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DIVALENT TRANSITION METAL β-KETO-ENOLATE COMPLEXES AS LEWIS ACIDS

D. P. GRADDON

School of Chemistry, University of New South Wales, Kensington, N.S.W. (Australia)

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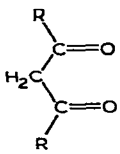
ABBREVIATIONS

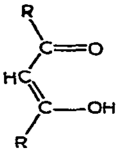
py = pyridine
2-mepy = 2-methylpyridine (2-picoline)
4-mepy = 4-methylpyridine (4-picoline)
2,6-me_2py = 2,6-dimethylpyridine (2,6-lutidine)
acac = acetylacetone
phen = 1,10-phenanthroline

A. INTRODUCTION

β-Diketones and related compounds capable of exhibiting keto-enol tautomerism (I, II) react with metal cations to form complexes, in which the metal replaces the enolic hydrogen and a six-membered chelate ring is produced (III)



I



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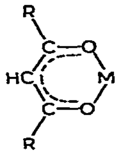


III

Since the enolate ion carries a single negative charge, divalent metal atoms react with two enolate ions to give neutral molecules, ML_2 (LH = β-diketone), in which there are four donor oxygen atoms to each metal atom. If the normal coordination number of the metal towards oxygen atoms is four, the result is an inner complex, or neutral molecule. The complexes formed by beryllium are typical examples and are usually comparatively low-melting solids, soluble in organic solvents; the beryllium atom is coordinately saturated.

The larger divalent ions of transition metals usually have coordination numbers towards oxygen greater than four. The neutral molecules, ML_2, then behave as Lewis acids, forming addition compounds with bases such as water, ammonia, pyridine or additional enolate ions. In these cases the normal preparative methods for β-keto-enol complexes give hydrates; for example β-diketone complexes of cobalt(II) and nickel(II) are usually obtained as dihydrates, $ML_2(H_2O)_2$, in which the coordination number of the metal atom is raised to six. Numerous examples of such complexes have been reported in the literature; the following series, derived from metal acetylacetonates[1] serve as examples:

$ML_2(NH_3)_2$, M = Mn, Co, Zn, Cd, Mg
$ML_2 \cdot py_2$, M = Co, Ni
$ML_2 \cdot bipy$, M = Mn, Co, Ni, Zn, Cd
$ML_2 \cdot phen$, M = Mn, Co, Ni, Zn, Cd
ML_3^-, M = Mn, Fe, Co, Ni, Zn, Cd, Mg

Removal of water from the hydrated complexes or of base from the base adducts leaves the anhydrous complex, ML_2, as a highly reactive Lewis acid; it also contains oxygen atoms, which are potential Lewis bases, and varying degrees of self-association have been observed, in which the coordination number of the metal atom is raised to five or six.

The literature on metal β-keto-enol complexes is now very extensive and a number of reviews of various aspects of this chemistry has appeared in recent years[2–7]. The present article will be restricted to a survey of the behaviour of the transition metal complexes ML_2 from manganese to zinc as Lewis acids and the way in which variation of the metal atom and the structure of the β-diketone affects this behaviour.

B. SELF-ASSOCIATION

Evidence for self-association of the anhydrous β-diketone complexes, ML_2, in solution has been obtained from determination of molecular weights and from variations in magnetic and spectroscopic properties. Association in the solid state is suggested by the much greater heats of sublimation of the cobalt(II) and nickel-(II) complexes of acetylacetone and some other β-diketones than of the corresponding complexes of beryllium(II), aluminium(III) and iron(III), in which the metal atom is coordinately saturated; data are given in Table 1.

TABLE 1

MELTING POINTS, SUBLIMATION TEMPERATURES AND MOLAR HEATS OF SUBLIMATION OF METAL ACETYLACETONATES[8]

Complex	*M.p., °C*	*Sub., °C*	*ΔH, Kcal. g-at^{-1}*
BeL_2	108	37	8.51
AlL_3	112	74	4.58
FeL_3	179	69	4.67
CoL_2	sub. > 120	100	15.0
NiL_2	d. 230	185	16.5
CuL_2	d. 230	72	–

The occurrence of self association is confirmed by X-ray analyses of the acetylacetonates of cobalt, nickel and zinc.

(i) Zinc, manganese

The structures of the zinc and manganese complexes are of interest as providing evidence for the sort of structures which may be expected in the absence of crystal-field effects.

Remarkable confusion has arisen between hydrated and anhydrous bis(acetylacetonato)zinc(II). The compound was first prepared by Gach in 1900,[9] who showed that on heating it could be vapourised, the vapour density corresponding to the formula $(C_5H_7O_2)_2Zn$. It was reported again in 1908 as forming yellow crystals, m.p. 130°, with the normal, monomeric, molecular weight in ethanol[10]. A white, crystalline compound, m.p. 138°, was obtained in 1914 by Morgan and Moss[11], who concluded that it was anhydrous on the basis of a metal analysis. Since that time anhydrous bis(acetylacetonato)-zinc(II) appears to have been accepted as a well documented compound, described by Sidgwick[12] as "not being hydrated even when crystallised from water". However, when preparing the compound in 1960 for X-ray analysis, Lippert and Truter[13] observed that their main product was in fact the monohydrate $(C_5H_7O_2)_2Zn(OH_2)$ and the properties of this have since been shown to correspond with those of the so-called anhydrous compound of earlier reports[14].

Anhydrous bis(acetylacetonato)zinc(II) can be readily obtained from the hydrate by heating in an oven at 105°, or in a drying pistol over phosphorus pentoxide at 60° or by azeotropic removal of water from a toluene solution; it is a white solid, m.p. 152° with decomposition, and with normal molecular weight in the non-donor solvents triphenylmethane, diphenyl and diphenylamine[14]. Preliminary X-ray investigation suggested that the anhydrous compound was probably trimeric in the solid state[15] and this has since been confirmed by single crystal analysis[16].

The structure of the trimer is based on a central 6-coordinate, approximately octahedral zinc atom, flanked by 5-coordinate, approximately trigonal-bipyramidal zinc atoms. The octahedron shares edges with the two trigonal bipyramids (Fig. 1).

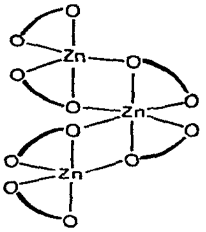


Fig. 1. Trimeric molecule of bis(acetylacetonato)zinc(II).

By contrast with bis(acetylacetonato)zinc(II), bis-(dipivaloylmethanato)-zinc(II), purified by vacuum sublimation, has been found to be monomeric and tetrahedral in the solid state[17]. In this molecule the chelate rings are symmetrical; details of bond angles and lengths are shown in Fig. 2.

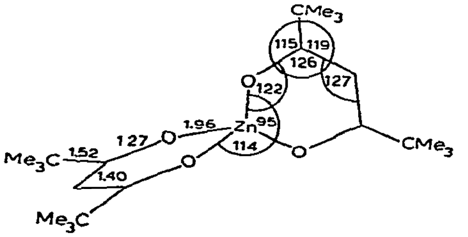


Fig. 2. Bond angles and distances (A.u.) in tetrahedral molecule of bis(dipivaloylmethanato)-zinc(II).

No other zinc complexes of β-diketones have been examined by X-ray methods, but bis(benzoylacetonato)zinc(II) and bis(dibenzoylmethanato)zinc(II) have been shown to be monomeric, and presumably tetrahedral, in non-donor solvents[18,19].

