring) (48)
		404 (0)	418 (1)	420 (0)	441 (0)	427[d]	ν(M–O) + δ(C–CH$_3$)
ν_{10}		(404) (0)	(418) (1)	(420) (0)	427 (0)	419 (0)	ν(M–O) + δ(C–CH$_3$)
ν_{11}	383 (35)[e]	389 (26)	393 (26)	399 (34)	388 (32)	395 (32)	quin δ,γ-ring (13, 36) + ν(M–N)
ν_{12}		274 (0)	275 (0)	277 (0)	283 (0)	204 (0)	δ(O–M–O)
ν_{13}		227 (1)	252 (0)	251 (0)	264 (0)	158 (1)	δ(O–M–O)
ν_{14}	178 (12)	206 (30)	198 (26)	192 (15)	195 (22)	188 (11)	quin γ(ring) (25)
ν_{15}		169 (2)	219 (7)	238 (3)	225 (3)	231 (3)	ν(M–N)

[a] Data in parentheses are the shifts (cm^{-1}) to lower wavenumber induced by quinoline deuteration. [b] The figures in parentheses for quinoline modes are the band numbers in the notation of McClellan and Pimentel [69]. [c] Band not resolved from 558 cm^{-1} band in the unlabelled complex but observed at 578 cm^{-1} in the deuterated complex. [d] Masked by ν_9 in the labelled complex. [e] Mean of 390 (39) and 375 (30) bands.

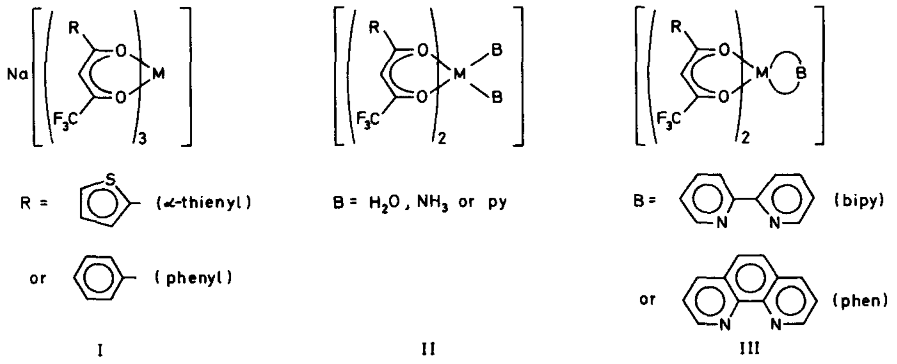


Fig. 25. Structures of TTA and BTA complexes.

the IR band near 400 cm^{-1} which exhibits maximum sensitivity to the coordinated metal ion (the sensitivity being in the sequence of CFSEs) and which generally occurs in a region free from ligand absorption, has been assigned to ν(M—O). These are the solid bands depicted in Fig. 26. The large shift in ν(Cu—O) observed for the H_2O and py adducts of the copper(II) β-ketoenolates is due to the lower coordination number of these complexes. There is no evidence of tetragonal distortion in the copper complexes with bipy and phen as adducting bases.

The most interesting feature of the spectra of these base adducts is that they provide an example of how IR spectra (rather than the more usually employed electronic spectra) may be used to derive a spectrochemical series of ligands. If the complex anion of the compounds Na[ML_3] is represented as $[ML_2B]^-$ (in this case B = L) then the series of complexes examined may be represented by the single general formula $[ML_2B]^{n-}$. In the complexes of manganese(II), compounds of this formula were synthesized with B = $2H_2O$, $2NH_3$, (NH_3+H_2O), 2py, TTA, bipy and phen. Figure 27 shows that ν(M—O) in this series of complexes moves in the sequence $2H_2O > (NH_3+H_2O) >$ TTA $> 2NH_3 >$ 2py $>$ bipy $=$ phen. The calculated f values (from $10Dq = fg$) of these ligand combinations are in the same sequence. Hence the potential usefulness of IR spectra to the problem of crystal field strength determination in these complexes has been demonstrated.

G. URANYL AND VANADYL β-KETOENOLATES

As normally prepared, uranyl acetylacetonate is obtained as the monohydrate $[UO_2(AA)_2(H_2O)]$ which is readily dehydrated to $[UO_2(AA)_2]$. The

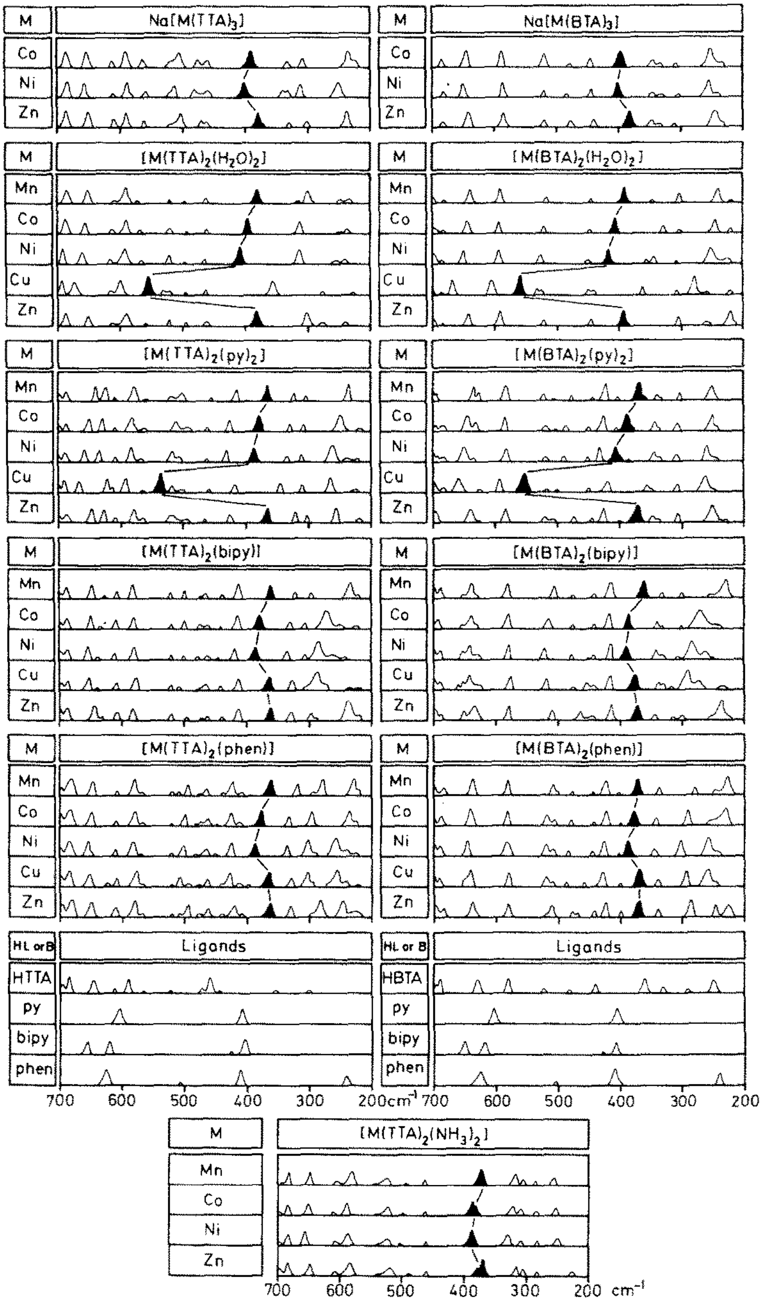


Fig. 26. IR spectra (700–200 cm^{-1}) of complexes Na[ML$_3$] and [ML$_2$B]. Solid bands are ν(M–O). In the aqua and pyridine adducts the copper complexes are anhydrous square planar and five-coordinate square pyramidal, respectively.

