*The Infra-red Spectra of Chelate Compounds. Part II.** *Metal Chelate Compounds of β-Diketones and of Salicylaldehyde.*

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The carbonyl absorptions of metal chelate compounds of β-diketones are not wholly dependent upon the double-bond strength of the enol, and no direct relation could be traced between these frequencies and the stabilities of copper complexes with various ligands. A linear relation exists, however, in the case of chelate compounds of salicylaldehyde with different bivalent metals. In more symmetrical structures the frequency differences are much reduced so that, although the carbonyl frequencies of chelate compounds of α-thenoyltrifluoroacetone can be shown to follow the expected order of stability, the values for acetylacetone chelate compounds are essentially the same for all metals. The reasons for this are discussed.

Very little work is recorded on the infra-red spectra of metal chelate compounds although the visible absorption spectra have been used by several workers in the study of bond types. Thus, Plumb, Bersworth, and Martell (*J. Phys. Coll. Chem.*, 1950, **54**, 1208) have shown that ionic metal complexes of ethylenediaminetetra-acetic acid show a shift of the visible absorptions to higher frequencies which is proportional to the stability of the chelate compound formed. Barnes and Dorough (*J. Amer. Chem. Soc.*, 1950, **72**, 4045) found a similar shift in alkali-metal porphine derivatives, which contrasts with a shift in the opposite direction shown by other porphine chelate compounds, such as those of copper and zinc in which the bonds are largely covalent. On the other hand, McKenzie, Mellor, Mills, and Short (*J. Proc. Roy. Soc. N.S. Wales*, 1944, **78**, 70) found very little difference between the visible spectra of acetylacetone and its nickel chelate derivative, and Geyer and Smith (*J. Amer. Chem. Soc.*, 1941, **63**, 3071) found that chelate compounds of 1-hydroxyanthraquinone show similar absorption frequencies but considerable differences in intensity.

In the infra-red field interest has been centred almost wholly on the acetylacetone complexes which have been studied by Morgan (U.S. Atomic Energy Commission, 1949, No. 12,569, p. 16), by Lecomte (*Discuss. Faraday Soc.*, 1950, **9**, 125), and by Duval *et al.* (*Compt. rend.*, 1950, **231**, 272; *Bull. Soc. chim.*, 1952, 106). Bellamy, Spicer, and Strickland (*J.*, 1952, 4653) also examined a few acetylacetone complexes and some derivatives of curcumin. In all these cases, however, interest has been centred on the structure of the ligand and no work has been done on the possible use of infra-red measurements in relation to the character or stability of the chelate bonds.

It has been shown (Part I *) that in hydrogen-bonded chelate compounds of β-diketones the carbonyl frequency is determined almost wholly by the character of the adjacent double bond. In the case of metal chelate compounds, however, in which the metal cannot be co-linear with the oxygen atoms other factors will operate. Thus the O · · · · O distances might change with alterations in the covalent or ionic radii of the metal atoms, and they should also depend to some extent on the configuration of the metal atom. For example, chelate rings with different angles might be expected from square and from tetrahedral structures. These changes would be expected to be reflected in the infra-red spectra and in particular in the carbonyl frequencies and we have made a preliminary examination of a number of metal chelate compounds from this point of view. In the first instance we have sought to find whether any relation exists between the stability of chelate compounds and these absorption frequencies and have examined a series of copper chelate compounds with a number of different β-diketone ligands. Changes following alteration of the metal atom have also been studied in three different ligands, and the results obtained form the subject of this communication.

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* Part I, preceding paper.

EXPERIMENTAL

Spectra were obtained by means of a Perkin-Elmer 21B recording spectrometer with a rock-salt prism. Samples were examined in chloroform solution in 0·4 mm. cells, a similar cell containing solvent being used in the reference beam. Samples which were not soluble in chloroform were examined as pastes in paraffin oil. The results obtained are given in the tables and are discussed below. In all cases in which more than a single band has appeared in the expected region the carbonyl absorption has been identified with that having the greatest intensity. This follows the observation by Rasmussen, Tunnicliff, and Brattain (*J. Amer. Chem. Soc.*, 1949, **71**, 1068) that the intensities of carbonyl absorptions in resonance chelated β-diketones were greater than those of normal carbonyl absorptions by a factor of at least 100.

