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CARBON-BONDED BETA-DIKETONE COMPLEXES

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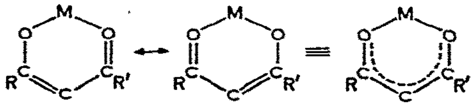
CONTENTS

A. INTRODUCTION

Beta-diketone complexes are known for nearly every metal and many non-metals. These complexes usually contain the beta-diketone bonded as a bidentate chelating agent via the two oxygen atoms forming a six membered planar ring as shown in Scheme 1**. The first examples of beta-diketone complexes containing metalcarbon bonds were established by Truter[1,2] from crystal structure determinations on the complexes $[Me_3Pt(C_3H_7CO \cdot CH \cdot CO \cdot C_3H_7)]_2$ and dipy.



Scheme 1

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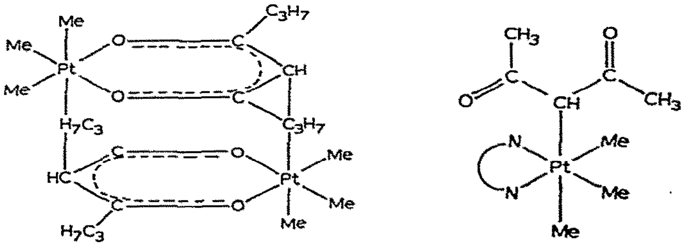
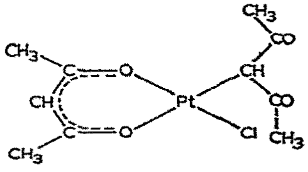
** This type of bonding will be referred to in future as oxygen-bonding.

$Me_3Pt(C_3H_7CO \cdot CH \cdot CO \cdot C_3H_7)$. The structures of these complexes, illustrated in Scheme 2, are examples of the two types of carbon-bonded beta-diketonates known. The first type (Scheme 2a), prepared by the reaction of Me_3PtI with $Tl(C_3H_7CO \cdot CH \cdot CO \cdot C_3H_7)$ in benzene solution[15], contains a tridentate bridging diketone with two metaloxygen bonds as well as a bond from the metal to the central carbon atom*; the six membered ring is essentially planar as is the case with simple oxygen-bonded complexes. The second type (Scheme 2b) is prepared from the first by the action of dipyridyl[16] and contains a unidentate diketone bonded to the metal via the central carbon atom only**. These are the only two definitely established forms of carbon-bonding in metal beta-diketone complexes. There are no reported examples in which metal atoms are bonded to a side chain although in some tellurium compounds with acetylacetone, prepared by Dewar *et al.*[3], this form of bonding occurs; there are also no known examples in which a metal atom is bonded directly to a carbonyl carbon atom.



Scheme 2 a b

The complex $KPtAcac_2Cl$, first prepared by Werner[4] by the reaction of K_2PtCl_4 with potassium acetylacetonate in aqueous solution, was shown by a crystal structure determination[5] to have one carbon-bonded and one oxygen-bonded ligand (Scheme 3). The carbon-bonded ligand in this complex differs from that in the dipyridyl platinum(IV) complex[2], where the two carbonyl groups point in opposite directions and have considerably different bond lengths. In $KPtAcac_2Cl$ the two carbonyl groups point in the same direction and the bond lengths are essentially the same; the platinum–carbon bond distance (2.13 ± 0.025 Å) in the Pt^{II} case is also somewhat shorter than in the Pt^{IV} complex (2.30 ± 0.03 Å).



Scheme 3

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* This type of bonding will be referred to in future as bridged bonding.

** This type of bonding will be referred to in future as carbon-bonding.

On the basis of the crystal structure of $KPtAcac_2Cl$, Lewis and Oldham[6] have established spectroscopic criteria for distinguishing carbon-bonded and oxygen-bonded ligands. In the p.m.r. spectrum of this complex, the 3-CH proton resonance of the carbon-bonded ligand is split by the ^{195}Pt isotope ($I = \frac{1}{2}$, Abundance 33%), into a doublet with a coupling constant of 120 cycles per second. A splitting is also observed for the 3-CH proton on the oxygen-bonded ligand but this is only 2 c.p.s. due to the greater distance of this proton from the metal atom. A similar situation occurs with the methyl groups of the two ligands, those on the carbon-bonded group being split by 10 c.p.s. while those on the oxygen-bonded group are split by only 6 c.p.s. The position of the resonances of both the 3-CH and methyl groups on the carbon-bonded ligand are, however, within the ranges usually associated with the resonances of the corresponding protons of oxygen-bonded groups[29]. In the absence of spin–spin coupling therefore, n.m.r. spectroscopy is not a good method of distinguishing the two types of bonding.