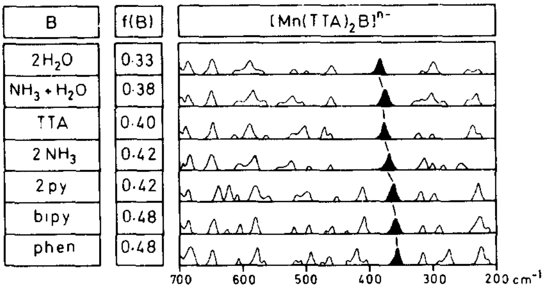


Fig. 27. IR spectra (700–200 cm^{-1}) of manganese(II) complexes $[Mn(TTA)_2B]^{n-}$. Solid bands are ν(Mn–O).

IR spectra of uranyl complexes have been widely studied but earlier work [71–77] was directed mainly to the problems of band assignments and the conformation of the UO_2 group. A systematic study of the IR spectra of a large range of uranyl β-ketoenolates was made in 1971 by Haigh and Thornton [78] who studied the complexes depicted in Fig. 28.

Theoretical and empirical evidence [52,71,76] unanimously support the assignment of the sharp intense band near 900 cm^{-1} in the spectra of all uranyl compounds to the asymmetric uranyl stretching frequency ν(U=O). Assignment of ν(U–O) is more difficult. On the basis of a theoretical study [52], the band at 433 cm^{-1} in the spectrum of $[UO_2(AA)_2]$ was so assigned but the equivalent band is not observed in the majority of the spectra studied by Haigh and Thornton [78]. Bands corresponding to those at 528 and 403 cm^{-1} in $[UO_2(AA)_2]$ were present in nearly all spectra and were the principal bands in the far-IR region to exhibit appreciable substituent sensitivity. Their assignment to ν(U–O) was therefore preferred. Moreover, the corresponding bands in the spectrum of $[Cu(AA)_2]$ (at 615 and 455 cm^{-1}) were reliably assigned [10] on the basis of normal coordinate [17,79] and ^{18}O labelling [18] studies to ν(Cu–O). That ν(U–O) is of lower frequency than ν(Cu–O) is expected in view of the greater mass and higher coordination number of the uranium atom.

Correlation of group frequencies with the substituent electronic effects requires some quantitative index of the latter. Use of the Hammett param-

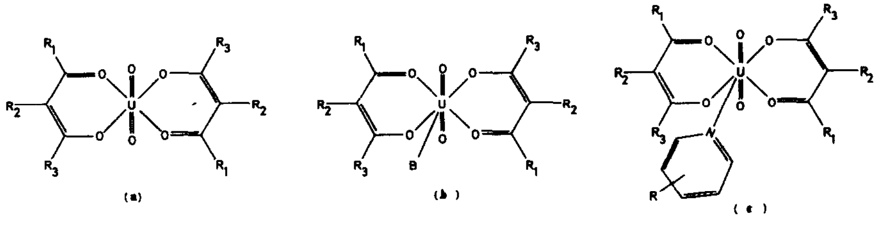


Fig. 28. Formulae of uranyl β-ketoenolates.

eters [43] (σ_m and σ_p) would assume aromaticity of the β-ketoenolate ring. Although there is evidence [80] of some electron delocalization in the chelate ring, the metal ion provides a barrier to complete freedom of movement of the π electrons [38,81,82]. Therefore it is preferable to employ the pure field (F) and pure resonance (R) parameters which are independent of the site of substitution (Table 16). The joint electronic effect ($\Sigma\ \sigma$) of the β-ketoenolate substituents is given by eqn. (5)

$$\Sigma\ \sigma = f\ \Sigma\ F + r\ \Sigma\ R \tag{5}$$

where f and r are the relative weightings of F and R. Earlier work [10] had shown that, except for phenyl substituents, use of $f=0.75$, $r=0.25$ yielded values of $\Sigma\ \sigma$ which decrease monotonically with increase in ν(Cu–O) in a series of copper(II) β-ketoenolates (see Section E). Since [38]

$$\sigma_m = 0.78F + 0.22R \tag{6}$$

it transpires that $\Sigma\ \sigma$ is very nearly equated with $\Sigma\ \sigma_m$. Phenyl-substituted β-ketoenolates require an increased contribution from R to yield values of $\Sigma\ \sigma$ which are consistent with the order of ν(Cu–O) values. This has been attributed [10,15] to the significant contribution of the forms (Figs. 29(a)–29(c)) to the resonance hybrid. The NMR spectra of the complexes $[UO_2L_2B]$ (B = pyridine, pyridine N-oxide) (Table 17) provide independent support for this hypothesis since the resonance structures depicted in Fig. 29 require that the ring $>$CH proton is magnetically shielded relative to that of the β-ketoenolates without phenyl substituents. Accordingly, the complexes of benzoylacetone and dibenzoylmethane yield the maximum upfield shift of the ring $>$CH proton signal.

The ligand orbitals of β-diketones are group theoretically, energetically and occupationally suitable for participation in both donor (U→L) and

TABLE 16

Substituent data for uranyl β-ketoenolates $[UO_2L_2]$ and $[UO_2L_2B]$ (Figs. 28(a) and 28(b))

L	R_1	R_2	R_3	$\sum F$	$\sum R$	f	r	$\sum \sigma$	ν(Cu–O)[a] (cm^{-1})
TFA	CF_3	CH_3	H	+0.58	+0.05	0.75	0.25	+0.45	445
EAA	OC_2H_5	CH_3	H	+0.31	−0.58	0.75	0.25	+0.09	
AA	CH_3	CH_3	H	−0.10	−0.28	0.75	0.25	−0.15	455
BA	C_6H_5	CH_3	H	+0.08	−0.23	0.25	0.75	−0.16	459
DBM	C_6H_5	C_6H_5	H	+0.28	−0.18	0.00	1.00	−0.18	465
PA	$C(CH_3)_3$	CH_3	H	−0.15	−0.28	0.75	0.25	−0.18	466
MAC	CH_3	CH_3	CH_3	−0.16	−0.42	0.75	0.25	−0.20	
DPM	$C(CH_3)_3$	$C(CH_3)_3$	H	−0.20	−0.28	0.75	0.25	−0.22	496

[a] For $[CuL_2]$ see ref. 10.

