PART II

REACTIVITY OF METAL CHELATES OF
β-DICARBONYL COMPOUNDS
An extensive field is encompassed by the term 'reactivity of metal chelates of \(\beta\)-dicarbonyl compounds'. In the present context, it refers to susceptibility of the metal chelates to electrophilic substitution (Chapters 1, 2, 3 and 4), residual affinity of metal atom in metal chelates (Chapter 5) and replaceability of the ligands (Chapter 6).
CHAPTER 1

NITRATION OF
METAL ACETYLACETONATES
NITRATION OF METAL ACETYLACETONATES

Most of the substitution studies in metal acetylacetonates have been confined to robust chelates. In addition to those of transition metal chelates, acetylacetonates of beryllium(II) and aluminium(III) have been chosen for study in this investigation since the latter two acetylacetonates have excellent solubility behaviour, apart from moderate stability. Furthermore, these diamagnetic compounds are amenable to proton magnetic resonance spectral analysis.

Nitration of metal acetylacetonates cannot be carried out by the familiar nitric-sulphuric acid mixture, since the complexes are rapidly decomposed in it. The most successful nitrating agent reported for metal acetylacetonates is a mixture of copper nitrate trihydrate and acetic anhydride. This nitrating agent has been found to be of general applicability to robust acetylacetonates. In the present investigation, however, the method was found to yield copper nitroacetylacetonate when used for the nitration of labile acetylacetonates of aluminium and

* 2,4-pentanedionates.
beryllium. This prompted the need to look for other nitrating agents.

Two new nitrating agents, aluminium nitrate in acetic anhydride and concentrated nitric acid in acetic anhydride, have been introduced in the course of this investigation as nitrating agents of general applicability.

Aluminium nitrate and nitric acid as nitrating agents for metal acetylacetonates

A metal nitrate which showed great promise as a nitrating agent for metal acetylacetonates is aluminium nitrate, Al(NO₃)₃·3H₂O. Conditions have been standardized for using it as a nitrating agent for robust and labile chelates alike. Metal acetylacetonates nitrated, using this nitrating agent in cold acetic anhydride are of cobalt(III), chromium(III), copper(II) and beryllium(II).

An interesting nitrination brought about by this reagent has been in the preparation of the nitroacetylacetonate* of aluminium in a single step. Acetylacetone and aluminium nitrate reacted in acetic anhydride yielding the aluminium

* 3-nitro-2,4-pentanedionate.
nitroacety lacetonate. This elegant preparation obviates the need to prepare aluminium acety lacetonate as an intermediate in the preparation of aluminium nitroacety lacetonate.

Under carefully controlled conditions, nitric acid in acetic anhydride proved to be even better a nitrating agent than aluminium nitrate in acetic anhydride. All the nitration achieved with aluminium nitrate - acetic anhydride mixture, were accomplished in greater yield with the nitric acid - acetic anhydride mixture.

The nitration brought about by nitric acid, particularly in the labile acety lacetonates is very encouraging, since it shows that even drastic reagents can be used for carrying out reactions in metal chelates, provided, of course, the right conditions are found and adopted.

The following table is illustrative of the comparative merits of the two nitrating agents. The yields reported are of purified materials. Robust chelates could be purified by chromatography on acid-washed alumina. The labile chelates, particularly the aluminium compound was found to leave a streak on its way down the column, showing partial decomposition. A chromatographic adsorbent found
suitable for the purification of the aluminium compound is polycaprolactam powder (commercial nylon-6 beads, treated with hydrochloric acid at room temperature, washed, dried and pulverized to 100-200 mesh. Thin layer chromatography on calcium sulphate was used to examine homogeneity of the products.

<table>
<thead>
<tr>
<th>Nitroacetylacetonate of</th>
<th>Method of preparation</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium(III)</td>
<td>( \text{Al(NO}_3\text{)}_3 + \text{Ac}_2\text{O} + \text{acetylacetone} )</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>( \text{Al(acac)}_3 + \text{Ac}_2\text{O} + \text{HNO}_3 )</td>
<td>57</td>
</tr>
<tr>
<td>Chromium(III)</td>
<td>( \text{Cr(acac)}_3 + \text{Ac}_2\text{O} + \text{Al(NO}_3\text{)}_3 )</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>( \text{Cr(acac)}_3 + \text{Ac}_2\text{O} + \text{HNO}_3 )</td>
<td>25</td>
</tr>
<tr>
<td>Cobalt(III)</td>
<td>( \text{Co(acac)}_3 + \text{Ac}_2\text{O} + \text{Al(NO}_3\text{)}_3 )</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td>( \text{Co(acac)}_3 + \text{Ac}_2\text{O} + \text{HNO}_3 )</td>
<td>47</td>
</tr>
<tr>
<td>Beryllium(II)</td>
<td>( \text{Be(acac)}_2 + \text{Ac}_2\text{O} + \text{Al(NO}_3\text{)}_3 )</td>
<td>46</td>
</tr>
<tr>
<td></td>
<td>( \text{Be(acac)}_2 + \text{Ac}_2\text{O} + \text{HNO}_3 )</td>
<td>66</td>
</tr>
<tr>
<td>Copper(II)</td>
<td>( \text{Cu(acac)}_2 + \text{Ac}_2\text{O} + \text{Al(NO}_3\text{)}_3 )</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>( \text{Cu(acac)}_2 + \text{Ac}_2\text{O} + \text{HNO}_3 )</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td>( \text{Cu(NO}_3\text{)}_2 + \text{Ac}_2\text{O} + \text{Be(acac)}_2 )</td>
<td>46</td>
</tr>
<tr>
<td></td>
<td>( \text{Cu(NO}_3\text{)}_2 + \text{Ac}_2\text{O} + \text{Al(acac)}_3 )</td>
<td>53</td>
</tr>
</tbody>
</table>