The only β-diketone complex of manganese(II) to have been studied is bis-(acetylacetonato)manganese(II), obtained readily by dehydration of the dihy-

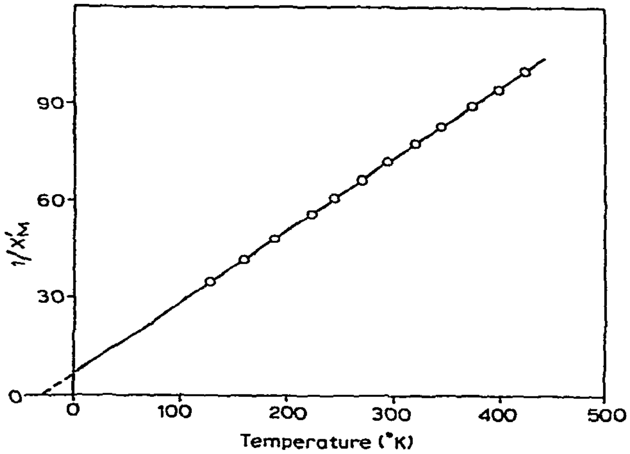


Fig. 3. Magnetic susceptibility of bis(acetylacetonato)manganese(II) from 120–420 °K.

drate[20]. The structure of the solid has not been determined but the compound has a molecular weight corresponding to a trimer in hydrocarbon solvents. The magnetic moment of 5.68 Bohr magnetons at 17° is far enough below the spin-only value of 5.92 to suggest possible anti-ferromagnetic interaction, but variation of the temperature over the range 128–418 °K reveals only a slight decrease[21], consequent upon following a Curie–Weiss law with $\theta = -25°$, and any significant degree of spin pairing must occur at temperatures below this range (Fig. 3).

(ii) Copper

A very large number of copper(II) complexes is known with β-diketones, β-ketoesters and related compounds. Typically they are neutral compounds, insoluble in water, soluble to some extent in organic solvents and monomeric in solution, blue to green in colour or sometimes bronzy, with magnetic moments in the range 1.8–2.0 Bohr magneton. Many of these compounds are extremely stable; bis(acetylacetonato)copper(II), for example, can be sublimed at atmospheric pressure, and electron diffraction studies are consistent with a planar molecular structure in the vapour phase[22].

In the crystalline compound[23,24] the molecules are also planar, but are packed in the crystal so that there is weak interaction between the copper atoms of one molecule and the middle carbon atoms of the chelate rings of neighbouring molecules; the chelate rings are slightly distorted out of the CuO_z plane[31] so as to bring these carbon atoms closer to the copper atoms (Fig. 4). This weak interaction can be considered as arising from attraction of the carbon p_z electrons by the neighbouring copper atom.

Similar close approaches between the copper atom of one molecule and the

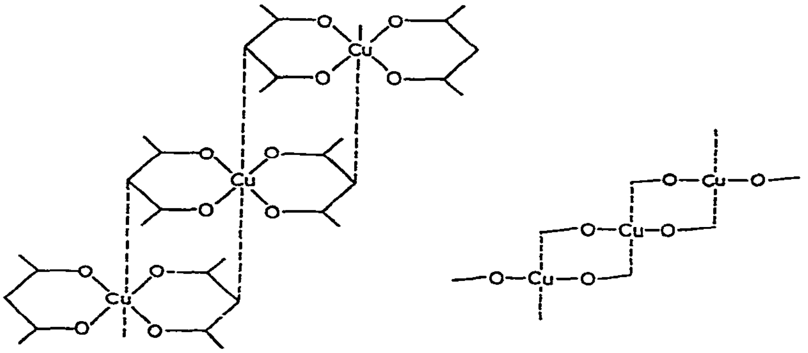


Fig. 4. Arrangement of molecules of bis(acetylacetonato)copper(II) in crystal.

middle carbon atoms of the chelate rings of neighbouring atoms have been observed in a variety of other β-diketone complexes of copper(II) and are summarised in Table 2. These results have been variously interpreted as showing weak intermolecular bonding or not showing it. In the case of bis(salicylaldehydato)copper(II), two forms have been obtained; in one of these the fifth and sixth coordination sites of the copper atoms are occupied by the aromatic rings of neighbouring molecules and in the other by phenolic oxygen atoms. In bis(dibenzoylmethanato)copper(II) and bis(dipivaloylmethanato)copper(II), on the other hand, these sites are vacant and these compounds are undoubtedly truly 4-coordinate planar complexes. Planar molecules have also been observed in bis(tropolonato)copper(II), and in this case intermolecular interaction possibly occurs with a neighbouring C_7 ring.

TABLE 2

DISTANCES OF NEAREST NEIGHBOURS (A.u.) IN COPPER(II) β-DIKETONE TYPE COMPLEXES, CuL_2

Ligand, LH	*2 O*	*2 O*	*Neighbour*	*Dist.*	*Ref.*
Acetylacetone	1.92	1.92	3-carbon	3.08	24
3-Methyl-acac	1.91	1.91	3-carbon	3.22	31
3-Phenyl-acac	1.91	1.91	3-carbon	3.5	26
Benzoylacetone	1.91	1.93	3-carbon	3.02	25
Dibenzoylmethane	1.91	1.91	none	–	30
Ethyl acetoacetate	1.91	1.91	3-carbon	3.12	27
Salicylaldehyde	1.86	1.98	arom. ring	3.21	28
Salicylaldehyde	1.90	1.94	phenolic O	3.15	29
Tropolone	1.83	1.98	C_7 ring	~3.3	33

Reflectance spectra of the solid compounds show a broad absorption in the visible region with two maxima near 15,000 and 17,500 cm^{-1}, separated by a shallow trough from high-intensity absorption in the near ultraviolet (Fig. 5). Single crystal polarized spectra reveal three or four components of the broad, double-

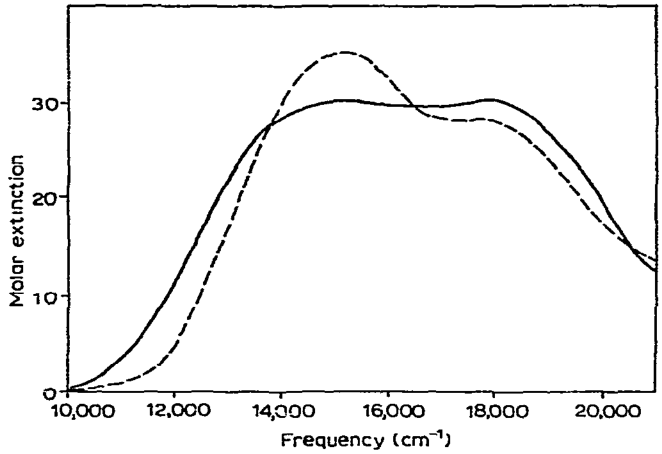


Fig. 5. Absorption spectra of bis(acetylacetonato)copper(II) in chloroform solution,——, and in the solid state----.

peaked enveloped in the 14,000–19,000 cm^{-1} region and detailed assignments of these bands to appropriate d → d transitions are still the subject of controversy[34–44] In the near ultra-violet there is a band of medium intensity near 26,000 cm^{-1}, almost certainly not a ligand-field band. At higher frequencies there are high-intensity bands, characteristic of the ligands.

These features are preserved when the compounds are dissolved in non-donor solvents, such as benzene and chloroform, the solution spectra being almost identical with the reflection spectra and only slightly affected by variation of solvent. This can be taken as evidence of the preservation of essentially planar mole-

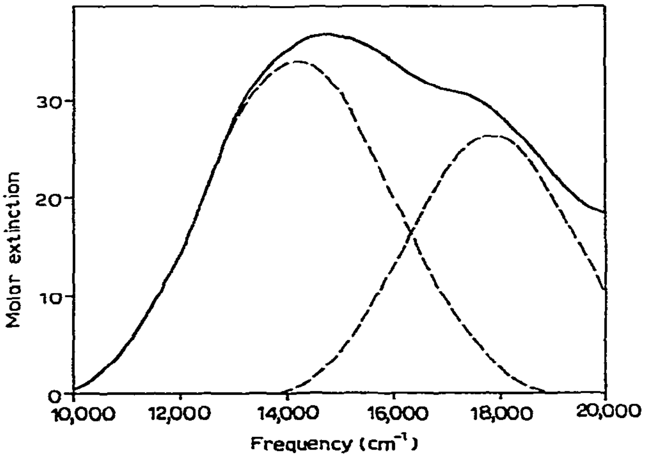


Fig. 6. Analysis of the absorption spectrum of bis(ethylacetoacetato)copper(II) in benzene solution into two Gaussian components.

cules in solution and also of the very small contribution made by intermolecular interactions to the ligand-field in the crystalline compounds.