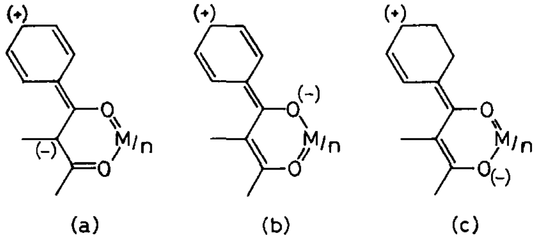


Fig. 29. Resonance forms of phenyl-substituted metal β-ketoenolates.

TABLE 17

IR and NMR data for uranyl β-ketoenolates [UO_2L_2] and [UO_2L_2B] (Figs. 28(a) and 28(b))

L	$\sum \sigma^a$	ν(U=O) (cm^{-1})	ν(U–O) (cm^{-1})		ν(C–O) (cm^{-1})	Chemical shift^b (δ) (ppm)			
						2-H	3-H	4-H	Ring >CH
UO_2L_2									
AA	−0.15	928	528	403	1565				
BA	−0.16	918	555	413	1552				
DBM	−0.18	904	606	430	1541				
$UO_2L_2 \cdot H_2O$									
TFA	+0.45	929	568	412	1624				
AA	−0.15	922		404	1583				
BA	−0.16	919	555	412	1561				
DBM	−0.18	915	605	451, 432	1540				
$UO_2L_2 \cdot py$									
TFA	+0.45	922	562	408	1621	9.20	7.75	8.12	6.28
EAA	+0.09	918	571	423	1605	9.47	7.72	7.98	5.31
AA	−0.15	913		403	1570	9.57	7.73	7.96	5.85
BA	−0.16	911	553	412	1555	—^{c}	—^{c}	—^{c}	—^{c}
DBM	−0.18	909	605	453, 428	1539	9.63	7.73	7.88	7.24
PA	−0.18	916	621	479, 416	1584	9.46	7.73	7.98	5.96
MAC	−0.20	907	653	541, 452	1582	9.59	7.73	7.95	
DPM	−0.22	917	607	479, 409	1560	9.36	7.73	8.00	6.11
$UO_2L_2 \cdot pyNO$									
TFA	+0.45	915	561	403	1620	9.09	7.70	7.63	6.24
AA	−0.15	896		403	1585	8.95	7.61	7.55	5.78
BA	−0.16	905	554	411	1560	9.03	7.57	7.53	6.50
DBM	−0.18	898	605	454, 426	1542	9.03	7.57	7.52	7.18
DPM	−0.22	903	605	480, 409	1560	9.13	7.56	7.46	6.10

[a] For derivation see Table 16. [b] Downfield shifts in deuterochloroform (internal standard, tetramethylsilane). [c] Insoluble.

acceptor (L→U) π-interaction with the uranyl ion [77,81,83]. Convincing evidence [77] has been adduced that U→L π-bonding provides a significant contribution to the bonding in uranyl complexes whereas in copper(II) β-ketoenolates Cu→O π-bonding is generally considered relatively weak [82,84]. Assuming the different extents of π interaction in the copper(II) and UO_2(II) β-ketoenolates to be real, some differences between the substituent dependence of ν(M–O) in the two series (Tables 16 and 17) may be anticipated.

Electron-withdrawing substituents will decrease the donor capacity of the carbonyl groups. This is evident from high ν(C–O) values in both copper and uranyl trifluoroacetylacetonates and is a general feature of all transition and non-transition metal β-ketoenolates comprising electron-withdrawing substituents [10]. At the same time, U→O π-bonding will be facilitated by such substituents, leading to a positive contribution to ν(U–O). Thus the monotonic increase in ν(Cu–O) with electron-releasing capacity of the substituents (expected for minimal π interaction) is replaced in the uranyl series by a trend to increasing values of ν(U–O) at the two extremes of the $\Sigma\,\sigma$ scale.

An early study [77] of ligation effects on ν(U=O) in a series of complexes $[UO_2(NO_3)_2L_2]$ revealed that the shift in ν(U=O) induced by varying the ligand L, may be expressed as

$$\Delta\nu = (\text{electrostatic effect}) - \sigma(L \rightarrow U) - \pi(L \rightarrow U) \pm \pi(U \rightarrow L) \qquad (7)$$

where a negative sign implies a shift to lower frequency and the adoption of positive sign for the last term is generally more probable. Equation (7) predicts that ν(U=O) will shift to lower frequency as the ligand field strength of L increases except where U→L π-bonding is of major importance and provides a positive contribution to $\Delta\nu$. Values of the ligand field parameter (f) are now available [83,85] for a majority of the ligands studied and enable the relationship to be placed on a quantitative basis (Table 18). The magnitude of ν(U=O) decreases monotonically with f except for L = pyridine. Pyridine and ammonia occupy similar positions in the spectrochemi-

TABLE 18

Comparison of ν(U=O) and ligand parameter (f) for complexes $[UO_2(NO_3)_2L_2]$

L	f	ν(U=O) (cm^{-1})
F	0.90	960
H_2O	1.00	945
NCS	1.03	898
py	1.25	926
NH_3	1.25	895
en	1.28	888
CN	1.70	873

cal series but ν(U=O) is far higher in the pyridine complex. This was attributed to the capacity of pyridine for entering into strong U→L π-bonding. In support of this conclusion it was observed that strongly electron-releasing substituents (such as the tertiary butyl group) in the complexes $[UO_2L_2py]$ are expected to facilitate U–pyridine π-bonding and therefore according to eqn. (7) should also shift ν(U=O) to higher frequencies. Thus high values of ν(U=O) are realized for $[UO_2(PA)_2py]$ and $[UO_2(DPM)_2py]$ (Table 17) while in the hydrate $[UO_2(DPM)_2(H_2O)]$, ν(U=O) has the value expected from the magnitude of $\Sigma\ \sigma$ for two tertiary butyl groups.