The infrared spectrum of $KPtAcac_2Cl$ shows several important differences between carbon and oxygen-bonded groups, as established by deuteration studies[6]:

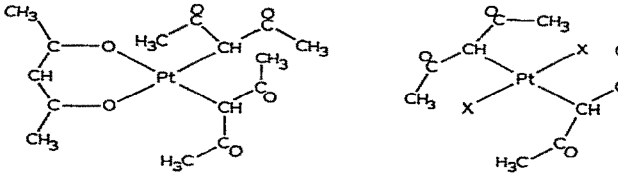
a) The 3-CH stretching frequency which occurs for oxygen-bonded ligands at 3080 cm^{-1} is replaced by a frequency at 2940 cm^{-1} for carbon-bonded ligands. In oxygen-bonded complexes the six membered ring formed by the metal and the ligand is planar and the carbon and oxygen atoms in the ring are essentially sp^2 hybridized with a pi-electron system above and below the plane of the ring. This is similar to the situation which occurs in aromatic molecules and the 3-CH stretching frequency of the diketone is therefore found to occur in the aromatic CH stretching region. In the carbon-bonded ligand the proton is bound to an atom which is more like a simple aliphatic carbon atom with sp^3 hybridization and the stretching frequency is correspondingly lower.

b) The carbonyl stretching frequencies of oxygen-bonded beta-diketonates occur 100 cm^{-1} lower than for carbon-bonded groups. In the chelate structure of the oxygen-bonded complex, the carbon–oxygen bond order is about 1.5 while in the unidentate carbon-bonded structure the carbonyl groups are more nearly like organic carbonyl groups with a bond order of 2.

c) The 3-CH in- and out-of-plane bending frequencies of the chelate ring are absent from the spectrum of the carbon-bonded group as this group is not planar. Since the out-of plane vibration usually gives a sharp strong peak in the spectra of oxygen-bonded complexes this is a useful negative test for the presence of carbon-bonding.

d) In the region 400–600 cm^{-1}, metal–oxygen stretching frequencies occur below and metal–carbon stretching frequencies above 500 cm^{-1}.

From these observations, the complexes $KPtAcac_3$, $Na_2PtAcac_2Cl_2 \cdot 2H_2O$ and $Na_2PtAcac_2Br_2 \cdot 2H_2O$ were shown to contain carbon-bonded acetylacetone groups[6]. The former compound contains one oxygen-bonded group and two *cis* carbon-bonded groups and in the latter two compounds there are two *trans* carbon-bonded groups. The structures of all these complexes are shown in Scheme 4. The ions $PtAcac_2X_2^{2-}$, where X = Cl, Br, and their deuterated analogues have been the subjects of a normal coordinate analysis by Nakamoto[7] which largely confirmed the above observations for carbon-bonded acetylacetone groups. The 3-CH stretching mode was predicted to occur at 2982 cm^{-1}, but was not observed. The two frequencies at 1652 and 1626 cm^{-1} were shown to be the symmetric and asymmetric carbonyl stretching modes respectively. In the 400–600 cm^{-1} region, a band at 567 cm^{-1} was assigned to a mainly platinum–carbon stretching mode but a band at 536 cm^{-1} was shown to be a bending mode of the methyl group. A corresponding normal coordinate analysis of an oxygen-bonded complex[8] showed the latter vibration to occur at least 100 cm^{-1} lower.


(a)
(b) X=Cl, Br

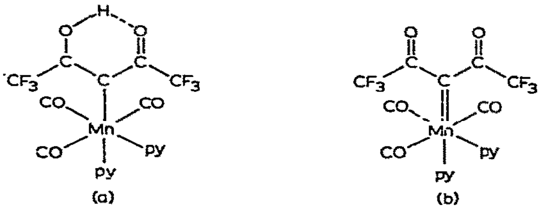
Scheme 4

Bridging groups are more difficult to identify from spectroscopic data. The carbonyl stretching frequencies will be determined by the relative strengths of the metal–oxygen and metal–carbon bonds. In $(Me_3PtAcac)_2$ despite the presence of a platinum–carbon bond a six membered planar ring is found, so that frequencies associated with this ring should still occur.

B. COMPLEXES HAVING CARBON-BONDED BETA-DIKETONE GROUPS

(i) *Manganese(I)*

Wojcicki[9] has suggested that the hexafluoroacetylacetone complex $Mn(CO)_3$-py_2HFA contains the beta-diketone bonded to the metal via the 3-carbon atom of the enol form as shown in Scheme 5a. He observed a carbonyl stretching frequency at 1701 cm^{-1} and an OH peak at 3250 cm^{-1}. The carbonyl stretching frequency is considerably lower than would be expected for a simple carbon-bonded derivative of this ligand as the electron withdrawing effect of the fluorine atoms in HFA normally causes an increase in the carbonyl stretching frequency of 50–70 cm^{-1} compared to an acetylacetone analogue. A second possibility is that the hydroxyl-band is due to water and that the ligand is bonded in a carbene type structure as shown in Scheme 5b; however the p.m.r. spectrum of this compound has not been observed. An alternative possibility is that the compound is a

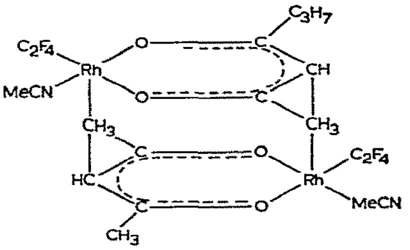


Scheme 5

trifluoroacetate, arising from the hydrolysis of hexafluoroacetylacetone (which readily occurs in the presence of atmospheric water and metal complexes).