acac = \( \text{C}_5\text{H}_7\text{O}_2 \), acetylacetonate anion.
\( \text{Ac}_2\text{O} \) = acetic anhydride.
From vapour pressure measurements in the nitric acid-acetic anhydride systems, Vandoni and Viola concluded that for solutions containing low percentage of nitric acid, most of the acid is converted to acetyl nitrate.

$$\text{Ac}_2\text{O} + \text{HNO}_3 \longrightarrow \text{AcO}_2\text{NO}_2 + \text{AcOH}$$

At higher concentrations of the acid, appreciable amounts of dinitrogen pentoxide are formed

$$\text{Ac}_2\text{O} + 2\text{HNO}_3 \longrightarrow \text{N}_2\text{O}_5 + 2\text{AcOH}$$

Considerable evidence from Raman spectra, vapour pressure measurements and infrared spectra support the conclusions of Vandoni and Viola.

Under conditions of the chelate nitration, acetyl nitrate

$$\text{CH}_3\text{COONO}_2 \longrightarrow \text{CH}_3\text{COO}^- + \text{NO}_2^+$$

is, therefore, considered responsible for the nitro-substitution. The greater efficiency of nitric acid-acetic anhydride mixture over that of aluminium nitrate-acetic anhydride, is probably due to the greater facility of formation of acetyl nitrate from the acid than from aluminium nitrate.

Infrared spectral evidences have been very useful in characterizing the nitration products. Metal acetyl-acetonates absorb strongly in the 1600-1800 cm$^{-1}$ region
and a doublet is usually observed. A very useful observation\textsuperscript{10} has been that in metal acetylacetonates substituted at the third carbon atom, the lower frequency band is conspicuously absent, unless the substituent absorbs in this region. The disappearance of the lower frequency band has been ascribed to mass effect of the substituent\textsuperscript{10}.

A medium intensity band at 1200 cm\textsuperscript{-1} is observed in the parent acetylecetonates. From deuteration studies this band has been assigned to $\gamma$-CH vibration\textsuperscript{11}. In the 3-substituted acetylacetonates this band does not occur indicating the entry of the group in this position\textsuperscript{11}. Other changes do occur but are of less significance. The above-mentioned changes in the spectra, and the occurrence of bands characteristic of the substituent can be taken as evidence of substitution in metal acetylacetonates.

In all the nitroacetylacetonates, the 1600-1600 cm\textsuperscript{-1} region of the spectra, showed two strong absorptions. The lower 1520 cm\textsuperscript{-1} band is attributable to the asymmetric nitro stretching frequency\textsuperscript{2}. A characteristic feature of the spectra is the appearance of a strong peak around 826 cm\textsuperscript{-1}, which is presumed to be a nitrogen-oxygen mode\textsuperscript{2}. The 1200 cm\textsuperscript{-1} region, as expected, did not show any absorption. Infrared spectra of aluminium acetylacetonate and aluminium nitroacetylacetonate are shown in Figs. 8 and 9.
respectively. These are typical of all acetylacetonates and nitroacetylacetonates.

Proton magnetic resonance spectra were recorded for the aluminium chelates in benzene. The signals for the ring hydrogen and methyl hydrogens occurred at 310.2 and 106.0 cps respectively in the integrated intensity 1:6 in the parent acetylacetonate. Signal for the methyl hydrogens of the nitroacetylacetonate, occurred at 115.0 cps. The region of the ring hydrogen did not show any absorption, indicating complete substitution.