In the 22 adducts of uranyl acetylacetonate with variously substituted pyridines (Fig. 28(c), Table 19) the substituent effects originate in the adduct rather than the chelate ring. The Hammett substituent parameters [43] are

TABLE 19

Substituent and IR data for complexes $[UO_2(AA)_2(R\text{-}C_5H_4N)]$ (Fig. 28(c); $R_1=R_2=CH_3$; $R_3=H$)[a]

R	σ	ν(U=O) (cm^{-1})	ν(U–O) (cm^{-1})	ν(C–O) (cm^{-1})
3-CN	+0.68	909	402	1567
4-CN	+0.63	909	403	1570
4-$CO_2C_2H_5$	+0.52	910	403	1571
4-$COCH_3$	+0.52	908	403	1567
4-COC_6H_5	+0.46	910	403	1578
3-$CO_2C_2H_5$	+0.40	910	404	1572
3-Br	+0.38	908	402	1571
3-Cl	+0.37	909	402	1568
3-$COCH_3$	+0.31	908	403	1567
4-C_6H_5	+0.01	910	403	1573
H	0	913	403	1570
3-CH_3	−0.08	909	404	1585
4-*n*-C_3H_7	−0.13	910	404	1572
3,5-di-CH_3	−0.14	907	404	1573
4-C_2H_5	−0.15	910	404	1574
3-NH_2	−0.16	908	404	1568
4-CH_3	−0.17	909	404	1572
4-*t*-C_4H_9	−0.20	910	404	1584
3,4-di-CH_3	−0.24	908	404	1577
4-OH	−0.36	898	408	1587
4-NH_2	−0.66	894	410	1582
3,4-di-NH_2	−0.82	890	413	1582

[a] Pyridines with substituents such as –CN, $-NH_2$ are bound to uranium through the heterocyclic nitrogen since the characteristic group frequencies of the substituents in the complexes are close to those of the free amines.

TABLE 20

Antisymmetric U = O stretching frequencies of complexes $[UO_2L_2(R{-}C_5H_4N)]$

R	σ_p	ν(U=O) (cm^{-1})			
		L = DPM	L = DBM	L = BA	L = AA
4–CN	+0.63	913	907	908	909
$4{-}CO_2C_2H_5$	+0.52	911	906	911	910
$4{-}CH_3$	−0.17	916	905	917	909
$4{-}NH_2$	−0.66	893	895	914	894

used as an index of the electronic effects. These have been shown [55] to apply very satisfactorily to substituted pyridines.

Electron-releasing pyridine substituents will increase the donor capacity of the heterocyclic nitrogen atom. According to eqn. (7) the resulting increased ligand field strength will shift ν(U=O) to lower frequencies (particularly since the π(U→pyridine) term is minimized at the negative end of the σ scale). Accordingly, ν(U=O) exhibits a marked decrease for strongly electron-releasing substituents. In order to ascertain the generality of this effect, ν(U=O) was also determined for two strongly electron-releasing and two strongly electron-withdrawing pyridine adducts of three further β-ketoenolates (Table 20). Except for L = BA, a decrease in ν(U=O) at the extreme negative end of the σ scale was observed.

Pyridine substituents at the positive end of the σ scale will facilitate U–pyridine π-bonding and increase the contribution of the π(U→L) term in eqn. (7). A positive contribution to ν(U=O) is expected. Although ν(U=O) is shifted 19 cm^{-1} in the expected direction between the extremes of σ values, it is not significantly sensitive to the range of substituents with positive σ.

Electron-releasing β-ketoenolate substituents lead to a decrease in both ν(U=O) and ν(C–O). Figure 30 shows that while ν(C–O) exhibits similar substituent sensitivity within each series of complexes studied, ν(U=O) is especially sensitive to the substituent in the anhydrous complexes. This suggests that, in the adducts, the electronic effects of the substituents are transmitted to influence not only the electron density in the chelate ring and U=O bonds but also within the adducted molecule. This was substantiated by the NMR spectra of the complexes $[UO_2L_2py]$ (the IR spectra do not provide any suitable characteristic vibration of the pyridine ring which is sufficiently sensitive to detect any relatively minor perturbation of the electron density in the pyridine ring caused by β-ketoenolate substituents). The NMR data (Table 17 and Fig. 31) show that those β-ketoenolate

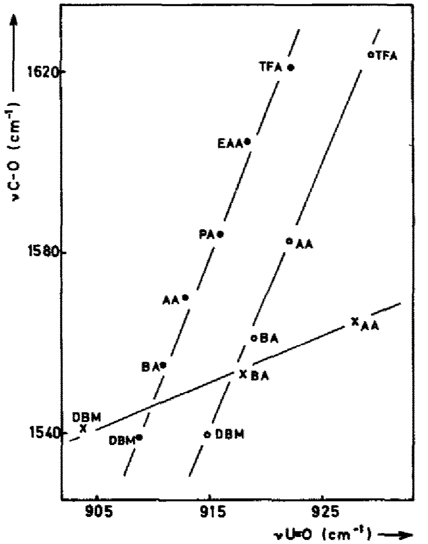


Fig. 30. Relationship between ν(C–O) and ν(U=O) for complexes $[UO_2L_2B]$ (●, B = pyridine; ○, B = H_2O; X, B absent). The points for L = DPM lie far off the plots and are excluded.

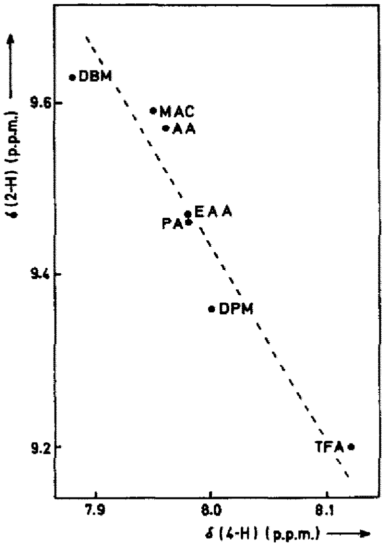


Fig. 31. Relationship between chemical shifts (δ) of pyridine 2- and 4-protons in complexes $[UO_2L_2(C_5H_5N)]$.

substituents which lead to deshielding of the pyridine proton in the 4-position correspondingly shield that in the 2-position and vice versa, while the 3-proton is unaffected. This observation and the relative insensitivity of the magnetic shieldings of the heterocyclic ring protons in the pyridine *N*-

oxide complexes towards β-ketoenolate substitution suggests that the degree of interligand conjugation is an important factor in determining the extent of transmission of the electronic effects to the heterocyclic ring. Nevertheless spatial (field) effects cannot be excluded since the 2- (and 6-) protons which are nearest to the source of perturbation exhibit the maximum chemical shift.

We have lastly to consider whether the electronic effects of the pyridine substituents are transmitted to affect the electron density distribution in the β-ketoenolate ring in the complexes $[UO_2(AA)_2(R{-}C_5H_4N)]$. It is observed (Table 19) that the decrease in ν(U=O) induced by electron-releasing pyridine substituents is accompanied by an increase in both ν(U–O) and ν(C–O). This implies that the transfer of negative charge to uranium (which leads to increased electrostatic repulsion in the U=O bond and hence lowers ν(U=O)) is partly relieved by U→O π-bonding.