Various authors have resolved the solution spectra into two, three or four Gaussian components in attempts to establish the number of d → d transitions involved. It is, however, possible to resolve any of these spectra into only two Gaussian components with maxima about 15,000 and 17,500 cm^{-1}, $\varepsilon \sim 30$ (Fig. 6), and as any Gaussian curve can itself be resolved into any number of others, resolutions into more than two components are probably meaningless; this does not, of course, mean that there are only two d → d absorption bands contained within the envelope, but simply that the experimental resolution is not capable of producing *unique* results for any number of Gaussian components greater than two.

TABLE 3

FREQUENCIES (CM^{-1}) AND EXTINCTIONS OF ABSORPTION BANDS RESOLVED INTO TWO COMPONENTS

Ligand	*Solvent*	ν_1	ε_1	*Width*	ν_2	ε_2	*Width*	*Ref.*
Acetylacetone	$CHCl_3$	15,190	34	3380	18,810	26	3920	34
Acetylacetone	C_6H_6	14,900	37	3400	18,600	33	3800	41
3-Methyl-acac	C_6H_6	15,100	40	3500	19,200	41	3800	41
3-Benzyl-acac	C_6H_6	15,100	44	3400	19,300	45	4000	41
3-Phenyl-acac	C_6H_6	15,300	49	3700	19,300	47	3500	45
Benzoylacetone	$CHCl_3$	14,800			18,600			36
Dibenzoylmethane	$CHCl_3$	14,900	39	4100	18,200	40	3300	46
Ethyl acetoacetate	$CHCl_3$	14,500			18,000			35
Ethyl acetoacetate	C_6H_6	14,300	34	4000	17,800	26	3600	36
Ethyl benzoylacetate	$CHCl_3$	14,400	30	3600	17,800	30	4300	46
Salicylaldehyde	$CHCl_3$	14,400	45	3400	17,300	35	3100	47

When the absorption spectra are resolved into only two components, their frequencies can be taken to give an indication of the strength of the ligand-field; this varies little from one ligand to another and there is no obvious relationship between the structure of the ligand and the frequencies of the components absorption bands. Table 3 gives some results of resolutions into two component bands.

(iii) Nickel

Anhydrous bis(acetylacetonato)nickel(II) can be obtained from the dihydrate by azeotropic distillation with toluene or by sublimation *in vacuo*. It is a green solid, magnetic moment 3.15–3.22 Bohr magneton over the temperature[48] range 20–200°. The paramagnetism of the compound was for long interpreted as indicating a tetrahedral molecule[49], but crystal structure determination has revealed a trimeric molecule in which NiO_6 octahedra share faces[50] (Fig. 7). This structure leads to ferromagnetic interaction of the nickel atoms at low temperatures, so that the magnetic moment per nickel atom rises to 4.1 Bohr magneton at 4.3 °K (ref. 51).

The reflectance spectrum of the solid is typical of octahedral high-spin nickel(II), the main features being two absorption bands at 8480 and 15,000 cm^{-1}; this spectrum is almost identical with that of the dihydrate[52]. Solution spectra in non-donor solvents are similar (Fig. 8) and molecular weight measurements in benzene and triphenylmethane[53,54] show that the trimeric molecule is preserved in these solvents.

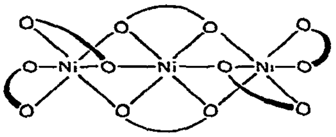


Fig. 7. Trimeric molecule of bis(acetylacetonato)nickel(II).

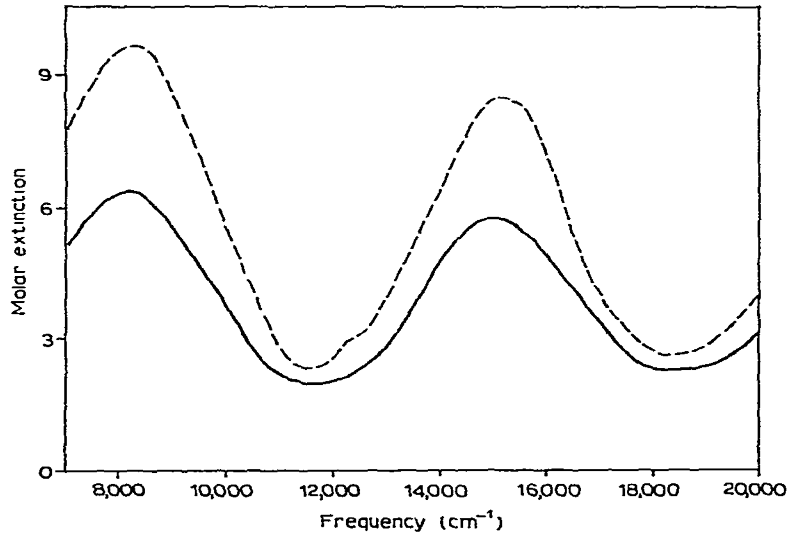


Fig. 8. Absorption spectra of anhydrous bis(acetylacetonato)nickel(II) in toluene solution,——, and in the solid state,- - - -.

In solutions in diphenylmethane at high temperatures, above 150°, a new absorption band about 18,000 cm^{-1} begins to appear, attributable to the low-spin, monomer[55] and electron-diffraction studies of the vapour at 170° show that this consists of planar, monomeric molecules[56]. The behaviour of bis(acetylacetonato)-nickel(II) in a variety of circumstances can thus be represented as an equilibrium:-

$$\begin{array}{ccc} Ni_3L_6 & \rightleftharpoons & 3NiL_2 \\ \text{high-spin} & & \text{low-spin} \\ \text{Ni, octahedral} & & \text{Ni, planar} \end{array}$$

where LH = acetylacetone.

Many other nickel(II) β-diketone complexes exhibit a similar high-spin/low-spin equilibrium, but the position of the equilibrium at room temperature varies considerably from one compound to another. In extreme cases only one form may be known whatever the conditions. Thus bis(trifluoroacetylacetonato) nickel(II) is known only in the green form[8] and bis(dipivaloylmethanato)nickel(II) only in the red, low-spin form[32,57,58]; in some other cases both forms have been isolated. The two forms can be readily distinguished by their colour, absorption spectra and magnetic properties. The high-spin forms with $\mu_{eff} \sim 3.1$ Bohr magneton are green with absorption bands near 9000 and 15,000 cm^{-1} ($\varepsilon < 20$), of which only the second has been observed in most cases, due to instrumental limitations. The trimeric nature of these compounds has been established, not only by the crystal structure of the acetylacetonate, but also by molecular weight determinations of this compound and the benzoylacetonate[59] and equilibrium studies on the 3-ethyl- and 3-benzyl-acetylacetonates[60].

The low-spin forms, with $\mu_{eff} = 0$, are reddish in colour, with a single absorption band about 19,000 cm^{-1} ($\varepsilon \sim 40$) appearing on the tail of high-intensity absorption in the near ultraviolet. The planar structure of these compounds has been established by X-ray analysis[32] of bis(dipivaloylmethanato)nickel(II), for which details of bond lengths and angles are shown in Fig. 9.

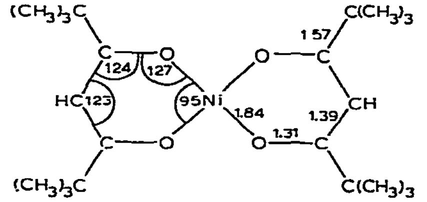


Fig. 9. Bond angles and distances in planar molecule of bis(dipivaloylmethanato)nickel(II).