Action of reducing agents on aluminium nitroacetylacetonate

Reduction of nitro group to amino was attempted, since the amino group, if can be diazotized, could be a potential intermediate for quite a number of substituted chelates. Sodium aluminium hydride was used to this end. In tetrahydrofuran the metal chelate reacted vigorously with the complex hydride. A white crystalline material was obtained from the reaction mixture which, however, proved to be only aluminium acetylacetonate. An unusual reaction like this was reported\textsuperscript{12}, wherein zinc dust in pyridine converted chromium nitroacetylacetonate back to chromium acetylacetonate.
Hydrazine hydrate in conjunction with Raney nickel is known to effect specific reduction of nitro groups in delicate systems\textsuperscript{13}. It was, therefore, of interest to try this method on aluminium nitroacetylacetonate.

Hydrazine hydrate and Raney nickel reacted with a suspension of aluminium nitroacetylacetonate in alcohol. The brown sticky substance obtained was extracted with ether; from the ether extract a metal-free white crystalline material was obtained which melted sharply at 125\degree C.

The formation of the metal-free product was thought to be due to the lability of the metal chelate itself. Hence, the same reaction was re-examined using stable chromium nitroacetylacetonate. However, the same metal-free product was obtained. This was subsequently identified as 4-nitro-3,5-dimethylpyrazole\textsuperscript{14} from melting point, analysis and infrared spectrum\textsuperscript{15}. Under similar conditions aluminium acetylacetonate yielded 3,5-dimethylpyrazole\textsuperscript{16,17}, which is obtainable also from acetylacetone and hydrazine hydrate\textsuperscript{18}.

In preference to reduction, it was condensation of the \( \beta \) -diketone with hydrazine, that occurred. The preparation of 4-nitro-3,5-dimethylpyrazole by this method
is significant, since aluminium nitroacetylace tone has been used as intermediate in the place of non-existent 3-nitroacetylace tone.

**Attempted preparation of 3-nitroacetylace tone**

Since 3-nitroacetylace tone is reported as non-existent, an attempt was made to obtain it by indirect means. Copper nitroacetylace tone was suspended in cold dilute sulphuric acid and was extracted with ether. The ether extract after drying was allowed to evaporate, when a pale yellow thick liquid was obtained. On careful distillation under vacuum, a colourless liquid was obtained which solidified to a pale yellow material on standing. From melting point, analysis and infrared spectrum it was found to be nitroacetone.

Nitroacetylace tone seems to have undergone hydrolytic carbon-carbon cleavage resulting in the formation of acetic acid and nitroacetone. Such a C-C cleavage has been reported for acetylace tone, although in alkaline medium.
Experimental

Acetylacetonates of aluminium(III), chromium(III), cobalt(III), copper(II) and beryllium(II) were prepared and purified according to reported methods\(^{21,22,23}\).

\[
\begin{align*}
\text{Al(acac)}_3 & \quad \text{Found: C, 65.60; H, 6.62\%. Calcd.: C, 65.55; H, 6.48\%.} \\
\text{Cr(acac)}_3 & \quad \text{Found: C, 51.61; H, 6.23\%. Calcd.: C, 51.58; H, 6.02\%.} \\
\text{Co(acac)}_3 & \quad \text{Found: C, 50.71; H, 6.88\%. Calcd.: C, 50.68; H, 6.90\%.} \\
\text{Cu(acac)}_2 & \quad \text{Found: C, 45.95; H, 6.61\%. Calcd.: C, 45.90; H, 6.56\%.} \\
\text{Be(acac)}_2 & \quad \text{Found: C, 57.12; H, 6.71\%. Calcd.: C, 57.37; H, 6.76\%.
}\end{align*}
\]

Single-step preparation of aluminium nitroacetylacetonate

Acetylacetone (3 ml; 0.03 mole) and acetic anhydride (20 ml.) were taken in a conical flask and the mixture stirred magnetically, in an ice bath. Crystals of aluminium nitrate, \(\text{Al(NO}_3\text{)}_3 \cdot 3\text{H}_2\text{O}\), (3.75 g.; 0.01 mole) were pulverized and added in six portions to the stirred solution during 30 min. After stirring for 1 hr. the flask was taken out of the ice bath, but the stirring was continued. The contents of the flask slowly became yellow through an exothermic reaction. Pressure developed inside the flask was released by occasional lifting of the stopper, and undue rise in temperature was promptly checked by dipping the flask.
in ice-cold water. A yellow deposit was formed after the clear solution had become orange and then turbid. The mixture was stirred for 4 hr. at room temperature and then poured into 200 ml. of ice-cold water containing sodium acetate and stirred for 1 hr. The yellow residue obtained on filtration was washed first with water and then with ethanol. After air drying, the product was crystallized twice from benzene; yield, 2.3 g.

A part of the material (0.3 g.) was further purified by column chromatography on polyacrylam powder (30 g., 2 cm. dia. column). Benzene was used for both development and elution (total volume 86 ml.), yellow glistening crystals were obtained from the eluate. Yield, 0.21 g.