(ii) *Rhodium(I)*

Parshall and Jones[10] have prepared two series of compounds from the reaction of various ligands with $(C_2F_4)_2RhAcac$. The first series are monomeric in solution, and have the formulation $(C_2F_4) \cdot L \cdot RhAcac$ where L is $(n\text{-}Bu)_3P$, Ph_3P, Me_2SO or pyridine. Their p.m.r. and infrared spectra are consistent with the presence of oxygen-bonded acetylacetone ligands; the carbonyl stretching frequencies occuring in the range 1580–1612 cm^{-1}. The second series are dimeric in solution, and have the formulation $[(C_2F_4)(RCN)RhAcac]_2$ where R is Me, Ph. In these complexes, the 3-CH proton of the diketone is split by 4 cycles per second by the isotope ^{103}Rh ($I = \frac{1}{2}$, Abundance 100%), which has a low magnetic moment, and couplings to protons are not usually observed unless the proton is very close to the metal. The carbonyl stretching frequencies of the dimeric complexes are at 1660 cm^{-1}, considerably higher than in the monomers. The proposed structure (Scheme 6) involves a bridging acetylacetone group and seems likely to be correct. The bonding however may differ considerably from that of the complex $(Me_3PtAcac)_2$ since the infrared spectra of the two compounds are different.



Scheme 6

(iii) *Iridium(III)*

When potassium chloroiridate(III) reacts with potassium acetylacetonate in aqueous solution under conditions similar to those used in the preparation of the anionic carbon-bonded platinum(II) complexes (*i.e.* with a large excess of the acetylacetonate ion), several products may be obtained. The characterization of these complexes has proved difficult and is not complete. Some $IrAcac_3$ is formed together with anionic, polymeric oxygen-bonded complexes of the type $K_2Ir\text{-}Acac_2XY \cdot nH_2O$ where X, Y = Cl, OH in several apparently isomeric forms. A complex containing carbon-bonded acetylacetone is also obtained and the most probably formulation for this is $K_2Ir_2Acac_7Cl \cdot H_2O$ although due to its apparently amorphous character this formulation is by no means certain. It is highly soluble in water, alcohols, acetone, benzene toluene, chloroform and carbon tetrachloride, although some decomposition occurs. It is obtained in a non-crystalline state from all of these solvents; it is insoluble in ether and petrol ether. In benzene solution a molecular weight of 1500–2000 is observed.

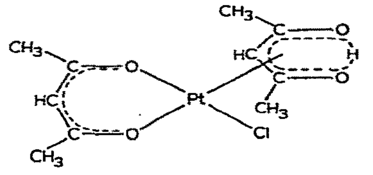
The p.m.r. spectrum indicates the presence of a very complex molecule. Five separate 3-CH resonances are observed in D_2O with intensities 1:1:2:2:1 approximately at 379, 361, 338, 334 and 325 c.p.s. down field from TMS. There are a greater number of methyl resonances centered on 128 c.p.s., none of whose intensities appears to bear an integral relation to the others. In non-aqueous solvents (CD_3COCD_3 and $CDCl_3$) an OH peak appears at 185 c.p.s. This spectrum is unchanged through successive preparations. By contrast the oxygen-bonded derivatives described above show only one peak in the 3-CH resonance region at 348 c.p.s. The infrared spectrum is very similar to that of $KPtAcac_2Cl$, with strong bands at 1678 and 1634 cm^{-1} due to the carbon-bonded ligands and at 1560 and 1518 cm^{-1} due to the oxygen-bonded species. Bands observed in the remainder of the spectrum are quite broad; in particular, the 3-CH out-of-plane band of the oxygen-bonded ligands at 775 cm^{-1} which, as mentioned previously, is normally a sharp peak. This is probably due to the several stereochemically different types of oxygen-bonded species which may occur in this complex. The low frequency region (400–600 cm^{-1}) shows bands which can be attributed to both metal–carbon and metal–oxygen stretching frequencies.