The effect on the U–O and C–O bond orders of electron-releasing pyridine substituents is precisely similar to that of electron-withdrawing β-ketoenolate substituents (Section E). By contrast, electron-withdrawing pyridine substituents in the complexes *trans*-$[Ni(AA)_2(R{-}C_5H_4N)_2]$ cause ν(Ni–O) to decrease [45]. The difference clearly hinges on the relatively greater capacity of uranium for participating in U→O π-bonding.

Vanadyl β-ketoenolates have distorted square pyramidal structure (Fig. 32), the vanadium atom being displaced from the basal plane of the four β-ketoenolate oxygen atoms towards the apical multiply bonded oxygen atoms [86–89]. Compared with regular square pyramidal structure, this distortion leads to some loss of π function by the vanadyl $d\pi$ orbitals (d_{xz}, d_{yz}) and severely restricted interligand conjugation [90]. The latter implies a considerable limitation in the capacity of the substituents for resonance interaction with the V–O and V=O bonds. Quite apart from such symmetry constraints to π interaction, the vanadium(IV) ion has only a single electron available for participation in π(V→O) bonding. Nevertheless, thermochemical measurements [91] show that the V–O bond energy in vana-

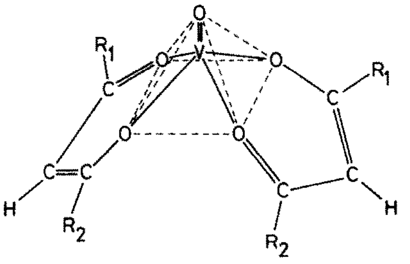


Fig. 32. Structure of vanadyl β-ketoenolates.

dyl acetylacetonate (324 kJ mol^{-1}) is at least 10% higher than the M–O bond energies of the acetylacetonates of uranyl(II), copper(II), magnesium(II), cobalt(III) and iron(III). Furthermore, bond length data (V=O, 1.57 Å; V–O, 1.97 Å) establish [87,88] a very short V–O distance which has been attributed [90,92] to very strong σ-bonding. Hence, while L→V π-bonding cannot be ruled out, there is probably an appreciable ionic contribution to the short V–O distance.

Equation (7), applicable to uranyl complexes, has been considered to apply also to vanadyl complexes [93]. However, in the vanadyl β-ketoenolates, the interligand conjugation implicit in the forms shown in Fig. 29 ($M = VO$, $n = 2$) is only allowed to a small extent. Accordingly (Table 21), ν(V=O) correlates with $\Sigma\ \sigma_m$ without assuming any increase in the weighting of R for vanadyl benzoylacetonate and dibenzoylmethanate (unlike the situation with the uranyl analogues) [93]. In practice, it transpires that the ν(V=O) values are qualitatively parallel to those of F so that it is not necessary to assume any resonance contribution to the bonding.

Further evidence for diminished π-interaction in vanadyl β-ketoenolates arises from the opposed direction of shift in ν(U=O) and ν(V=O), induced by ligands spanning the range of $\Sigma\ \sigma_m$ values (Table 22). Thus substitution of L = DPM for L = TFA leads to an increase of 75 cm^{-1} in ν(V=O) and a decrease of 21 cm^{-1} in ν(U=O). In the uranyl series, electron-releasing substituents transfer charge by σ (L→M) and π(L→M) contributions into orbitals which are pure uranium orbitals in $D_{\infty h}$ symmetry [77]. This charge transfer to uranium increases the electrostatic repulsion between the U and O atoms in the O=U=O bonds leading to a decrease in ν(U=O). In the vanadyl series, a large ionic contribution to the bonding in the V–O bond will (for electron-releasing substituents) lead to a polarization of this bond in the sense O^-–V^+ and thus promote the V-to-O attraction in the V=O bond, thereby increasing ν(V=O).

Electron-withdrawing substituents will reduce the σ-donor capacity of the carbonyl oxygen atom for the metal ion, evident from the high values of ν(C–O) observed [10] for all metal trifluoroacetylacetonates. Superimposed on this effect will be substituent-induced π(M→L) bonding, where allowed (i.e. in the uranyl but not in the vanadyl series). Thus ν(M–O) should serve as a sensitive index to detect differences in the relative significance of π(M→L) bonding in the uranyl and vanadyl β-ketoenolates (Table 22). Accordingly, theoretical evidence for strong π(U→O) bonding is supported by the observed high value of ν(U–O) in $[UO_2(TFA)_2]$ in contrast with a low value of ν(V–O) in the analogous vanadyl complex. At the opposite end of the Σ σ scale, strongly electron-releasing substituents will provide σ(L→M) and π(L→M) contributions to the total M–O bonding. Both effects provide a positive contribution to ν(M–O) although their relative

TABLE 21

Substituent parameters and vibrational frequencies of vanadyl β-ketoenolates, [VOL_2]

L	R_1	R_2	$\sum F$	$\sum R$	$\sum \sigma$	$\sum \sigma_m$	$\nu(V=O)$ (cm^{-1})	$\nu(V-O)$ (cm^{-1})	$\nu(C-O)$ (cm^{-1})	$\nu(C-C)$ (cm^{-1})
TFA	CF_3	CH_3	+0.58	+0.05	+0.50	+0.36	931	602 449	1616	1540
PTA	CF_3	$C(CH_3)_3$	+0.53	+0.05	+0.46	+0.33	945	607 456	1604	1530
DBM	C_6H_5	C_6H_5	+0.28	−0.18	+0.21	+0.12	996	589 467	1544	1531
BA	C_6H_5	CH_3	+0.08	−0.23	+0.03	−0.01	998	575 462	1562	1526
AA	CH_3	CH_3	−0.10	−0.28	−0.13	−0.14	999	611 488	1564	1536
DPM	$C(CH_3)_3$	$C(CH_3)_3$	−0.20	−0.28	−0.19	−0.21	1006	648 490	1552	1508
MDBM	*p*-$CH_3O-C_6H_4$	*p*-$CH_3O-C_6H_4$					991	652 485	1531	1507

TABLE 22

Summary of differences in substituent sensitivity of vibrational frequencies (cm^{-1}) in vanadyl and uranyl β-ketoenolates

L	$\sum \sigma_m$	$[VOL_2]$			$[UO_2L_2(H_2O)]$		
		$\nu(V=O)$	$\nu(V-O)$	$\nu(C-O)$	$\nu(U=O)$	$\nu(U-O)$	$\nu(C-O)$
TFA	+0.36	931	602 449	1616	929	412	1624
AA	−0.14	999	611 488	1564	922	404	1583
DPM	−0.21	1006	648 490	1552	908	413	1548

weightings undoubtedly differ in the vanadyl and uranyl series. Accordingly, high values of $\nu(M-O)$ are realized for vanadyl and uranyl dipivaloylmethanate (Table 22). Evidence has been cited for the relatively small contribution of the quinonoid forms to the bonding in phenyl-substituted vanadyl β-ketoenolates compared with their uranyl analogues. In both series, substitution of methyl by phenyl groups leads to the expected decrease in $\nu(C-O)$ and $\nu(M=O)$. Furthermore, the smaller shifts in the vanadyl series are in accordance with the diminished role of quinonoid resonance in this series. It is possible to induce an increased contribution from the forms (Fig. 29, $M=VO$, $n=2$) by incorporating a *p*-methoxyl substituent in the phenyl rings since this substituent participates in strong resonance interaction with an aromatic ring (Fig. 33). Thus, in the series of complexes $[VOL_2]$, both $\nu(V=O)$ and $\nu(C-O)$ decrease in the order L = AA > BA > DBM > MDBM, i.e. as the resonance interaction of the substituent with the chelate ring increases.