The properties of most of the known complexes of this type are summarised in Table 4, in which the ligands are arranged in order of decreasing acidity. The Table shows clearly the relationship between ligand donor strength, expressed as pK_a, and the properties of the nickel complexes. When $pK_a < 13.5$ only the high-spin form of the nickel complex can be obtained whilst when $pK_a > 14.2$ only the low-spin form occurs; between these limits it is often possible to isolate both forms and it is in these cases that an equilibrium mixture of the two forms is obtained in solution in non-donor solvents at room temperature. An exception to these generalisations is provided by the complex with dimesitoylmethane which is known only in the red, low-spin form despite the comparatively low pK_a of 12.48; in this case it seems likely that polymerisation, necessary to stabilise the high-spin form, is sterically prevented by the very bulky mesityl groups. Steric interference to poly-

TABLE 4

PROPERTIES OF NICKEL(II) β-KETO-ENOL COMPLEXES AT ROOM TEMPERATURE

Ligand LH	*pK_a**	*NiL_2 colour*	*Solid μ_{eff}*	*NiL_2 solvent*	*Solution $\nu(cm^{-1})$*	*ε*	*Ref.*
$CH_3COCH_2COCF_3$	8.83	green					8
$C_6H_5COCH_2COCF_3$	9.14	green					8
2-Acetylcyclopentanone	11.60	green	3.14	xylene	15,000	4.7	61
2-Benzoylindanone	12.23	green	3.25	benzene	14,800	11	61
Dimesitoylmethane	12.48	red	0	toluene	18,700	42	62
$CH_3COCH_2COCH_3$	12.70	green	3.15	C_6H_{12}	15,000	9	79
$C_6H_5COCH_2COCH_3$	12.85	green	3.22	xylene	14,900	–	59
$C_6H_5COCH_2COC_6H_5$	13.75	green brown	3.2 0	benzene	14,800	–	61
$CH_3COCHC_6H_5COCH_3$	13.76	red	0	toluene	18.700	42	55
$(CH_3)_2CH.CO.CH_2CO.–CH(CH_3)_2$	13.94	green	3.41	toluene	15,200	–	58
2-Acetylcyclohexanone	14.1	green red	3.10 0	$CHCl_3$	18,900	41	61
2-Acetylcycloheptanone	14.1	green red	3.13 0	$CHCl_3$	18,900	45	61
$CH_3COCH(CH_3)COCH_3$	14.3	red	0	toluene	19,300	36	60
$CH_3COCH(C_4H_9)COCH_3$	14.8	red	0	toluene	19,500	36	60
2-Benzoylcyclohexanone	14.9	red	0	$CHCl_3$	17,700	48	61
$(CH_3)_3C.COCH_2CO.C(CH_3)_3$	15.9	red	0	toluene	18,700	60	58

* In 75% dioxan. For refs see ref. 60.

merisation has been proposed as the reason for the occurrence of the dipivaloylmethane and 3-phenylacetylacetone complexes in the low-spin, monomeric form. However the electronic effect seems a more probable explanation, particularly as the 3-methylacetylacetone complex also has the low-spin structure and it is not easy to see how steric effects could prevent trimerisation in this case.

The equilibrium between high-spin and low-spin forms of the complexes with 3-alkylacetylacetones has been studied in toluene solution at room temperature[60]. The form of the equilibrium constant:

$$K = \frac{[Ni_3L_6]}{[NiL_2]^3}$$

confirms the trimeric nature of the high-spin forms. Values of log $K \sim 2$ have been obtained, from which, by assuming an entropy change of about -40 e.u., bond energies of about 7 Kcal are obtained for each additional Ni-O bond formed in the polymer; this value is of interest for comparison with the bond energies observed for addition of bases to molecules of this type (see below, C, ii).

The equilibrium between high-spin and low-spin forms has also been studied in toluene solutions of bis(diisobutyrylmethanato)nickel(II)[54] and bis (3-phenylacetylacetonato)-nickel(II)[55] over a range of temperatures from 3–50°. Assuming a monomer-trimer equilibrium:-

$$3NiL_2 \rightleftharpoons Ni_3L_6$$

thermodynamic values for the enthalpy and entropy of reaction were derived as follows:-

diisobutyrylmethane	$\Delta H = -15.0$	$\Delta S = -31$
3-phenylacetylacetone	$\Delta H = -10.3$	$\Delta S = -18$

corresponding to Ni-O bond energies of 7.5 and 5.1 Kcal, respectively. These values for the Ni-O bond energies are supported by the data quoted above (Table 1), which show that nickel and cobalt acetylacetonates have heats of sublimation about 10 Kcal mole^{-1} greater than the monomeric complexes of beryllium, aluminium and iron.

(iv) Cobalt, iron

The cobalt(II) and iron(II) β-diketone complexes have been much less extensively studied than those of nickel(II) or copper(II). They are less stable to hydrolysis and consequently more difficult to prepare and the anhydrous compounds are very sensitive to aerial oxidation.

Anhydrous bis(acetylacetonato)cobalt(II), like the nickel(II) complex, is trimeric in benzene[63] or triphenylmethane[59]. However, crystal structure analysis[64] has shown that the solid contains tetrameric molecules, in which all the cobalt atoms have approximately octahedral environments, the linear tetramer being built up by edge-sharing of two pairs of face-sharing octahedra (Fig. 10).

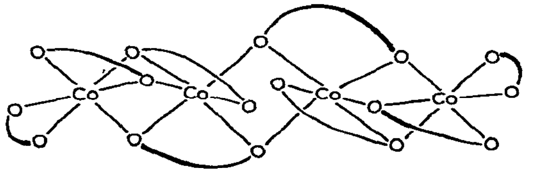
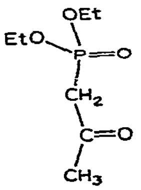


Fig. 10. Tetrameric molecule of bis(acetylacetonato)cobalt(II).

A trimeric structure has, however, been observed by X-ray analysis[65] of the analogous cobalt(II) complex of diethoxyphosphonylacetone (IV) (Fig. 11).



IV

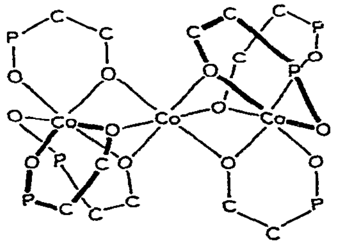


Fig. 11. Trimeric molecule of bis(diethoxyphosphonylacetonato)cobalt(II).

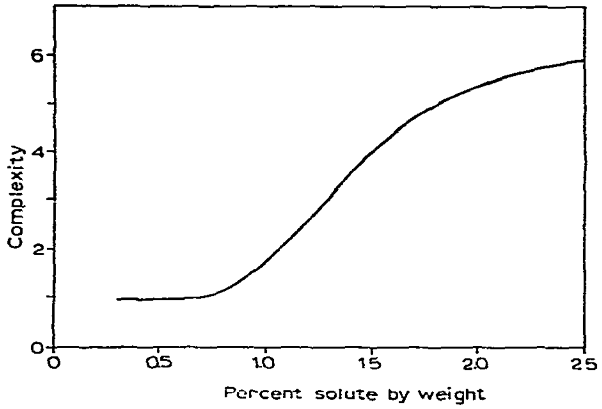


Fig. 12. Complexity of benzene solutions of bis(acetylacetonato)iron(II).

In benzene solutions the molecular weight of bis(acetylacetonato)iron(II) has been determined over a wide range of concentrations by the cryoscopic (5°) and ebullioscopic (80°) methods[66]. The results show a gradual increase in complexity from monomer at low concentrations to nearly hexamer in 2·4% solutions at 5° (Fig. 12); complexities are lower at 80°; there is evidence for the presence in the equilibrium mixture of species intermediate between $Fe(acac)_2$ and $[Fe(acac)_2]_6$. Molecular weight data on bis(trifluoroacetylacetonato)iron(II) and bis(hexafluoroacetylacetonato)iron(II) also show some association, but the highest complexity observed is less than 2 and it is not possible to estimate the size of the polymer involved. Bis(dipivaloylmethanato)iron(II) is monomeric in solution and has been shown to be tetrahedral and isomorphous with the zinc compound in the solid state[67].

Bis(dipivaloylmethanato)cobalt(II) is also isomorphous with the zinc compound and tetrahedral[68]; absorption spectra support the preservation of this stereochemistry in solution; molecular weight measurements have not been done. A planar structure for bis(trifluoroacetylacetonato)cobalt(II) has been proposed on the basis of dipole moment measurements[69] but this explanation of the results now seems unlikely.

C. BASE ADDUCT FORMATION

(i) Copper

The weak interactions between copper atoms in molecules of the β-diketone complexes and electron-rich regions of neighbouring molecules are parallelled by reaction of the complexes with Lewis bases to form addition compounds.