The chemical properties of this substance are similar to those of $KPtAcac_2Cl$ (see next section). A bright yellow precipitate is formed with various strong acids. This is unstable, however, rapidly decomposing to a brown solid from which no derivative analogous to the "acid" complex $HPtAcac_2Cl$ can be isolated. With divalent metal ions of both the transition and non-transition series, salts of the type $M^{II}(Ir_2Acac_7Cl)Cl$ can be obtained. These have been characterized for Co, Ni, Cu and Cd. The formation of these compounds is accompanied by a decrease of 20–40 cm^{-1} in the carbonyl stretching frequency of the carbon-bonded ligand. Such behavior is also observed in the formation of metal salts of the anionic platinum(II) complexes and these complexes presumably contain bridging acetylacetone groups. While the precise nature of these iridium complexes is still in doubt, the presence of carbon-bonded acetylacetone groups seems beyond question.

(iv) *Platinum(II)*

Complexes of divalent platinum containing carbon-bonded acetylacetone were first prepared by Werner[4] at the beginning of the century. They were not shown to contain this ligand, however, until 1962 when the structure of $KPtAcac_2Cl$ was determined[5]. In addition to the complexes mentioned previously, the bromo-analogue of $KPtAcac_2Cl$, and corresponding complexes with trifluoroacetylacetone, $KPtTFA_2Cl$ (and Br) and benzoyl acetone $KPtBA_2Cl$ (and Br) have also been prepared[11].

$KPtAcac_2Cl$ reacts with strong acids (such as hydrochloric, sulphuric and phosphoric acids, but not acetic acid) in aqueous solution forming a bright yellow precipitate[12] of the "acid" complex $HPtAcac_2Cl$, soluble in organic solvents but insoluble in water. In the p.m.r. spectrum of this complex the resonances of the two methyl groups in the oxygen-bonded ligand are not the same indicating an assymetric molecule, and a further resonance is observed from a ligand having two equivalent methyl groups. The splitting by the ^{195}Pt isotope of the central CH proton of this ligand (80 cps) is considerably less than that observed for the corresponding proton in $KPtAcac_2Cl$ (120 cps) and is close to that observed for olefinic protons on groups bonded to platinum. An OH resonance is also observed. In the infra-red spectrum of the complex, the high carbonyl stretching frequency of the parent anion disappears and a weak band is observed at 1640 cm^{-1} together with a broad OH stretching frequency at 3400 cm^{-1}. Bands due to the oxygen-bonded group remain. On the basis of this evidence, the presence of a pi-bonded acetylacetone group is suggested with the ligand bonded as the neutral enol form of the diketone (Scheme 7). If correct this is the first example of the stabilization of the enol form of a diketone by a metal atom.



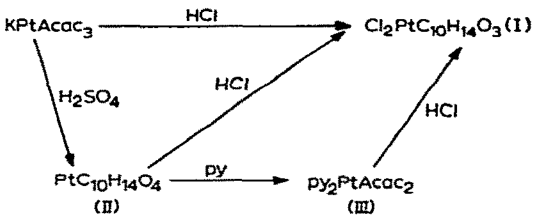
Scheme 7

The complex can be reconverted to the original potassium salt by treatment with potassium hydroxide. The pi-bonded diketone ligand is readily displaced by a variety of donor groups giving substituted acetylacetone complexes of the types L · PtAcacCl, where L is a phosphine, phosphite, amino or mono-olefin, and

$L(PtAcac_2Cl)_2$ where L is a conjugated or non conjugated diolefin. With dipyridyl however, the complex dipyPtAcacCl is formed. This insoluble complex which has a carbonyl stretching frequency in the infrared at 1673 cm^{-1} apparently contains a carbon-bonded acetylacetone group.

A similar but very unstable acid complex can be obtained from the benzoylacetone analogue of $KPtAcac_2Cl$. No product is obtained from $KPtTFA_2Cl$. Acid derivatives cannot be obtained from the complexes $Na_2PtAcac_2X_2 \cdot 2H_2O$ (X = Cl, Br), but in the presence of 2:4 dinitro-phenylhydrazine compounds containing one mole of 2:4-DNP per diketone are obtained. This behavior indicates that the free carbonyl groups have the normal ketonic reactivity.

With the complex $KPtAcac_3$, which contains two *cis* carbon-bonded groups, the reaction products with acids vary according to the acid used, as indicated in Scheme 8. With halogen acids, the dienyl complex (I) is precipitated from aqueous solution but is soluble in many organic solvents. Displacement of the oxygen-bonded group and condensation of the two carbon-bonded groups still attached to the metal atom occurs, with the elimination of a molecule of water. The unusual structure of (I) has been confirmed by X-ray structural analysis[13]. With all other strong acids (sulphuric, phosphoric and perchloric acids) formation of an insoluble polymeric materials occurs (II) which is isomeric with $PtAcac_2$. However, the infra-red spectrum is very different from that of a simple oxygen-bonded complex; two strong bands in the carbonyl region at 1666 and 1597 cm^{-1} suggest the presence of carbon-bonded groups. This is confirmed by the reaction of the compound with pyridine to give $py_2PtAcac_2$(III). In this complex the presence of two equivalent carbon-bonded acetylacetone groups is confirmed by both p.m.r. and infra-red spectral data. The retention of the *cis* orientation of the two metal carbon in both bonds (II) and (III) is shown by their reaction with hydrochloric acid to give the dienyl complex (I). (II) probably contains bridging acetylacetone groups, similar to those in the metal derivatives (see below) which give it its polymeric nature; one half of the carbonyl oxygen atoms being used to maintain a coordination number of four around the platinum atom.