H. DERIVATIVES OF METAL ACETYLACETONATES IN WHICH ONE OR BOTH O ATOMS HAVE BEEN SUBSTITUTED BY NH, S OR Se

The relationship between the complexes discussed here and those referred to in earlier sections of this review is illustrated in Table 23. The IR spectra of these complexes [94–109] have not been as widely studied as those of their parent metal acetylacetonates. The more significant IR studies are shown in Table 24. They include all of the examples given in Table 23, except for the complexes of formula $[M(NS)_2]$, simple examples of which have not yet been described [110].

The complexes $[M(NA)_2]$, $[M(SA)_2]$ and $[M(SS)_2]$ are all square planar for M = Co, Ni, Cu, Pd and Pt while $[Zn(SA)_2]$, $[Cd(SA)_2]$ and $[Pb(SA)_2]$ are probably tetrahedral. The complexes $[M(NA)_2]$ (M = Ni, Cu) are trans planar while $[M(SA)_2]$ (M = Ni, Cu) are cis planar. The point group symmetries and the number of IR-active modes are shown in Table 25.

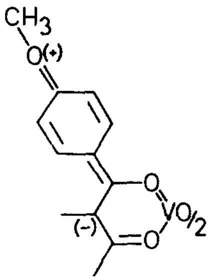
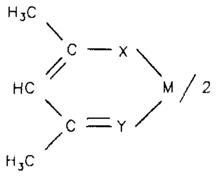


Fig. 33. Resonance interaction of *p*-methoxyl group in [VO(MDBM)$_2$] (of Fig. 32, $R_1 = R_2 = p$-CH_3O–C_6H_4–).

TABLE 23

Formulae and nomenclature of complexes



X	Y	Abbreviated formula	Generic name	Trivial name
O	O	[M(AA)$_2$]	Metal(II) 2,4-pentanedionate	Metal(II) acetylacetonate
NH	O	[M(NA)$_2$]	Metal(II) 4-imino-2-pentanonate	Metal(II) bis(acetylacetoneimine)
S	O	[M(SA)$_2$]	Metal(II) 4-thioxo-2-pentanonate	Metal(II) monothioacetylacetonate
S	S	[M(SS)$_2$]	Metal(II) 2,4-pentanedithionate	Metal(II) dithioacetylacetonate
NH	S	[M(NS)$_2$]	Metal(II) 4-imino-2-pentanethionate	Metal(II) bis(monothioacetylacetoneimine)
Se	Se	[M(SeSe)$_2$]	Metal(II) 2,4-pentanediselenonate	Metal(II) diselenoacetylacetonate

The spectra of the complexes listed in Table 26 (Fig. 34) have received the widest attention and they are therefore selected as examples for discussion. The frequencies and assignments over the range 4000–50 cm^{-1} have been taken from the most recent IR work on these species [107].

The acetylacetonates of nickel, copper and zinc (used as a basis for comparison) have the composition *trans*-[Ni(AA)$_2$(H$_2$O)$_2$], [Cu(AA)$_2$] and [Zn(AA)$_2$(H$_2$O)]. The presence of coordinated water in the nickel and zinc complexes is readily detected by ν(O–H) bands near 3400 cm^{-1} (nickel) and 3300 cm^{-1} (zinc). These bands are absent from the spectrum of the anhydrous copper complex. Bands within the range 3200–2900 cm^{-1} originate in

TABLE 24

Significant IR studies of substituted metal acetylacetonates

Complex	Metals	Range (cm^{-1})	Ref.
$[M(NA)_2]$	Cu	4000–650	94
	Ni	1000–400	95
	Ni, Cu, Pd (NCA)[a]	4000–20	96
	Ni, Cu	4000–50	107
$[M(SA)_2]$	Ni, Cu, Zn, Pd, Cd, Pb (NCA)[a]	1700–300	99
	Ni, Pd (Also Raman)	1700–50	101
	Ni, Pd (Resonance Raman)	1700–100	102
	Ni, Cu, Zn	4000–50	107
	Ni, (NCA)[a]	1700–350	104
$[M(SS)_2]$	Co, Ni	1700–400	103
	Co, Ni (NCA)[a]	1700–350	104
	Fe[b], Co, Ni, Pd, Pt (NCA)[a]	4000–300	105
	Co, Ni, Pd, Pt	Review	106
	Ni	4000–50	107
$[M(SeSe)_2]$	Ni (NCA)[a]	1700–350	104
$[M(SS)_3]$	Fe, Ru, Os	1700–300	108
	Co, Rh, Ir	1700–300	109

[a] Includes normal coordinate analysis. [b] Spurious compound [106].

TABLE 25

Point group symmetries (PGS) and expected number of IR-active metal–ligand modes for the complexes $[M\{CH_3C(X)CHC(Y)CH_3\}_2]$

M	X	Y	Structure	PGS	ν(M–X)	ν(M–Y)	δ(L–M–L)
$[M(AA)_2]$							
$Ni \cdot 2H_2O$	O	O	Trans octahedral	D_{4h}	1[a]	—	3[b]
Cu	O	O	Square planar	D_{2h}	2	—	3
$Zn \cdot H_2O$	O	O	Square pyramidal	C_{4v}	2[a]	—	3[b]
$[M(NA)_2]$							
Ni	O	NH	Trans square planar	C_{2h}	1	1	4
Cu	O	NH	Trans square planar	C_{2h}	1	1	4
$[M(SA)_2]$							
Ni	O	S	Cis square planar	C_{2v}	2	2	7
Cu	O	S	Cis square planar	C_{2v}	2	2	7
Zn	O	S	Tetrahedral	C_2	2	2	9
$[M(SS)_2]$							
Ni	S	S	Square planar	D_{2h}	2	—	3

[a] Also ν($M-OH_2$).

[b] Also δ($L-M-OH_2$).

the methyl groups while the δ-methine C–H stretches are weakly observed just above 3000 cm^{-1}.