The first of these compounds to be isolated was the quinoline adduct of bis-

(acetylacetonato)copper(II), obtained by crystallisation of the complex from quinoline[70]. Many similar adducts have since been isolated including the 1:1-adducts of pyridine with bis(benzoylacetonato)copper(II)[36] and of 4-methylpyridine with bis(acetylacetonato)copper(II)[71] and bis(benzoylacetonato)copper(II)[36] and adducts of bis(ethylacetoacetato)copper(II) with two molecules of pyridine or 4-methylpyridine[36]. A variety of 1:1 and 1:2 adducts of *o*-hydroxyarylcarbonyl compounds has also been obtained[47]. All these adducts are dark green or bright green in colour and are unstable, decomposing on exposure with loss of base, leaving a residue of the β-diketone complex. Magnetic moments of the solid adducts are normal, in the range 1.8–2.0 Bohr magneton. Reflectance spectra of the solid 1:1-complexes resemble those of solutions of the β-diketone complexes in pure base or base-solvent mixtures, though the adducts dissociate in solution in the absence of excess base.

The absorption spectra of the 1:1-adducts in solution, like those of the β-diketone complexes themselves, can be resolved into two Gaussian components, though this does not necessarily mean that there are only two absorption bands in the envelope. The resolution reveals two rather unequal components at about 12,000 cm^{-1} ($\varepsilon \sim 20$) and 15,000 cm^{-1} ($\varepsilon \sim 70$); some examples of resolutions into two component bands are given in Table 5.

TABLE 5

FREQUENCIES (CM^{-1}) AND EXTINCTIONS OF COMPONENTS OF ABSORPTION OF 1:1-ADDUCTS

Ligand	*Base*	ν_1	ε_1	*Width*	ν_2	ε_2	*Width*	*Ref.*
Acetylacetone	py	12,500	32	2800	15,300	73	3600	41
3-Methyl-acac	py	13,100	34	2800	16,000	84	3700	41
3-Phenyl-acac	py	13,180	44	4400	15,950	81	3500	45
Dibenzoylmethane	4-mepy	12,000	28	3000	15,000	80	4000	46
Ethyl acetoacetate	py	11,200	43	3600	14,400	70	4000	35
Ethyl benzoylacetate	4-mepy	11,100	40	3600	14,100	70	4200	46
Salicylaldehyde	4-mepy	11,700	58	3600	14,700	100	4200	47

The effect of solvent and ligand variation on these spectra has been interpreted as indicating a square-pyramidal structure, and this in confirmed by X-ray analysis of bis(acetylacetonato)-quinoline copper(II)[72] (Fig. 13).

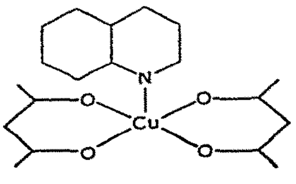


Fig. 13. Square-pyramidal molecule of quinoline adduct of bis(acetylacetonato)copper(II).

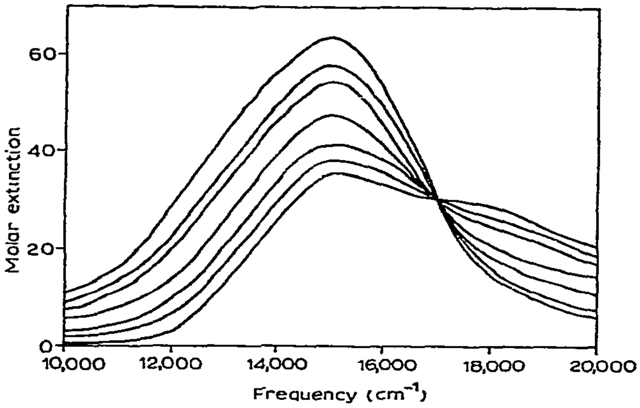


Fig. 14. Absorption spectra of bis(acetylacetonato)copper(II) in benzene (curve 1) and with increasing concentrations of pyridine.

In this structure the copper atom is at the centre of an approximately square pyramid, the base formed by the four oxygen atoms of the β-diketone and the apex by the nitrogen atom. The Cu-N bond is distinctly longer than the Cu-O bonds as is common in copper(II) complexes of this stereochemistry. The structures of the adducts with two molecules of base are not known.

Addition of successive amounts of base to solutions of the copper(II) β-diketone complexes in non-donor solvents, such as benzene or chloroform, gives a series of absorption spectra passing through a sharply defined isosbestic point (Fig. 14), from which equilibrium constants have been obtained[73] for the reaction:

$$\mathrm{CuL_2 + B \rightleftharpoons CuL_2B}$$

$$K = \frac{[\mathrm{CuL_2B}]}{[\mathrm{CuL_2}] \times [\mathrm{B}]}$$

The effects of variation of solvent, base and β-diketone on the value of K have been studied in some detail[36]. In different solvents the value of K increases in the order

chloroform < acetone < benzene

which is the order of decreasing solvation energy of the base. With a series of substituted pyridines the adducts increase in stability in the order

2,6-me$_2$py < 2-mepy < py < 4-mepy

which is what might be expected from a combination of electronic and steric effects.

Thermodynamic data have been obtained for the reaction of bis(acetylacetonato)copper(II) with a series of bases in benzene solution[74]. The enthalpy of reaction was evaluated both from variations of the equilibrium constant over a temperature range and by calorimetry; unfortunately the two sets of results do not agree too well, the first method giving values of ΔH between -1.3 and -3.4 Kcal mole^{-1} and the second method values between -0.7 and -11.5 Kcal mole^{-1} for the same systems. Despite this discrepancy it is evident that the value of ΔH, which may be taken to approximate the Cu-N bond energy, lies in the range -2 to -10 Kcal mole^{-1}, which is comparable to the Ni-O bond energies observed from studies of the polymerisation of the anhydrous nickel β-diketone complexes.

Formation constants have been obtained for the addition of bases to some twenty-five copper(II) complexes in either benzene or chloroform. Some typical values of K at room temperature are shown in Table 6.

TABLE 6

FORMATION CONSTANTS OF 1:1-ADDUCTS OF COPPER(II) β-DIKETONE COMPLEXES WITH BASES

β-Diketone	*Solvent*	*2-Mepy*	*Py*	*4-Mepy*	*Ref.*
Acetylacetone	$CHCl_3$	0.66	2.0	2.7	36
Benzoylacetone	$CHCl_3$	0.74	2.8	3.9	36
Ethyl acetoacetate	$CHCl_3$	1.6	3.3	8.0	36
Ethyl acetoacetate	C_6H_6	9.6	29	59	36
3-Methyl-acac	C_6H_6	1.00	2.35	3.51	41
3-Phenyl-acac	C_6H_6	1.62	4.60	8.5	45

Incorporation into the β-diketone of electron withdrawing groups, although it lowers the stability of the copper(II) complex towards hydrolysis, increases its strength as a Lewis acid and gives more stable adducts. With the copper(II) complexes of trifluoroacetylacetone[75] thenoyltrifluoroacetylacetone and hexafluoroacetylacetone[76,77] adducts have been obtained with both one and two molecules of base and these are more stable than the adducts of ordinary β-diketones. Spectroscopic studies show that two molecules of 4-methylpyridine can be added successively in solution, though formation constants have not been reported. Bis(hexafluoroacetylacetonato)copper(II) forms a, presumably six-coordinate, dihydrate and the anhydrous complex, though readily obtained, is hygroscopic[78].