Calcium sulphate, for thin layer chromatography, was prepared from an aqueous solution of calcium chloride and an equivalent quantity of sulphuric acid according to the method of Matlis et al. The material was washed thoroughly with water until entirely free of acid and dried at 115-120°C. Ground and sieved. The powder which passed through 200 mesh was used.

About 4 g. of the absorbent was slurred with 12 ml. of water and was used to coat four thoroughly degreased
glass plates (3.6 x 15 cm.). Dried at 100-110°C for 2 hr. and cooled in a desiccator over silica gel.

The applicator used for obtaining a uniform layer of 0.5 mm. and the technique adopted have been described in detail recently by Gupta and Sukdev. When the solvent (benzene) front reached the 10 cm. mark, the spot of the aluminium nitroacetylacetone had reached 8.4 cm. (Rf = 0.84). The spot did not show any separation. Melting point, 260-261°C. Found: C, 33.44; H, 4.07; N, 3.31; Al, 6.03%. C_{16}H_{16}N_{3}O_{12}Al requires: C, 33.22; H, 3.92; N, 3.15; Al, 6.88%.

Nitrilation using aluminium nitrate

**Beryllium nitroacetylacetone** = Beryllium acetylacetone (3.1 g., 0.015 mole) and acetic anhydride (25 ml.) were taken in a conical flask, cooled and stirred. Powdered aluminium nitrate (3.75 g., 0.01 mole) was slowly added. The rest of the procedure was the same as in the single-step preparation described earlier. The product was sucked dry on a filter. Extracted with benzene. A yellow material obtained from the extract was crystallized from hot ethanol as lustrous yellow needles, m.p., 196.5°C. Found: C, 40.53;
Copper, cobalt and chromium acetylacetonates were nitrated similarly.

**Copper nitroacetylacetonate** - Green crystals, m.p., 233-234°C (decomp.). Found: C, 34.27; H, 3.63; N, 8.03; Cu, 13.17%.
C$_{10}$H$_{12}$N$_2$O$_8$Cu requires: C, 34.14; H, 3.41; N, 7.97; Cu, 13.03%.

**Chromium nitroacetylacetonate** - Red-violet needles; m.p., 257°C. Found: C, 37.41; H, 3.98; N, 8.31; Cr, 10.90%.
C$_{16}$H$_{18}$N$_3$O$_1$$_2$Cr requires: C, 37.19; H, 3.72; N, 8.68; Cr, 10.74%.

**Cobalt nitroacetylacetonate** - Green needles, m.p., 194-196°C (decomp.). Found: C, 36.31; H, 3.93; N, 8.51; Co, 11.38%.
C$_{16}$H$_{18}$N$_3$O$_1$$_2$Co requires: C, 36.67; H, 3.67; N, 8.55; Co, 12.00%.

**Nitration using nitric acid**

**Aluminium nitroacetylacetonate** - Aluminium acetylacetonate (2.25 g.; 0.01 mole) was suspended in ice-cooled and magnetically stirred acetic anhydride (25 ml.). To this was added, drop by drop, conc. nitric acid (16N; 2.2 ml; 0.036 mole) which was previously cooled to 0°C. A clear yellow solution was obtained when the cooling bath was removed after 1 hr., but
when the stirring was continued yellow deposition slowly occurred. After stirring for 4 hr., the reaction mixture was worked up as in the case of nitration with aluminium nitrate. Yield, 2.6 g. Analytical data were similar to those obtained for the product from the single-step process.

Nitration of the other metal acetylacetonates was conducted similarly. Attempted nitration of aluminium and beryllium acetylacetonates, using copper nitrate (whereby copper nitroacetylacetonate was formed) was also conducted similarly.

Nitration products obtained by different methods gave identical IR spectra and similar analytical data.

Attempted reduction of aluminium nitroacetylacetonate with sodium aluminium hydride

Sodium aluminium hydride (0.64 g.; 95% pure) in tetrahydrofuran (25 ml.) was added to a solution of aluminium nitroacetylacetonate (1.15 g.; 0.0025 mole) in the same solvent (80 ml., drop by drop. The solution became warm and viscous. This was carefully neutralized with dilute hydrochloric acid. The product obtained was removed, sucked dry and crystallized from benzene. Yield: 0.68 g. of aluminium acetylacetonate.
Attempted reduction of nitroacetylacetoneates with hydrazine hydrate

Aluminium nitroacetylacetoneate (1.16 g.; 0.026 mole) in alcohol (30 ml.) was treated with hydrazine hydrate (4 ml.; 0.08 mole) and a pinch of Raney nickel. Refluxed over a water bath for 3 hr. The hot solution was filtered and evaporated to dryness. Extracted with ether. Colourless needles; yield, 0.9 g. (82%). Found: C,43.01; H,4.89; N,29.80%. Required for \( \text{C}_6\text{H}_7\text{N}_3\text{O}_2 \): C,42.65; H,4.99; N,29.79%.