DISCUSSION

(a) *Copper Chelate Compounds with Various* β*-Diketone Ligands.*—The copper complexes of β-diketones differ from the parent hydrogen-bonded materials in a number of important respects. In particular, as has been shown by earlier workers on acetylacetone complexes, the complete resonance between forms (I) and (II) leads to a modification of the character of both the C=O and C–O links. As a result both take on an intermediate double-bond character. Two bands of approximately equal intensity are shown in the spectra and, by analogy with the ionised carboxyl group, these have been assigned by Lecomte (*loc. cit.*) to the asymmetric and symmetric vibrations of these two groups. The splitting of the carbonyl absorption in this way prevents the direct application of the equation derived by Hunsberger, Ketcham, and Gutowsky (*J. Amer. Chem. Soc.*, 1950, **72**, 5626) relating the shift of the carbonyl absorption and the proportions of the canonical forms. It is, however, interesting to find that if the mean value of the two observed frequencies is substituted in this equation the values for the proportions of (I) and (II) in the β-diketones listed in Table 1 lie close to the 50 : 50 equilibrium which would be expected. Salicylaldehyde is an exception as only one strong band is shown, presumably indicating that owing to the weaker double bond involved the resonance is less complete.

(I)

(II)

TABLE 1. *Copper chelate compounds : carbonyl frequencies (cm.$^{-1}$) measured in dilute chloroform solutions.*

Ligand		
Acetylacetone	1580	1389
Salicylaldehyde	1608	—
α-Thenoyltrifluoroacetone	1570	1309
Benzoylacetone	1550	1389
Dibenzoylmethane	1524	1391
Ethyl 2-oxo*cyclo*hexanecarboxylate	1590	1290
Ethyl 1-oxotetralin-2-carboxylate	1592	1287
2-Formyl*cyclo*hexanone	1592	1353
Acetoacetic ester	1570	1282

The frequencies found in this region which can be assigned to the vibrations of the modified C=O and C–O groups are listed in Table 1. It will be seen that the double-bond character of the enol bond no longer plays the dominant role in determining the frequency which it appears to do with hydrogen chelate compounds (Part I). Conjugation effects, for example, clearly influence the frequency considerably as shown by the series of copper complexes of acetylacetone, benzoylacetone, and dibenzoylmethane. However, there is no obvious relation between these frequencies and the stabilities of the corresponding chelate compounds, which in these compounds are very similar (Van Uitert, Thesis, Pennsylvania State Coll., 1951).

(b) *Metal Chelate Compounds of Salicylaldehyde.*—Chelate compounds of salicylaldehyde differ from those of β-diketones in not showing any second C–C absorption comparable in intensity with the first, and in some cases the carbonyl absorption is not far removed from that of salicylaldehyde itself. It therefore appears reasonable to conclude that in these cases the carbonyl group retains at least a proportion of its original character and that interference from coupling effects is relatively small. The values for this carbonyl frequency for a variety of metals are given in Table 2. The metals chosen were those for which reliable stability constants are available from the work of Mellor and Maley (*Nature*, 1947, **159**, 370; 1948, **161**, 436) but cadmium, iron, and manganese were omitted as there appears to be some doubt as to whether they are disalicylaldehyde complexes.

It will be seen that the carbonyl shifts follow the order Pd > Cu > Ni > Co > Zn > Mg, which is the usual order of stabilities for bivalent-metal complexes, and when the carbonyl frequencies are plotted directly against the stabilities (log K_1K_2) given by Mellor and Maley (*loc. cit.*) a straight line relation is found (Fig. 1). It should therefore be possible to utilise infra-red measurements to determine directly the stabilities of other chelate compounds of bivalent metals with salicylaldehyde. In addition a plot of atomic number against carbonyl frequency results in a curve (Fig. 2) which is similar in shape to that derived by Irving and Williams (*Nature*, 1948, **162**, 746). They have shown that the stability constants of a number of bivalent-metal chelate compounds follow the same trend in relation to atomic number, and show a gradual increase through a transition series to copper, followed by a fall at zinc which is the first member of the series which is unable to form octahedral d^2sp or square dsp^2 orbitals.

FIG. 1.