The unique ν(N–H) bands of the [M(NA)$_2$] complexes occur near 3300 cm^{-1}. The considerable controversy concerning the ν(C=O) and ν(C=C) assignments has been discussed in Section B and it is now generally agreed that the band near 1600 cm^{-1} is ν(C=O) and that near 1500 cm^{-1} is ν(C=C) with a weak combination band between the two visible in some spectra. In support of these assignments is the absence of the band near 1600 cm^{-1} in the spectrum of [Ni(SS)$_2$] whereas the ν(C=C) band is present, as would be expected. Further bands unique to the complexes [M(NA)$_2$] occur near 1460 cm^{-1} [δ(N–H)$_{\text{ip}}$], 1380 cm^{-1} [ν(C–N)] and 830–800 cm^{-1} [δ(N–H)$_{\text{oop}}$].

For the [M(SA)$_2$] complexes, Chaston et al. [112] assigned ν(C–S) bands near 1200, 840 and 800 cm^{-1}. However, normal coordinate analysis of the complexes [M(SA)$_2$] [101] and [Ni(SS)$_2$] [104, 105] subsequently showed ν(C–S) to occur near 700 cm^{-1}. This is supported by the observation that the latter bands are markedly sensitive to metal ion substitution. The assignment is also in accord with studies on the IR spectra of dithiooxalato [113, 114], dithiooxamido [115] and xanthato [116] complexes where ν(C–S) has been found in the range 850–550 cm^{-1}. Clearly, the low frequency of the ν(C–S) mode implies largely single bonding between the carbon and sulphur atoms as has been proposed on other grounds [99].

The far-IR spectra of the complexes [M(NA)$_2$], [M(SA)$_2$] and [Ni(SS)$_2$] (Fig. 34) are most readily discussed in relation to those of the acetylacetonates (see Sections B, D and F) despite the fact that the nickel and zinc complexes incorporate coordinated water and are therefore not square planar.

Substitution of an oxygen atom of the acetylacetonate anion by the imino group –NH yields trans square planar complexes [M(NA)$_2$] with C_{2h} point group symmetry [94–96]. The spectra of [Cu(AA)$_2$] and [Cu(NA)$_2$] (both square planar) have very similar band patterns. The two νM–L bands expected for C$_{2h}$ symmetry are observed at 454 and 288 cm^{-1} in [Cu(AA)$_2$] and 463 and 277 cm^{-1} in [Cu(NA)$_2$]. In [Ni(NA)$_2$] which is also trans square planar, these bands occur at 481 and 315 cm^{-1}. Distinction between ν(Ni–O) and ν(Ni–N) has been made on the basis of the effect of deuterating the imino group [96] which decreases the wavenumber of the band of lower frequency only, indicating that this band (at 315 cm^{-1}) is ν(Ni–N). The band at 481 cm^{-1} is unaffected by deuteration of the imino group and is therefore ν(Ni–O). The corresponding bands in the spectrum of [Cu(NA)$_2$] have been similarly assigned, i.e. ν(Cu–O) at 463 cm^{-1} and ν(Cu–N) at 277 cm^{-1}. The bending mode assignments have been made by comparison between the spectra of [Cu(AA)$_2$] and [Cu(NA)$_2$] and then extended to the [Ni(NA)$_2$] complex.

TABLE 26

Frequencies (cm^{-1}) and assignments for IR bands in the spectra of the complexes [M(AA)$_2$], [M(NA)$_2$], [M(SA)$_2$] and [Ni(SS)$_2$]

[M(AA)$_2$]			[M(NA$_2$)]		[M(SA)$_2$]			[M(SS)$_2$]	Assignment
Ni	Cu	Zn	Ni	Cu	Ni	Cu	Zn	Ni	
3409		3300							ν(O−H)
			3283	3287					ν(N−H)
3074	3075	3070	3038	3034	3010		3014	3030	ν(C−H)[(γCH)]
2986	2992	2992	2985	2984	2978	2976	2973		ν(C−H)(CH$_3$)
	2960	2957	2951	2952			2950		
2920	2920	2919	2915	2915	2911	2911	2911	2920	
1652		1615							δ(O−H)
1605	1577	1598	1591	1587	1565	1573	1584		ν(C=O)
	1550		1553	1531	1520	1520	1552		combination
1518	1527	1510	1525	1522	1474	1491	1489	1491	ν(C=C)
			1475	1455					δ(N−H)
1461	1455	1455	1434	1435	1440		1439	1430	δ(C−H) deg def
1407	1415	1398			1420	1422	1413	1415	
			1382	1380					ν(C−N)
1360	1352	1368	1351	1349	1371	1352	1363	1348	δ(C−H) sym def
					1338	1337	1338		
1260	1272	1258	1244	1225	1234	1224	1225	1229	ν(C−C) + ν(C−CH$_3$)
			1229	1214	1227	1202			
1197	1187	1187	1188	1187	1117	1112	1112	1156	δ(C−H) ip
			1180	1176					
1019	1018	1017	1020	1015	1016	1013	1020	1009	ρ(CH$_3$)
			952	938					
					985	960	979	979	ρ(CH$_3$) + ν(C−S)
928	935	929	933	928	935	928	925	925	ν(C−CH$_3$) + ν(C = O)
			830	819					δ(N−H) oop
			808	811					
765	779	772	789	786	813	811		826	δ(C−H) oop
		769	755	756	809	806	805	801	
					720	711	703	747	ν(C−S)
675	682	653	703	686					Ring def + ν(M−L)
			681	647					
658	651	(653)			672	675		703	Ring def
			658	617	662	636	639	648	
589	611	570	623	582	642	614	615		Ring def + ν(M−O)
					620	570			
550	550	552	552	554	498	503	(499)	556	δ(C−CH$_3$) + ring def
		555							ν(Zn−O)
		433							ν(Zn−OH$_2$)
427	454	408	481	463	492	471	499		ν(M−O)
		388							

TABLE 26 (continued)

$[M(AA)_2]$			$[M(NA_2)]$		$[M(SA)_2]$			$[M(SS)_2]$	Assignment
Ni	Cu	Zn	Ni	Cu	Ni	Cu	Zn	Ni	
(427)	430	421	456	436					Ring def
			421	408					ν(M−L)
			361	334					
			315	277					ν(M−N)
275									$\nu(Ni-OH_2)$
255	288	239			409	387	398		ν(M−O)
					396	379	386	390	ν(M−S)
(255)	265	262	292	296	373	361	364	374	Ring def
					308	264	274	286	ν(M−S)
		210[a]	(234)[b]	230[b]			247	240	δ(L−M−L)
220	217	171	234	228	252	217	221	227	
195			195	185	196	184	197	216	
139	166								
107	102		100	103	149	147	152	149	Ring def oop
85	90	88	125	120	112	96	140	122	δ(L−M−L)
					84	85	91	95	
	74	81	75	74		78	78	82	Lattice + $\delta(CH_3)$ oop
60	60	66	60	67	53		62		

[a] This band has been assigned to a C−C−C bend since it is unaffected by ^{18}O or $^{64,68}Zn$ labelling [111].