Scheme 8

All of the anionic complexes of platinum(II) react with metal ions to give metal complexes[14]. In most cases, particularly with the transition elements, these are insoluble compounds which are precipitated from aqueous solution on addition of a solution of a metal salt. The complexes formed with zinc and cadmium are more soluble however. Thus, the reaction of $KPtAcac_2Cl$ with divalent metal ions affords complexes of the type $M^{II}(PtAcac_2Cl)_2$ where M is Mn, Fe, Co, Ni, Cu, Zn, Pd, and Cd. The formation of these complexes is accompanied by a reduction in the stretching frequencies of the free carbonyl groups by up to 50 cm^{-1}. This suggests that the carbonyls are involved in coordination to the metal atom thus forming a bridging group. The magnetic properties and the ultra-violet spectrum of the complexes $Co(PtAcac_2Cl)_2$ and $Ni(PtAcac_2Cl)_2$ have been studied and are consistant with octahedral coordination for the metal. The complexes are anhydrous and the nature of the groups occupying the two remaining positions on the metal atoms is uncertain; there are several possibilities i) coordination by the chlorine atoms bonded to the platinum ii) metal–metal bonds iii) formation of oxygen-bridged species as is observed with the simple acetylacetonates of nickel and cobalt[17,18]. The zinc and cadmium derivatives are monomeric in organic solvents although in this case the environment is presumably tetrahedral. The continued existence of a metal–carbon bond is indicated by a splitting of 100 cps for the 3-CH proton of the carbon-bonded group in the p.m.r. spectrum of the complexes. No metal derivatives have been obtained from $KPtTFA_2Cl$ or $KPtBA_2Cl$.

(v) *Platinum(IV)*

$(Me_3PtAcac)_2$ and dipy $Me_3PtAcac$ were first prepared by Lille and Menzies[15,16]. They were shown to contain carbon-bonded acetylacetone, in the former case of the bridging type, by Swallow and Truter[1,2] and were the first examples with these types of bonding. Analogues have been prepared with several other beta-diketones containing aliphatic side-chains and also with ethylacetoacetate. The crystal structure determination of $(n\text{-}Rh_3PtAcac)_2$ shows the presence of a planar diketone ring in many ways similar to the ring in oxygen-bonded beta-diketonates. The carbonyl stretching frequency at 1600 cm^{-1} is also quite close to that of oxygen-bonded complexes. It is low in comparison with other species containing bridging acetylacetone groups. In $Co(PtAcac_2Cl)_2$ this frequency occurs[14] at 1640 cm^{-1} and in $[(MeCN)(C_2F_4)RhAcac]_2$ at [10]1660 cm^{-1}, suggesting a considerable difference between the various types of bridging acetylacetone groups. The bonding in $(Me_3PtAcac)_2$ may be related to that of $HPtAcac_2Cl$ which can be inferred by the reactivity of these complexes with neutral ligands. With dipyridyl, the metal–oxygen bonds are broken in preference to the metal–carbon bonds giving a carbon-bonded species, but with other donor ligands the reverse is true and oxygen-bonded species are formed.

Oxidation of divalent platinum complexes provides a route to other tetravalent platinum complexes containing metal–carbon bonds. Thus oxidation of the complex dipy·PtAcacCl with chlorine in chloroform solution gives a small yield of dipy $PtAcacCl_3$, analogous to the compound investigated by Swallow and Truter. Some of the anionic complexes of platinum(II) can also be oxidized, the best oxidizing agent in this case being an aqueous solution of thallic chloride. The complexes $KPtAcac_2Cl$ and $KPtTFA_2Cl$ have been successfully oxidized in this way forming $KPtAcac_2Cl_3H_2O$ and $KPtTFA_2Cl_32H_2O$ respectively. That both of these complexes contain carbon-bonded groups is evident from their infra-red spectrum; in the acetylacetone complex a strong band is observed at 1712 cm^{-1} and in the trifluoroacetylacetone complex at 1756 cm^{-1}. This is an increase of 20–40 cm^{-1} in the stretching frequency of the carbonyl group as compared to the platinum(II) case and is also observed on going from dipyPtAcacCl to dipy-$PtAcacCl_3$. The splitting by the Pt isotope of the 3-CH proton resonance is observed in the p.m.r. spectrum of $KPtAcac_2Cl_3H_2O$ in aqueous solution although the magnitude is decreased by 20 cps. The splitting of the methyl group is not, however, observed. The chemical properties of these anionic platinum(IV) complexes are similar to those of the platinum(II) derivatives although no acid analogue is formed with strong acids, due to decomposition. With divalent metal ions however, complexes of the type $M^{II}(PtAcac_2Cl_3)_2$ are formed, where M = Mn, Fe, Co, Ni, Cu and Cd and there is a corresponding decrease of about 50 cm^{-1} in the free carbonyl stretching frequency in the infra-red. These compounds are slightly more soluble than are the platinum(II) metal-derivatives and the cadmium and nickel derivatives are monomeric in chloroform. The ultra violet spectrum of the cobalt and nickel salts suggest that the metal atom is in an octahedral environment.