Method was essentially the same when chromium nitroacetylacetoneate and aluminium acetylacetonate were treated with hydrazine hydrate. The product obtained from aluminium acetylacetonate gave the following analytical data: C,62.32; H,9.86; N,29.31%. Required for \( \text{C}_6\text{H}_8\text{N}_2 \): C,62.6; H,9.33; N,29.17%.

Attempted preparation of 3-nitroacetylacetone

Copper nitroacetylacetoneate (3.5 g.; 0.01 mole) was suspended in dilute sulphuric acid (60 ml., 10%) and shaken with ether (three times successively, using 30 ml. each time). The ether extract (pale yellow) was dried with sodium sulphate, solvent removed and the product distilled carefully in vacuum, when a colourless liquid was obtained.
which solidified to a pale yellow solid; m.p., 60°C.
Moderately soluble in water, the solution being acidic to litmus. Found: C, 34.66%; H, 4.87%; N, 13.21%. \( \text{C}_3\text{H}_5\text{NO}_3 \) requires: C, 34.36%; H, 4.85%; N, 13.63%. Infrared spectrum showed strong adsorption at 1732, 1550, 1306, 1200 and 747 cm\(^{-1}\).

In this chapter and unless otherwise stated, throughout the investigation covering this thesis, carbon, hydrogen and nitrogen were determined by micro analysis. Metal was determined after decomposing the compound with concentrated sulphuric-nitric acid mixture, by standard quantitative methods. Infrared spectra were recorded in a Perkin Elmer infracord spectrophotometer. Proton magnetic resonance spectra were obtained in a Varian Associates model A-60 spectrometer operating at 60 Mc with tetramethyl silane as an internal standard. Chemical shifts are expressed in cps downfield from TMS.
CHAPTER 2

BROMINATION OF
METAL ACETYLACETONATES
BROMINATION OF METAL ACETYLACETONATES

Bromine is reported to bring about destructive bromination of metal β-dicarbonyl chelates. Most of the bromination studies with metal acetylacetonates have been carried out using N-bromosuccinimide. The success of bromination using this reagent, has been ascribed to the absence of strongly acidic by-products. It was implied that the decomposition of metal chelates, on bromination with bromine, was due to the acidity of the hydrogen bromide liberated during the course of substitution. Bromination of six metal acetylacetonates was re-examined in this investigation using bromine in the presence of excess calcium carbonate, so that the acidity would be kept in check.

Bromination of aluminium(III), beryllium(II) and chromium(III) acetylacetonates was quite successful by this method. Though calcium carbonate was found effective in warding off the adverse effect of hydrogen bromide in bromination of the above three metal acetylacetonates, it was entirely ineffective in the
bromination of copper(II), cobalt(III) and manganese(III) acetylacetonates. In the decomposed products obtained in the bromination of the latter three metal acetylacetonates, copper(I), cobalt(II) and manganese(II) species respectively, have been found present.

Acidity of hydrogen bromide cannot be the reason for the decomposition of copper, cobalt and manganese acetylacetonates, since labile aluminium acetylacetonate has undergone non-destructive bromination under the same condition. The facility of reduction of compounds of copper(II), cobalt(III) and manganese(III) to stable lower oxidation states is well known. Reducibility of these metal ions should, therefore, be the cause of destruction of their metal chelates under the experimental conditions.

The results lead to the conclusion that the reducing nature of the hydrogen bromide is far more destructive than its acidity to acetylacetonates of certain transition metals, which have stable lower oxidation states.

The above findings are supported by the work of Nakamura and Kawaguchi, whose attempted bromination
of copper acetylacetonate with bromine, resulted in
the formation of cuprous bromide and γ-bromo-
acetylacetone. Furthermore, the formation of cupric
chloride, cuprous bromide and cuprous iodide from
copper(II) ethylacetoacetate on reaction with chlorine,
bromine and iodine respectively, is in conformity with
the above line of reasoning.

Bromination of beryllium(II), aluminium(III) and
chromium(III) acetylacetonates was conducted in both
carbon tetrachloride and chloroform. When the latter
solvent was used, bromoacetylacetonates of aluminium
and chromium were rendered insoluble by the formation
of chloroform clathrates. These clathrates were
completely desolvated on extraction with hot benzene
and drying the residue obtained from it in vacuo.

Analytical data and melting points of the three
bromoacetylacetonates agreed with those reported.
The infrared spectra of these compounds did not show
any absorption in the 1200 cm⁻¹ region. The 1500-1600 cm⁻¹
region was characterized by a single sharp absorption.
Infrared spectra of these compounds were superposable
with those of authentic samples. Melting points remained
undepressed on admixture with the authentic samples.
Infrared spectrum of beryllium bromoacetylacetonate is
shown in Fig.10, as a representative type.