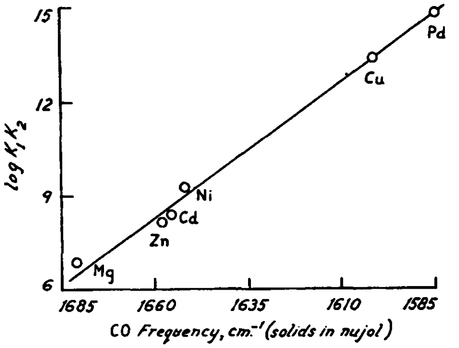

FIG. 2.

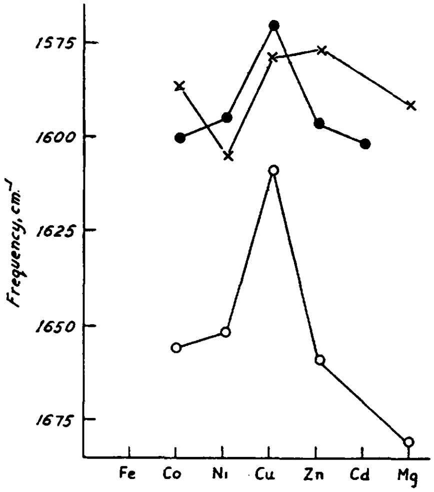

TABLE 2. *Carbonyl frequency (cm.⁻¹) of metal chelate compounds.*

	Salicylaldehyde *	Thenoyltrifluoroacetone †		Acetylacetone †	
Copper	1608	1570	1309	1580	1390
Cobalt	1656	1600	1305	1586	1373
Nickel	1652	1595	1266	1605	1389
Magnesium	1681	—	—	1590	1397
Zinc	1658	1597	1297	1577	1375
Iron	—	1575	1305	1575	1370
Cadmium	1585	1603	1287	—	—
Palladium	—	—	—	—	—

* Determined on paraffin pastes of the solids. † Chloroform solutions.

(c) *Metal Chelate Compounds of α-Thenoyltrifluoroacetone.*—The coupling effects observed in the copper chelate compounds with differing ligands come into play also with the metal chelate compounds of α-thenoyltrifluoroacetone. Two bands of about equal intensities are shown which correspond to modified C=O and C–O vibrations, and the separation of them is notably greater than in the acetylacetone complexes (see Table 2). This may perhaps indicate that the dissymmetry introduced by the thenoyl group and especially by the trifluoromethyl group results in their retention at least to a small extent of some measure of their original characters. The differences between the frequencies of the first of these two bands with different metals are very much less than those given by salicylaldehyde chelate compounds but it will be seen from Fig. 2 that they still follow the Irving and Williams's (*loc. cit.*) general stability pattern. Very few data are available on the absolute stability constants of these compounds but it is in any case doubtful whether the frequency differences are sufficiently great to permit of their use as a measure of stability.

(d) *Metal Chelate Compounds of Acetylacetone.*—As will be seen from Table 2 the frequencies of the first carbonyl absorption in metal acetylacetone complexes are essentially the same and only nickel and magnesium show any departure from the common value. Resonance effects are clearly operating sufficiently strongly to dwarf any variations in frequency which might have been expected to follow alterations on the metal. This finding is supported by the spectra obtained by Lecomte (*loc. cit.*) and the other workers cited, all of whom found that the first carbonyl absorption in acetylacetone derivatives of bivalent metals lie at about the same frequency. The second carbonyl absorption, near 1400 $cm.^{-1}$, shows rather more variation but shows no obvious relation with the stability.

Conclusions.—It appears, therefore, that no direct correlation between infra-red absorption frequencies and chelate stability exists in the β-diketones, despite the fact that there is a linear relation between these factors for salicylaldehyde derivatives. This is almost certainly due to the increased resonance and coupling effects occurring in β-diketones rather than to any difference in the type of linkage involved. The insolubility of the salicylaldehyde compounds in organic solvents might well be taken to indicate the presence of a more ionic type of linkage in these cases but the weight of evidence from magnetic and other measurements indicates that the vast majority of the β-diketone chelates are also ionic. In some ways the present findings are similar to those of workers on the acetylacetone compounds and other chelate compounds in the visible spectrum, and it may be that as with the visible spectra of 1-hydroxyanthraquinone derivatives the differences produced by variations in the metal will be more clearly shown in a careful comparison of the relative intensities of the carbonyl absorptions rather than by their absolute frequencies.

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