(ii) Nickel, cobalt, iron

The anhydrous nickel(II) complexes, whether low-spin monomers or high-spin trimers, react with excess base to form addition compounds of the type NiL_2B_2, where $B = H_2O$, NH_3, pyridine etc. Equilibrium studies of the reaction of pyridine in benzene or toluene solution with the high-spin, trimeric acetylacetone complex[79] and with the low-spin, monomeric, 3-butylacetylacetone complex[50] indicate that, in both cases, complexes of the type Ni_2L_4py are formed as intermediates. The acetylacetone complex, $Ni_2(acac)_4py$, has been isolated as green crystals, $\mu_{eff} = 3.31$ Bohr magneton. There is no evidence for any other intermediate species in the reaction and equilibrium constants have been obtained for the two steps: –

$$2Ni_3(acac)_6 + 3py \rightleftharpoons 3Ni_2(acac)_4py; \quad K_1 \sim 10^{10}\ l^2\ mole^{-2}$$
$$Ni_2(acac)_4py + 3py \rightleftharpoons 2Ni(acac)_2py_2; \quad K_2 = 2.7 \times 10^5\ l^2\ mole^{-2}$$

Equilibrium studies of the reaction of pyridine with the low-spin 3-alkylacetylacetone complexes also reveal a high-spin intermediate of similar type, though not isolated; there is, however, evidence for the existence of these intermediates in the decomposition of the adducts, NiL_2py_2, on a thermogravimetric balance. For the 3-butylacetylacetone complex equilibrium constants for the two steps have been evaluated as follows: –

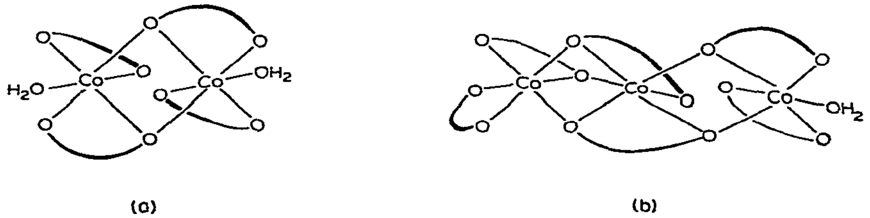
$$2NiL_2 + py \rightleftharpoons Ni_2L_4py \qquad K_1 = 1.3 \times 10^5\ l^2\ mole^{-2}$$
$$Ni_2L_4py + 3py \rightleftharpoons 2NiL_2py_2 \qquad K_2 = 7.9 \times 10^2\ l^2\ mole^{-2}$$

The values of K_1 in the two systems cannot be satisfactorily compared as the form of the equation is different. The value of K_2 is considerably smaller in the case of the butyl complex and this is reflected in the qualitatively different behaviour of the complexes NiL_2B_2 in solution: the acetylacetone complex dissolves without significant dissociation; the 3-alkylacetylacetone complexes dissolve with partial dissociation of pyridine.

The reaction of anhydrous bis(acetylacetonato)cobalt(II) with pyridine in benzene solution is apparently more complicated than that of the nickel(II) compound[63] and has been interpreted as involving three steps: –

$$2Co_3(acac)_6 + 3py \rightleftharpoons 3Co_2(acac)_4py \qquad K_1 \text{ very big}$$
$$Co_2(acac)_4py + py \rightleftharpoons 2Co(acac)_2py \qquad K_2 = 2.0$$
$$Co(acac)_2py + py \rightleftharpoons Co(acac)_2py_2 \qquad K_3 = 5.8 \times 10^3\ l.\ mole^{-1}$$

the middle step being the formation of a 1:1 adduct, apparently 5-coordinate. All species have the high-spin configuration and the adduct $Co_2(acac)_4py$ has been isolated and the crystal structure of the 1:1-hydrate $Co_2(acac)_4(H_2O)_2$ determined[80]. In this compound two octahedra share edges (Fig. 15a). In the hydrate $Co_3(acac)_6\ H_2O$ one of the terminal $(Coacac)_2$ units of $Co_4(acac)_8$ is replaced by H_2O (Fig. 15b)[80a].



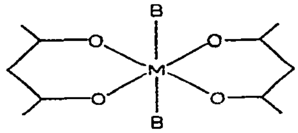
(a) (b)

Fig. 15. Molecules derived from the tetramer of bis(acetylacetonato)cobalt(II); (Fig. 10); (a) dimer of $Co(acac)_2OH_2$; (b) $Co_3(acac)_6OH_2$.

The end-product of the reaction of bases with the β-diketone complexes of nickel(II), cobalt(II) or iron(II) is normally the bis-adduct, ML_2B_2, though in a few cases compounds have been isolated containing more base; bis(dibenzoylmethanato)nickel(II) and cobalt(II), for example, crystallise from 4-methylpyridine as adducts of the type ML_2B_4, but the reflectance spectra of these, apparently 8-coordinate, compounds are similar to those of the 6-coordinate ML_2B_2 adducts and it seems likely that the additional base molecules are accomodated in the crystal lattice, rather than being coordinated to the metal atom[18].

Adducts of bis(acetylacetonato)nickel(II) of the type $Ni(acac)_2B_2$ have been reported with $B = H_2O$, C_2H_5OH[81], NH_3, pyridine[1], butylamine and benzylamine[82]. A wide variety of adducts of other nickel compounds and of corresponding complexes of cobalt and iron has been reported. All these adducts have the high-spin configuration. An interesting feature of the adducts of the cobalt(II) and iron(II) β-diketone complexes with heterocyclic bases is the protection which the base gives against oxidation of the metal atom.

Crystal structure determinations have shown that the compounds $Ni(acac)_2(H_2O)_2$[83] $Ni(acac)_2py_2$[84], $Co(acac)_2(H_2O)_2$[85], and $Co(acac)_2py_2$[86] form *trans*-octahedral molecules (Fig. 16). The two different metal–ligand distances in the compounds suggest that distortion from octahedral symmetry occurs to a greater extent than could be expected merely from the non-identity of the six donor atoms.



M	B	M–O	M–B
Co	OH_2	2.05	2.23
Ni	OH_2	2.02	2.14
Co	NC_5H_5	2.03	2.19

Fig. 16. Metal-ligand distances (A.u.) in base adducts of acetylacetonates of cobalt(II) and nickel(II).

Adducts have also been obtained with bidentate bases such as 1:10-phenanthroline and 2:2′-bipyridine[1] in which the structure is presumably *cis*-octahedral, though this has not been confirmed by X-ray analysis. A series of adducts of bis(ethyl acetoacetato)cobalt(II) with uni- and bi-dentate heterocyclic bases has recently been reported[87].

The absorption spectra of the nickel(II) complexes are typical of weakly tetragonal, high-spin nickel(II) species and are dominated by two absorption bands near 10,000 and 16,000 cm^{-1}, $\varepsilon < 20$. In the diaquo complexes these bands are observed at about 9,000 and 16,000 cm^{-1}; in the pyridine adducts they are shifted to about 10,000 and 17,000 cm^{-1}. Rather surprisingly, there is no significant shift in the frequency of these ligand–field bands when changes are made in the structure of the β-diketone (Table 7); evidently changes in the ligand–field due to varying donor power of the β-diketone are too small to be observed as shifts in the ligand–field bands.

TABLE 7

FREQUENCIES OF ABSORPTION MAXIMA OF NICKEL COMPLEXES, NiL_2B_2

LH	*B*	ν_1	ν_2	*Ref.*
Acetylacetone	pyridine	10,420	17,210	60
3-Methyl-acac	pyridine	10,200	17,210	60
3-Phenyl-acac	pyridine	10,420	17,700	45
Benzoylacetone	pyridine	10,120	17,090	45
Dibenzoylmethane	pyridine	10,130	17,210	45
Acetylacetone	2-mepy	9,870	16,610	88
3-Phenyl-acac	2-mepy	9,800	16,530	45
Benzoylacetone	2-mepy	9,850	16,670	45
Dibenzoylmethane	2-mepy	9,880	16,860	45
Acetylacetone	phen	9,870	16,610	45
3-Benzyl-acac	phen	9,650	16,810	60
Dibenzoylmethane	phen	9,970	16,950	45

Replacement of pyridine by 2-methylpyridine produces a shift in the ligand-field bands to lower frequencies, presumably due to steric interference of the methyl groups, which either cause lengthening of the Ni-N bonds or impose a *cis*-configuration: There is a comparable shift in the 1:10-phenanthroline adducts, in which there is necessarily a *cis*-configuration, but there no bond lengthening would be expected; this suggests that the shift observed in the 2-methylpyridine complexes is due to these having the *cis*-configuration.

(iii) Zinc, manganese

The isolation of bis(acetylacetonato)zinc as a monohydrate has been mentioned above. The structure of this compound has been determined[89]. The zinc atom is 5-coordinate, the ZnO_5 group being intermediate in shape between a square pyramid and trigonal bipyramid with five equal Zn-O linkages (Fig. 17). The molecule is preserved undissociated in triphenylmethane solution[14] though dilute solutions in hydrocarbons slowly deposit zinc hydroxide.