* 3-bromo-2,4-pentanedionates.
<table>
<thead>
<tr>
<th>Compound</th>
<th>m.p.°C</th>
<th>yield(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be(C₆H₆O₂Br)₂</td>
<td>177-179</td>
<td>90</td>
</tr>
<tr>
<td>Al(C₆H₆O₂Br)₃</td>
<td>215-216</td>
<td>50-60</td>
</tr>
<tr>
<td>Cr(C₆H₆O₂Br)₃</td>
<td>225-229</td>
<td>50-60</td>
</tr>
</tbody>
</table>

Yields reported are based on purified products.

The melting point (226-229°C) of the chromium bromoacetylacetone remained unaltered even after several crystallisations and is identical with the value reported by Collman et al. Kluiber, however, reported the melting point of this compound as 240-241°C.

The method, though not of general applicability to transition metal acetylacetonates, is still of interest, since the brominated chelate is easily separated from the calcium carbonate and calcium bromide. When N-bromosuccinimide is used for bromination, the separation of the brominated chelate from succinimide formed is often not easily achieved.

Beryllium and aluminium ethylacetoacetates, under these conditions, did not yield the desired substituted metal chelates. Instead, a metal-free liquid was obtained, which got analysed for bromoethylacetoacetate. It was not further characterized.
Experimental

Manganese(III) acetylacetonate: Prepared from manganous chloride, potassium permanganate and acetylacetone. Found: C, 51.34; H, 6.08%. Calculated: C, 61.17; H, 5.97%.

Aluminium ethylacetoacetate: Aluminium isopropoxide (10.2 g.; 0.06 mole), suspended in absolute alcohol (50 ml.), was stirred vigorously with freshly distilled ethylacetoacetate (19.52 g.; 0.15 mole). The mixture was subsequently evaporated to dryness over a water bath. Alcohol (50 ml.) was again added and the evaporation repeated. From the residue, very pure aluminium ethylacetoacetate was obtained by extraction with petroleum ether. Colourless crystals, m.p., 78-79°C. Yield, 19.5 g. (94%). Found: C, 52.30; H, 6.57; Al, 6.63%. Required for \( \text{C}_{18}\text{H}_{27}\text{O}_{9}\text{Al} \): C, 62.18; H, 6.52; Al, 6.52%.

Beryllium ethylacetoacetate: Prepared from beryllium chloride, ethylacetoacetate and aqueous ammonia. Found: C, 54.20; H, 6.85%. Calcd.: C, 53.94; H, 6.74%.

Beryllium bromoacetylacetonate: Beryllium acetylacetonate (2.07 g.; 0.01 mole) was dissolved in dry chloroform (40 ml.), cooled and kept stirred in a conical flask along with finely
powdered calcium carbonate (5 g.; 0.06 mole) using a magnetic stirrer. Bromine (3.2 g.; 0.02 mole) in chloroform (15 ml.) was slowly added from a dropping funnel fitted to the flask and provided with pressure equalizing arrangement and a calcium chloride drying tube. After complete addition which took about 1.5 hr., the contents were stirred at room temperature for an additional hour, filtered and the filtrate evaporated to dryness. The residue was extracted with benzene; the product obtained from the benzene extract was crystallized once from benzene-petroleum ether. Yield, 3.28 g.

Found: C, 33.10; H, 3.41; Be, 2.63%. C_{10}H_{12}Br_{0.5}Be requires: C, 32.90; H, 3.29; Be, 2.47%.

Bromination procedure was essentially the same for all chelates. Aluminium and chromium bromoacetylacetonates were found being precipitated out. Hence, after the reaction the solvent was removed by evaporation and the residue extracted with hot benzene. The material recovered from the benzene extract was heated in vacuum at 80°C. The products were further purified by crystallization from benzene-petroleum ether.

**Aluminium bromoacetylacetonate**: Found: C, 32.30; H, 3.43; Al, 4.32%. C_{16}H_{18}Br_{0.5}Al requires: C, 32.10; H, 3.21; Al, 4.82%.
Chromium bromoacetylacetonate:  
- Found: C, 30.37; H, 3.31; Cr, 8.33%.  
- Required for $\text{C}_6\text{H}_{12}\text{Br}_3\text{O}_6\text{Cr}$: C, 30.73; H, 3.07; Cr, 8.83%.

In the bromination of the acetylacetonates of cobalt(III), manganese(III) and copper(II), the filtrate did not contain any metal chelate, nor was the residue extractable with solvents in which the parent or substituted chelates are soluble. The filtrate, however, contained a metal-free oil presumably 3-bromoacetylacetone. Another metal-free oil was obtained in the attempted bromination of aluminium and beryllium ethylacetocetates.