[b] Assigned to $\tau(C-CH_3)$ [96].

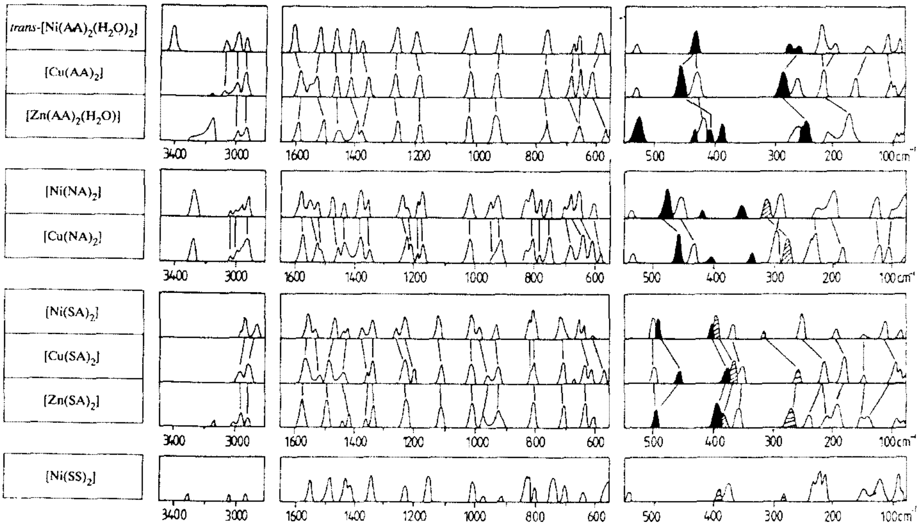


Fig. 34. IR spectra of the complexes $[M(AA)_2]$, $[M(NA)_2]$, $[M(SA)_2]$ and $[Ni(SS)_2]$.

It is interesting to note that the ν(M–L) assignments which have been proposed exhibit the sequence ν(Ni–O) > ν(Cu–O) and ν(Ni–N) > ν(Cu–N). This sequence is the opposite of that experienced for octahedral complexes in which the copper complex is stabilized by Jahn–Teller distortion such that ν(Ni–L) < ν(Cu–L). In square planar symmetry the stability sequence ν(Ni–L) > ν(Cu–L) is expected because the additional electron of the copper complex is antibonding.

Considering now the complexes [M(SA)$_2$] (M = Ni, Cu, Zn), the nickel and copper derivatives are cis square planar (C_{2v} symmetry), increasing the complexity of the far-IR spectra relative to the complexes of (NA) and (AA). The zinc complex is tetrahedral (C_2 symmetry) [101]. In all three complexes of formula [M(SA)$_2$] (M = Ni, Cu, Zn) two ν(M–O) and two ν(M–S) bands are expected to occur. Siimann et al. [101] assigned a doublet at 498, 492 cm^{-1} to δ(C–CH$_3$) + ring deformation in the spectrum of [Ni(SA)$_2$] but Bennett et al. [107] found that the 498 cm^{-1} component was insensitive to substitution of nickel by copper while the 492 cm^{-1} component was shifted to lower frequency ($\Delta\nu$ = 21 cm^{-1}) by copper substitution, suggesting that the latter component is ν(Ni–O). Again, the observed sequence ν(Ni–O) > ν(Cu–O) is expected for square planar structure, thus supporting the assignment proposed. In the spectrum of the tetrahedral zinc complex, Siimann et al. [101] proposed that a band near 640 cm^{-1} be assigned to ν(Zn–O). However, this band is less sensitive to metal ion substitution than others at lower frequency which are therefore preferentially assigned to ν(Zn–O) [107].

Bands at 410 and 396 cm^{-1} in the spectrum of [Ni(SA)$_2$] are shifted to 387 and 379 cm^{-1} by copper substitution. These have been assigned to ν(M–O) and ν(M–S) respectively [107]. Again, the expected sequence ν(Ni–L) > ν(Cu–L) is observed. A further band at 308 cm^{-1} in the nickel complex is also metal sensitive in the sequence nickel > copper. It has therefore been assigned to a further ν(M–S) band [107]. In this way the two ν(M–O) and two ν(M–S) bands expected for the C_{2v} symmetry of these cis square planar complexes have been accounted for. In the tetrahedral [Zn(SA)$_2$] complex, the two ν(Zn–S) bands occur at 386 and 274 cm^{-1}.

The square planar complex [Ni(SS)$_2$] with D_{2h} point group symmetry is expected to yield two ν(Ni–S) bands. Accordingly, the region 550–400 cm^{-1}, where ν(M–O) bands were observed in the spectra of the [M(NA)$_2$] and [M(SA)$_2$] complexes, is free from any IR bands in the spectrum of [Ni(SS)$_2$]. Bands at 390 and 286 cm^{-1} have been assigned to ν(Ni–S) on the basis of normal coordinate analysis [104, 105]. Comparison with the spectrum of [Ni(SA)$_2$] supports these assignments since ν(Ni–S) bands in the latter complex were found at similar frequencies of 396 and 308 cm^{-1}. Bands at 240, 227 and 216 cm^{-1} in the spectrum of [Ni(SS)$_2$] are clearly δ(S–Ni–S) bends, occurring at approximately half the frequency of the corresponding stretches.

The spectra of the complexes $[M(SA)_2]$ and $[M(SS)_2]$ (M = Pd, Pt) are very similar [99,105] to those of their nickel analogues so assignments are straightforwardly made. The ν(M–O) and ν(M–S) frequencies are in the expected sequence of platinum > palladium > nickel. The complex $[Ni(SeSe)_2]$ has a spectrum which is very similar to that of $[Ni(SS)_2]$ but the Ni–Se stretching frequencies have not been reported [104].

Finally, the complex $[Co(SS)_2]$ is of interest since its square planar structure yields an expected stability sequence cobalt > nickel for the unusual pair of square planar complexes $[M(SS)_2]$ (M = Co, Ni) [117]. Therefore we may anticipate that the sequence of metal–sulphur stretching frequencies would also be in the sequence ν(Co–S) > ν(Ni–S). From the data of Siimann and Fresco [105], this is true for the ν(M–S) band near 300 cm^{-1} where ν(Co–S) is at 292 cm^{-1} compared with ν(Ni–S) at 286 cm^{-1} but not for the ν(M–S) band near 400 cm^{-1}. This feature suggests that the ν(Co–S) assignments warrant further investigation.

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