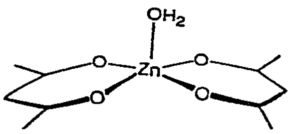


Fig. 17. Five-coordinate molecule of bis (acetylacetonato)aquo-zinc(II).

By reaction with heterocyclic bases, the water molecule can be replaced, giving compounds $Zn(acac)_2B$ (B = py, 2-mepy, 4-mepy) which are only slightly dissociated in benzene solution and presumably 5-coordinate[14]. Apparently six-coordinate complexes have been isolated of the form $Zn(acac)_2(NH_3)_2$, $Zn(acac)_2$-

(bipy), $Zn(acac)_2(phen)$[1] and $Zn(acac)_2(4\text{-}mepy)_2$,[14] the last of which dissociates in benzene with the loss of one molecule of 4-methylpyridine.

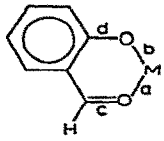
5- and 6-coordinate adducts have also been obtained from bis(benzoylacetonato)zinc[18] and bis(dibenzoylmethanato)zinc[19]. The 5-coordinate compounds include 1:1-adducts of both of these with pyridine and 2-methylpyridine and of the former with methanol and 4-methylpyridine. All except the pyridine-dibenzoylmethanate adduct are almost undissociated in benzene. Both compounds also form presumably 6-coordinate adducts, ZnL_2B_2, with pyridine and 4-methylpyridine, which lose one molecule of base in solution. Bis(dibenzoylmethanato)zinc also forms an adduct $ZnL_2(4\text{-}mepy)_4$, which loses three molecules of base in solution.

The dissociation behaviour of these adducts, together with the stability of the hydrate, $Zn(acac)_2(H_2O)$, and the structure of the trimer $Zn_3(acac)_6$ indicates the preference of the zinc atom for 5-coordination in β-diketone complexes. However, bis(hexafluoroacetylacetonato)zinc(II), like the copper(II) complex, forms some stable 6-coordinate adducts[77].

Bis(acetylacetonato)manganese(II) resembles the zinc complex in forming both 5- and 6-coordinate adducts. The former include 1:1-adducts with pyridine and 4-methylpyridine, which are monomeric in freshly prepared benzene solutions[90]. The 6-coordinate compounds include the hydrate, $Mn(acac)_2(H_2O)_2$,[91] 1:1-adducts with bipyridine and phenanthroline[1] and 1:2-adducts with pyridine, 2-methylpyridine and 4-methylpyridine[90] which dissociate in benzene solution, probably with the loss of one molecule of base. The 6-coordinate complexes appear to be rather more stable than those of zinc, but here too the preferred coordination number is probably five. In all these compounds the manganese has the high-spin configuration.

D. *o*-HYDROXYARYLCARBONYL COMPLEXES

Incorporation of the C=C double bond of a β-keto-enol into an aromatic system has the effect of destroying the equivalence of the two C—O bonds, which is such a characteristic feature of the metal complexes of β-diketones. Crystal structure determinations of the two forms of bis(salicylaldehydato)copper(II)[28,29] (Table 2) and of diaquobis(salicylaldehydato)nickel(II)[92] show in each case a distinct difference in bond length between the phenolic and ketonic C—O bonds, together with corresponding variations in the C—C and M—O bond lengths (Fig. 18).



M =	Cu(28)	Cu(29)	Ni(92)
a =	1.98	1.94	2.03
b =	1.86	1.90	2.03
c =	1.26	1.28	1.22
d =	1.32	1.32	1.30

Fig. 18. Bond lengths in metal salicylaldehyde complexes.

These differences are reflected in the infra-red spectra of metal complexes of these ligands. In typical β-diketone complexes the C=C and C=O stretching frequencies in the 1400–1750 cm^{-1} region are replaced by two very strong bands[93] near 1520 and 1600 cm^{-1}, characteristic of the symmetrical system with equivalent C—O and M—O bonds. In complexes of the *o*-hydroxyarylcarbonyl compounds on the other hand, the absorption near 1640 cm^{-1}, characteristic of the conjugated C=O group, is only slightly shifted to lower frequencies (Table 8).

TABLE 8

C=O STRETCHING FREQUENCIES (CM^{-1}) IN METAL COMPLEXES, ML_2, OF O-HYDROXYARYLALDEHYDES AND KETONES[47,94,95]

LH	*ν, LH*	*ν,CuL₂*	*ν,NiL₂*	*ν,CoL₂*
Salicylaldehyde	1660	1605	1625	1620
2-Hydroxyacetophenone	1650	1605	1620	1605
2-Hydroxypropiophenone	1640	1605	1620	1610
2-Hydroxybenzophenone	1640	1630	1610	–
2-Hydroxy-5-methylbenzophenone	1625	1635	–	1615

Copper(II) complexes of these ligands[47] closely resemble those of simple β-diketones. The anhydrous compounds, CuL_2, have magnetic moments in the range 1.8–2.1 Bohr magneton and absorption spectra which can be resolved into two bands at about 14,000 and 17,000 cm^{-1}. They are probably all planar molecules with varying amounts of weak intermolecular interaction in the solid state. Like the β-diketone complexes they react with Lewis bases to form adducts CuL_2B and CuL_2B_2, but the base adducts appear to be more stable than those of the simple β-diketone complexes.

Monohydrates, $CuL_2 \cdot H_2O$, are known of the complexes with 2-hydroxyacetophenone, 2-hydroxypropiophenone and 2-hydroxy-1-naphthaldehyde; these readily lose water to give the anhydrous compounds. Dihydrates, $CuL_2(H_2O)_2$, are obtained when LH = methyl or ethyl salicylate; these are quite stable and cannot be dehydrated without decomposition of the complex; the anhydrous compounds are unknown.

Bis(salicylaldehydato)copper(II) crystallises from pyridine as a dipyridine adduct, CuL_2py_2.[96] Adducts with two molecules of 4-methylpyridine[47] are formed when LH = salicylaldehyde, 5-chloro-2-hydroxybenzophenone, methyl or ethyl salicylate or 2-aceto-1-naphthol. Adducts with one molecule of 4-methylpyridine are formed with the complexes of a variety of other ligands. All these adducts with one or two molecules of water or base have magnetic properties typical of copper(II) complexes and the ligand C=O stretching frequency is observed in the 1600–1635 cm^{-1} region.

Reflectance spectra indicate that the 1:1-adducts are probably square pyramidal molecules with the nitrogen at the apex and this is confirmed by X-ray analysis of the 4-methylpyridine adduct of bis(2-hydroxyacetophenonato)copper(II)[97] details of which are shown in Fig. 19.

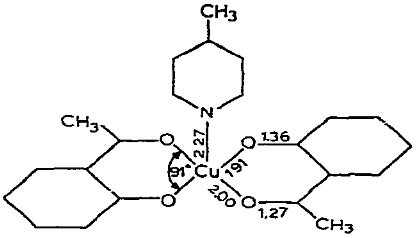


Fig. 19. Bond lengths in square-pyramidal adduct of 4-methylpyridine with bis(*o*-hydroxyacetophenonato)copper(II).

The copper(II) complex of 2-hydroxy-1-naphthaldehyde is obtained as a monohydrate[98] and spectroscopic evidence has been obtained for the formation of an adduct in pyridine solution.[99]

Equilibrium constants have been obtained for the addition of 4-methylpyridine to some of these compounds[47]. Despite the apparently greater stability of the solid adducts compared with those of the simple β-diketones, formation constants

$$K = \frac{[CuL_2B]}{[CuL_2]\times[B]}$$

are of the same order as those of the simple β-diketone complexes (Table 6). Compared with acetylacetone ($K = 2.7$ for 4-methylpyridine in chloroform), some ligands give less stable adducts, for example 2-hydroxypropiophenone ($K = 0.6$) and some give more stable adducts, for example salicylaldehyde ($K = 28.7$) and 5-chloro-2-hydroxybenzophenone ($K = 37.0$). The latter is the highest value of K yet observed in chloroform solution and there does not appear to be any particular relationship between these values and the nature of the ligand.