Yields obtained from carbon tetrachloride were comparable to those obtained from chloroform for the bromoacetylacetonates, of beryllium, aluminium and chromium.
CHAPTER 3
THIOCYANATION OF METAL ACETYLACETONATES
The direct replacement of a hydrogen atom by a thiocyanate, \((\text{SCN})\), group through the use of thiocyanogen, \((\text{SCN})_2\), is commonly termed thiocyanation. The non-destructive thiocyanation reported for certain robust metal acetylacetonates is significant, since this substitution reaction is limited mostly to aromatic amines and phenols, although a few particularly reactive aromatic hydrocarbons are also thiocyanated. It was, therefore, of interest to examine the possibility of thiocyanation of labile acetylacetonates of aluminium(III) and beryllium(II). Manganese(III) acetylacetonate was also included for study.

Thiocyanogen, which is a pseudo-halogen, is used in synthesis in essentially the same way as the halogens, with the exception that certain precautions must be observed owing to the instability of thiocyanogen. At room temperature, it polymerizes rapidly to pseudo- or para- thiocyanogen. Although stable in inert dry solvents, thiocyanogen may polymerize on standing, under the catalytic influence
of heat, light, moisture or oxygen. It is also readily hydrolysed. For these reasons, when thiocyanogen is employed in chemical reactions, it is prepared in solution or more commonly produced in situ. In this investigation, a fresh solution of it in ethylenedichloride was obtained from lead thiocyanate and bromine and was used immediately, after filtering under nitrogen.

Although aluminium(III) and beryllium(II) acetylacetonates yielded the fully substituted chelates, the product from manganese(III) acetylacetonate was metal-free. Aluminium and beryllium thiocyanatoacetylacetonates were characterized through their analytical data and infrared and proton magnetic resonance spectra. A sharp peak at 2176 cm\(^{-1}\) due to C≡N stretching and another around 740 cm\(^{-1}\) due to C-S stretching vibrations, characteristic of thiocyanato group, were observed in the infrared spectra of both the compounds (Figs. 11 and 12). The medium intensity peak at 1200 cm\(^{-1}\) of the parent chelates was absent in these substituted chelates. The 1600-1600 cm\(^{-1}\) region showed a single strong absorption. The proton

* 3-thiocyanato-2,4-pentanedionates*
magnetic resonance spectra of the compounds, as expected, showed only a single signal (methyl hydrogens).

<table>
<thead>
<tr>
<th></th>
<th>Signal at (cps)</th>
<th>Solvent</th>
</tr>
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<tbody>
<tr>
<td>Aluminium thiocyanatoacetylacetonate</td>
<td>163</td>
<td>CHCl₃</td>
</tr>
<tr>
<td>Beryllium thiocyanatoacetylacetonate</td>
<td>156</td>
<td>CCl₄</td>
</tr>
</tbody>
</table>

The metal-free product obtained from manganese(III) acetylacetonate proved to be 3-thiocyanatoacetylacetone from analysis and infrared spectrum.

It is very significant that acetylacetonates of two typical non-transition metals, namely beryllium and aluminium - one each of the first and second short periods of the periodic system - have undergone thiocyanation and other electrophilic substitutions in such a facile manner. This proves, beyond doubt, that the presence of d electrons and their delocalization are not essential to confer quasi-aromaticity to metal acetylacetonates. While aluminium has empty high energy d orbitals, beryllium has none.

Preparation of thiocyanatoacetylacetonate of aluminium, by a different method, has been reported.
**Experimental**

**Aluminium thiocyanatoacetylacetonate : Bromine**

(10.6 g.; 3.37 ml.; 0.066 mole) in 1,2-dichloroethane (20 ml.) was added slowly to a vigorously stirred suspension of anhydrous lead thiocyanate (21.4 g.; 0.066 mole) in the same solvent (80 ml.) kept cooled in a freezing-mixture. The red bromine colour was allowed to disappear before each successive addition of bromine. The mixture of thiocyanogen and lead bromide produced was stirred for 5 min. after the bromine addition was complete.

The solid lead bromide formed was allowed to settle and the colourless thiocyanogen solution was filtered with a filter-stick under nitrogen pressure, directly into the solution of aluminium acetylacetonate (6.6 g.; 0.02 mole) in 1,2-dichloroethane (50 ml.) kept cooled in a freezing-mixture. The mixed solutions were stirred and cooled for 2 hr. after which the contents were allowed to come to room temperature and react for an additional hour. At this stage an yellowish suspension was noticed, which was sent back into solution by adding 50 ml. more of the solvent.

The solution was extracted twice with water (150 ml. each time) after which the organic phase was dried with calcium chloride, filtered and evaporated to dryness in
vacuum. The residue obtained was recrystallized from methylene chloride - chloroform mixture. Grey material; yield, 7.5 g. (70-80%); m.p., 183-4°C. Found: C, 43.91; H, 4.00; N, 8.70; Al, 6.33%. C\textsubscript{13}H\textsubscript{18}N\textsubscript{3}O\textsubscript{6} requires: C, 43.64; H, 3.64; N, 8.48; Al, 6.45%.