(vi) *Silver(I)*

Silver nitrate and silver perchlorate have been shown to form adducts with several acetylacetone complexes of divalent and trivalent transition metal[19]. The perchlorates may contain one, two or three molecules of silver perchlorate per metal acetylacetonate group; two nitrate complexes are known, both with nickel bis(acetylacetonate), $AgNiAcac_32AgNO_3H_2O$ and $AgNiAcac_3AgNO_3H_2O$. The formation of these adducts was accompanied by a reduction in the carbonyl stretching frequency of the ligand at 1580 cm^{-1}. A crystal structure determination of the former complex has been carried out[20] and all three silver atoms have been shown to be bonded to the 3-carbon atoms of the acetylacetonate groups in addition to one oxygen atom, the metal–carbon bond length being 2.34 Å. The bridging acetylacetonate groups thus formed are similar but not identical to $(Me_3PtAcac)_2$. The chelating ring is bent slightly along a line connecting the two oxygen atoms although the dimensions of the ring are quite similar to those of conventional oxygen-bonded groups. The structures of the other complexes are presumably related to this compound.

(vii) *Gold(I)*

Phosphine and arsine gold halides of the type R_3EAuCl react with thallous beta-diketonates in organic solvents to give complexes of the general formula R_3EAu(beta-diketone)[21]. These complexes have been formed where R_3E is Et_3P, Ph_2EtP, Ph_3P and Ph_3As, and with the beta-diketones acetylacetone and benzoylacetone, although not with fluorinated beta-diketones. They are found to be soluble and monomeric in organic solvents.

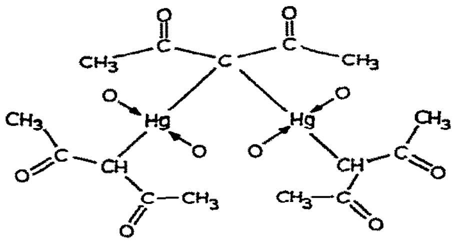
The p.m.r. spectrum of the complex $Ph_3PAuAcac$ has single 3-CH and CH_3 resonances indicating a symmetrical environment for the beta-diketone. The infra-red spectra of all the complexes are different from those of conventional oxygen-bonded beta-diketonates and show in particular carbonyl stretching frequencies around 1660 cm^{-1}. In view of this, and the fact that univalent gold normally has a coordination number of two with a linear stereochemistry it seems highly probably that these complexes contain carbon-bonded groups. No acid derivatives have been isolated and reaction with concentrated acid merely gives back the phosphine gold halides.

(viii) *Mercury(II)*

The compounds formed between mercury and beta-diketones are complex and are usually highly insoluble substances which are probably polymeric. They have not been fully characterized but the existance of mercury–carbon bonds of some form seems highly probable[22].

Several complexes are formed in the reaction of mercury derivatives with acetylacetone. Mercuric chloride reacts with neutral acetylacetone to form the insoluble complex Hg_2Cl_2Acac[30]. The infra-red spectrum of this complex shows one strong band at 1698 cm^{-1}. Sodium Acetylacetonate reacts with mercuric chloride in aqueous solution to precipitate the complex Hg_2Acac_3. This compound is also formed in a variety of other ways, for instance from the reaction of $(Ph_3P)_2HgCl_2$ with two moles of thallous acetylacetonate. It has been previously reported as $HgAcac_2$ but this has never been substantized by analytical data. The infrared spectrum contains several strong bands between 1690 and 1640 cm^{-1} and as with Hg_2Cl_2Acac, none between 1500 and 1600 cm^{-1}, where oxygen-bonded chelates absorb. The complex $Hg_2(CH_3CO_2)_2Acac$ has also been prepared. A complex of mercury with dipivoloylmethane, $HgDPM_2$ has been reported by Hammond *et al.*[23] and it is suggested on chemical evidence that here the diketone is bonded through one oxygen atom. However, this evidence is also consistent with bonding via carbon although on steric grounds it is not unusual for complexes of this ligand to differ from their acetylacetone analogues[24]. It seems likely that the mercury atom is bonded to either the 3- or the 1-carbon atom of at least one and probably all three ligands in Hg_2Acac_3 (in the latter case it would not be surprising if the DPM complex had a different formulation), with mercury–oxygen bonds affording a polymeric structure. A possibility is that one acetylacetone group acts as a bridging group between two mercury atoms via the 3-carbon atom, in a manner similar to that observed[3] in Se_2Acac_2. The most likely structure is shown in Scheme 9.