Complexes of *o*-hydroxyarylcarbonyl compounds with nickel(II) and cobalt(II) differ markedly from those of the simple β-diketones, particularly in the behaviour of the anhydrous complexes in solution. Usual preparative methods give these complexes[94,98,100,101–103] as dihydrates, $ML_2(H_2O)_2$. All of these have the high-spin configuration. The crystal structure of the nickel salicylaldehyde complex has been determined[92] and it is shown to have the *trans*-octahedral structure with unequal C—O bond lengths. Solid state reflectance spectra of the dihydrates are typical of octahedral, high-spin nickel(II) and cobalt(II).

Reaction of the dihydrates with bases gives base adducts of the type ML_2B_2. The pyridine adduct of bis(2-hydroxyacetophenonato)nickel(II)[104] and 4-methylpyridine adducts[94,100,103] of a range of *o*-hydroxyarylcarbonyl compounds have been obtained. All have magnetic and spectroscopic properties typical of high-spin octahedral complexes, and the infra-red absorption of the ketonic C=O is preserved at 1600–1630 cm^{-1}. These base adducts are less stable than those of high-spin β-diketone complexes, such as bis(acetylacetonato)nickel(II) and dissociate in solution in hydrocarbons. Molecular weight data in toluene indicate that dissociation occurs according to the equation: –

$$ML_2B_2 \rightleftharpoons ML_2B+B$$

or possibly incomplete dissociation: –

$$ML_2B_2 \rightleftharpoons ML_2+2B$$

This is comparable to the behaviour of the adducts of low-spin nickel β-diketone complexes.

Water or base can be removed from the adducts to give the anhydrous compounds ML_2. Preliminary X-ray data show that in solid bis(salicylaldehydato)nickel(II) there are twelve nickel atoms in the unit cell[105], suggesting that this compound may be a trimer similar to bis(acetylacetonato)nickel(II); it is too insoluble for molecular weight determinations to be made. Like all the other anhydrous nickel(II) and cobalt(II) complexes of this type it has the high-spin configuration and a reflectance spectrum typical of octahedrally coordinated metal atoms. These characteristic properties are retained in solutions of some of the more soluble cobalt(II) and nickel(II) complexes in hydrocarbon solvents. Molecular weight determinations in the same solvents reveal monomer–polymer equilibria, the main species present in concentrations below 10^{-2}M being monomeric.

These monomeric forms of the complexes ML_2 thus have the high-spin configuration and spectra typical of octahedral cobalt(II) or nickel(II). As theoretical considerations suggest that tetragonal distortion should have little effect on the absorption spectra of these complexes[52,106]; these results have been interpreted as indicating a high-spin square planar structure for these species*. This conclusion is supported by equilibrium studies[102] which show that some of nickel(II) complexes add 4-methylpyridine in two successive stages: –

$$NiL_2+B \rightleftharpoons NiL_2B$$
$$NiL_2B+B \rightleftharpoons NiL_2B_2$$

The equilibrium constants for the first step are similar to those for addition to the copper(II) complexes, for example, the successive equilibrium constants for addition to bis(2-hydroxypropiophenonato)nickel(II) in toluene at 21° are $K_1 = 8.8$, $K_2 = 0.42$.

The similarity of the absorption spectra of all the species in equilibrium

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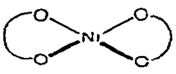
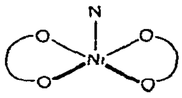
* I am grateful to the editor for drawing my attention to recent papers[116,117] showing that tetragonal distortion can have observable effects on Ni^{2+} spectra. So far, however, such effects have only been observed at very low temperatures with ligands of very different types, for example in $Nipy_4Cl_2$.

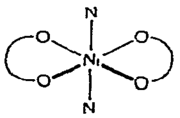
shows that all have the high-spin configuration and suggests that all are based on a planar NiL_2 structure, the intermediate NiL_2B being a 5-coordinate square pyramidal molecule: –



V



VI



VII

1:1-adducts of this type have recently been obtained from 4-methylpyridine and the cobalt(II) and nickel(II) complexes of 5-chloro-2-hydroxybenzophenone; they are monomeric in solution in hydrocarbon solvents and have spectra typical of the high-spin configurations[46].

E. CONCLUSION

In the anhydrous inner complexes, ML_2, formed by divalent transition metals and β-keto-enol compounds (LH), the metal atom is coordinately unsaturated and these compounds behave as Lewis acids, forming adducts with bases such as water, amines or further enolate ions and, in the absence of these, undergoing self-association to give polymeric species in which the oxygen atoms of one ML_2 moleculare are coordinated to the metal atom of another. This type of behaviour raises two questions:

1. How strong are these ML_2 molecules as Lewis acids?
2. How many base molecules can be taken up; that is, what are the preferred and maximum coordination numbers of the metal, and what is the stereochemistry of the adducts?

(i) *Strength of ML_2 as Lewis acids*

Though comparatively little work has been done, measurements of the heats of sublimation of the acetylacetone complexes of cobalt(II) and nickel(II), of the monomer–trimer equilibria of some of the nickel(II) complexes and of equilibrium constants and heats of reaction for the addition of bases to the copper(II) complexes, all lead to approximately similar values of about 5–10 Kcal $mole^{-1}$ for the dissociation energy of the additional metal–ligand bonds formed. Comparable values have been observed for the Lewis acid behaviour of some other types of coordinately unsaturated transition metal complex, for example, in the reaction of heterocyclic bases with diacetylbis(benzoylhydrazonato)-nickel(II)[107], bis(dimethyldithiocarbamato)zinc(II)[108] or with cobalt halide complexes of the type CoX_2base_2[109]. This bond energy of about 5–10 Kcal $mole^{-1}$ appears to be more or less independent of variations of the metal atom or even of changes of spin multiplicity.

The heat of reaction of ML_2 with bases is much less than that observed in most other Lewis acid-base reactions. For example, in a wide range of reactions of boron compounds with various bases, heats of reaction are nearly all[110] in the range 10–20 Kcal $mole^{-1}$ and for reactions of group V halides, MX_5, with a variety of bases, heats of reaction[111,112] range between 10–40 Kcal $mole^{-1}$. Various estimates have been made of the average bond energy of metal–ligand bonds in complex ions. Values in the range 50–120 Kcal $mole^{-1}$ per bond are estimated[113] for a variety of transition metal aquo and ammine complexes, ML_x^{n+} and values of about 60 Kcal $mole^{-1}$ per bond[114] for the reaction

$$M^{2+}{}_{(g)}+6NH_{3(g)} = M(NH_3)_6{}^{2+}{}_{(g)}$$

(ii) Coordination number and stereochemistry

Typically, transition metals exhibit coordination numbers of four and six, usually the latter, towards oxygen donors, though an increasing number of 5-coordinate compounds is being found[115]. In the zinc β-diketone compounds described above it is clear that the preferred coordination number is five, though both four and six are also observed; in the manganese compounds five and six appear to be preferred to four. These are examples where no stereochemistry is favoured by crystal field effects.

In the complexes formed by iron, cobalt and nickel, in which crystal field effects can be expected to stabilise octahedral 6-coordinate structures, these are clearly dominant. Tetrahedral 4-coordination is observed in the iron and cobalt complexes with dipivaloylmethane, presumably stabilised by the steric effect of the bulky tertiary butyl groups. In the case of nickel the 4-coordinate complexes are planar and have the low-spin configuration; the change of coordination number from six to four, accompanied by change of spin multiplicity, may be due to steric effects or to electronic effects. It occurs in the complexes with the strongest donor ligands, but these also are those which have bulky substituents. Reaction with bases gives 6-coordinate products and it is doubtful whether 5-coordination occurs in these compounds.

Fusion of the β-keto-enol system with an aromatic ring apparently stabilises the 4-coordinate cobalt and nickel species in the high-spin configuration, possibly due to π-bonding with the localised C=O group[95] and it is then possible to add base molecules one at a time, the first product being a 5-coordinate, presumably square-pyramidal, 1:1-adduct. This type of adduct is also the most usual product of reaction of the planar copper complexes with bases.

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