Other beta-diketones have also been investigated (*e.g.* benzoylacetone, dibenzoylmethane, trifluoracetylacetone and hexafluoroacetylacetone) and in these cases the situation is more complex. Stoichiometries of the type Hg_2X_2 (beta-diketone) are obtained where X = acetate, propionate, benzoate or beta-diketonate. With certain carboxylic acids, some of the benzoylacetone and dibenzoylmethane complexes are soluble in organic solvents and p.m.r. data indicates that the phenyl-ring is not involved in bonding to the mercury atom. This data, however, could not distinguish between 3-carbon, 1-carbon or oxygen bonding in the case of the complex $Hg_2(C_2H_5CO_2)_2(BA)$.



Scheme 9

Some complexes of the type Hg(beta-diketone) have also been obtained with acetylacetone and benzoylacetone. These still appear to contain divalent mercury however, and are probably derivatives of a $(\text{diketone})^{2-}$ species.

C. FACTORS INFLUENCING THE FORMATION OF CARBON-BONDED BETA-DIKETONATES

A beta-diketone may be regarded in one sense as a di-acyl substituted methane and the formation of carbon-bonded beta-diketonates can be related to the formation of metal alkyls in general. It has been shown by Jaffé that the low stability of metal carbon bonds is due to the low ionic resonance energy and low covalent contribution to these bonds[25]. The highest covalent contribution occurs with elements of high electronegativity. This can be seen in the formation of beta-diketone derivatives of the non-transition elements where the most electronegative elements, such as the halogens, sulphur and selenium form carbon bonded derivatives while less electronegative elements such as silicon, tin or aluminum form oxygen bonded compounds. The same effect is also seen with the transition elements. It has recently been suggested that the highest electronegativity values for the transition elements occur among the heavier elements of the second and particularly the third transition series[26]; it is these elements, which form the most stable simple alkyls and among these elements that nearly all carbon-bonded diketone complexes have been found.

The effect of electron withdrawing substituents, particularly fluorine, on a carbon atom bonded to a metal has been shown to increase the strength of the metal carbon bond, as the ionic nature of the bond is enhanced, and pi-bonding from the metal to the alkyl group can occur[27]. As acyl groups have a net electron withdrawing effect, a carbon-bonded beta-diketone should form a bond to a metal which is at least as strong as a corresponding alkyl complex. It should, therefore, be possible to form these complexes for all metals for which alkyls are known, especially in the presence of stabilizing ligands. There are, however, two competing factors in the formation of beta-diketone complexes i) the affinity of the metal for carbon ii) the affinity of the metal for oxygen and the resonance stabilization achieved by the formation of the chelate ring in oxygen-bonded complexes. Since most elements would be expected to form stronger bonds to oxygen than to carbon the second possibility is usually predominant. Only in cases where the electronegativity is sufficiently high to reduce the affinity of the metal for oxygen does the first case become evident. Even with platinum, however, the alternatives are finely balanced and it is only with univalent gold, where steric requirements prevent the formation of the chelate ring, that the first possibility occurs alone.

There are several examples in which the increased tendency of metals to form carbon-bonded complexes in going from the second to the third row of the transition series can be seen:

i) Carbon-bonded complexes of iridium are produced, together with oxygen-bonded complexes, in the reaction of potassium chloroiridate with the acetylacetonate ion in aqueous solution. Reaction of potassium chlororhodate with acetylacetone using 1:1 molar proportions for all reactants, produces oxygen-bonded complexes with the probable composition $K_2Rh_2Acac_3(OH)_5$. There is no evidence for the formation of carbon-bonded species in this reaction, or when the conditions and proportions of reactants are varied.

ii) Platinum forms several carbon-bonded beta-diketonates, which can be obtained in both oxidation states of the metal. However, the reaction of potassium chloropalladate with the acetylacetonate ion in aqueous solution, and similar reactions under a variety of conditions produce only the simple palladium bis-(acetylacetonate) complex.

iii) Phosphine and arsine gold(I) halides react with thallous beta-diketonates in aqueous solution giving complexes containing carbon-bonded beta-diketonates. Phosphine silver(I) halides of the type $(R_3PAgX)_4$ also react with thallous beta-diketonates but the products in this case are the three and four coordinate oxygen bonded complexes $R_3PAgAcac$ and $(R_3P)_2AgAcac$ where R = Ph. There is no evidence for the existence of metal–carbon bonds in the three coordinate complexes, even in the solid state.

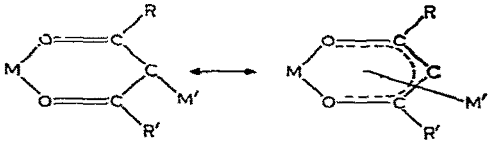
iv) Mercury(II) forms a wide range of complexes with beta-diketonates some of which appear to contain carbon-bonded diketone groups. Cadmium(II) however, appears to form only the simple bis(diketonate) complexes.

The two known examples of complexes of the second row elements which contain metal–carbon bonds to diketone groups are both examples of the bridging type of complex and appear to arise under rather special circumstances. In the case of the rhodium(I) complex, the metal–carbon bond is formed with one type of ligand only and a change of ligand is sufficient to split this bond. In the silver(I) case the metal–carbon bond is formed in the solid state, and from the nature of the complex, it is unlikely that it would exist otherwise. The only carbon-bonded complex known for a first row element is $Mn(CO)_3py_2HFA$. Hexafluoroacetylacetone has the most strongly electron-withdrawing substituents of any beta-diketone and a metal–carbon bond to this ligand should therefore be quite strong; the electron withdrawing effect will also tend to discourage the formation of a metal–oxygen bond as the oxygen atoms will tend to be fairly positive. It should, therefore, be the ligand most likely to form carbon-bonded complexes. However, attempts to form such complexes with third row elements have so far met with no success. Due to hydrolysis of the hexafluoroacetylacetone by a small amount of water, catalysed by the presence of metal complexes, trifluoroacetates are readily formed.

D. KETO-ENOL TAUTOMERISM IN CARBON-BONDED COMPLEXES

With the exception of the manganese complex described above, all the known simple carbon-bonded complexes contain the beta-diketone bonded to the metal in the reto form. P.M.R. and infra-red data show no evidence for the existence of the enol form of the diketone in any of these complexes although in general the enol content of neutral beta-diketones is between 80 and 100%. The stabilization of the keto form has been shown by p.m.r. studies to be related either to the electron-donor capacity of a substituent[27] on the central carbon atom or to steric effects. With electron withdrawing substituents such as chlorine, stabilization of the enol form occurs while electron donating groups such as alkyl groups increase the percentage of the keto form. On this basis, since stabilisation of the keto form occurs on coordination to a metal a net electron donation from the metal to the carbon atom is implied. This would be expected if the carbon-bonded ligand is regarded as a substituted methyl group with electron withdrawing acyl groups. Steric effects also appear to be important since increasing the size of the substituent in the 3-position is reflected in a decrease in the percentage of the enol form. Thus 3-substituted acetylacetonates with large groups in this position have a much reduced tendency to form conventional oxygen-bonded chelates than does acetylacetone. The presence of bulky metal-atoms in this position would, therefore, favor the keto form. In the complex dipy $Me_3PtAcac$, the crystal structure determination[2] has shown the two carbonyl groups to be oriented in opposite directions and this would certainly inhibit the formation of the enol. However, the study of $KPtAcac_2Cl$ shows that the carbonyl groups point in the same direction[5], yet there is still no evidence for the enol form in this complex.

In the bridged beta-diketonate complexes, the precise nature of the bonding is uncertain but is probably best represented as intermediate between the keto and enol forms of the diketone. In the infra-red spectra of bridged complexes, the stretching frequencies of the carbonyl groups vary from 1660 cm^{-1} for $[(MeCN)(C_2F_4)RhAcac]_2$ to less than 1580 cm^{-1} for $AgNi(Acac)_3 2AgNO_3 H_2O$ suggesting a considerable difference in the nature of the bonding. The metal complexes derived from the anionic carbon-bonded species of iridium(III), platinum(II) and platinum(IV) all show a reduced carbonyl frequency as compared with the corresponding alkali metal salts. The "acid" complex, $HPtAcac_2Cl$, which contains the neutral enol form of the diketone coordinated to the metal can be placed at the end of the series of metal complexes and probably represents one of the limiting structures. The diketone in $(Me_3PtAcac)_2$ is also apparently close to the limiting form since the crystal structure shows the planar chelate ring to be only slightly different from that found in a conventional oxygen-bonded chelate in which the diketone is in the enol form[1]; the carbonyl stretching frequency at 1600 cm^{-1} is consistent with this suggestion. For the silver(I) complex, $AgNiAcac_3 \cdot 2AgNO_3H_2O$ the chelate ring is apparently bent[20]. The two possible limiting forms of bonding of the metal atoms to the beta-diketone are shown in Schem 10 and the bonding of most bridged complexes is presumably intermediate between these.



Scheme 10

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