The same method was used for the thiocyanation of beryllium and manganese acetylacetonates; care being exercised to mix equivalent quantities of the reactants.

**Beryllium thiocyanatoacetylacetonate** - Crystallized twice from benzene-petroleum ether. Yellowish-brown material; yield, 65%; m.p., 147-8°C. Found: C, 44.87; H, 3.32; Be, 2.91%. C\textsubscript{12}H\textsubscript{12}N\textsubscript{2}O\textsubscript{4}Be requires: C, 44.86; H, 3.74; Be, 2.80%.

The metal-free residue obtained from manganese acetylacetonate, was recrystallized from ethylene dichloride-petroleum ether mixture. Brown residue; yield, 50%; m.p., 73-80°C. Found: C, 45.87; H, 4.37%. C\textsubscript{6}H\textsubscript{7}NO\textsubscript{2}S requires: C, 45.90; H, 4.46%. IR spectrum showed strong absorptions at 2174, 1724 and 1585 cm\textsuperscript{-1}.
CHAPTER 4
MERCURATION

Action of mercuric acetate on metal
chelates of β-dicarbonyl compounds
Mercuration is a typical aromatic reaction. Though the quasi-aromatic nature of metal chelates of \( \beta \)-dicarbonyl compounds has often been indicated and discussed, no attempt seems to have been made to mercurate the metal chelates. It was, therefore, thought desirable and timely to examine the possibility of this reaction on metal chelates of \( \beta \)-dicarbonyl compounds.

Mercuration of aromatic nuclei is accomplished by heating with such mercuric salts as the chloride, nitrate or acetate\(^{25}\).

\[
\text{ArH} + \text{HgX}_2 \rightarrow \text{Ar-Hg-X} + \text{HX}
\]

The product is an organo-metallic compound (involving direct metal-carbon bond).

In the present investigation, mercuric acetate was used, since the chloride and nitrate, if employed, would lead to the formation of strong mineral acids.

Mercuration reactions with mercuric acetate are
best conducted in glacial acetic acid. Copper acetylacetonate is soluble and stable in this medium. By reacting copper acetylacetonate with mercuric acetate in glacial acetic acid the desired product was not obtained. However, copper acetylacetonate was found to react slowly with warm aqueous mercuric acetate solution. White residue obtained was found to contain mercury and no parent metal. The blue filtrate contained copper quantitatively.

Other labile acetylacetonates like those of beryllium and nickel also reacted likewise. Analysis and infrared spectra showed that the products obtained from the various acetylacetonates were all identical.

Copper chelates of trifluoroacetylacetone, ethylacetoacetate, acetoacetanilide and acetoacet-orthochloroanilide, all yielded white residues under similar conditions.

From analytical data it was apparent that the materials obtained were the diacetoxymercuri derivatives of the ligands concerned.

In all these compounds, the mercury retains its salt-forming character and mercuric ions are split off with relative ease. For example, boiling the salts with
sodium or ammonium sulphide solution, or passing hydrogen sulphide through aqueous suspension, results in the deposition of mercuric sulphide, while alkaline stannous chloride solution immediately gives a dark grey precipitate of mercury. The latter test is in fact a very convenient one for identifying mercury compounds of the so-called 'half-complex' class in which one valence of mercury retains its salt-forming inorganic character, as distinguished from the 'full-complex' class in which the mercury is fully bound between two carbon atoms.³⁷

Substances containing mercury in the place of hydrogen atoms in reactive methylene group are unusually reactive towards hydrogen sulphide. The fast and facile precipitation of mercuric sulphide from these compounds by hydrogen sulphide (as has been mentioned earlier) is suggestive of the site of attachment of mercury to the organic moiety.

All the above organo-mercury compounds disintegrate in dilute hydrochloric acid, liberating the original ligand. Mercury bonded to a carbon atom in the α-position to a carbonyl group is known to be cleaved easily and such compounds have been shown to behave in like fashion to dilute acids. Decomposition of these materials in the presence of
dilute hydrochloric acid was made use of in estimating mercury in them.

Aqueous potassium iodide brought about a complete splitting of the mercury-carbon linkage in these compounds, with the liberation of alkali. This is to be expected from compounds containing mercury, substituted for the hydrogen atoms in the grouping -CO-CH₂-CO-\(^{40}\). Formation of one equivalent of alkali for each carbon-mercury linkage can be envisaged through the following reaction

\[
RH₂X + KI + H₂O \rightarrow RH + HgXI + KOH
\]

The amount of alkali liberated in each case was found to be in agreement with that calculated for diacetoxymercuri derivatives of the various \(\beta\)-dicarbonyl compounds. Determination of the rate of this reaction should give a comparative account of the stability of carbon-mercury bond in these compounds. This was attempted, but the extreme fastness of the reaction precluded such a possibility.

The instantaneous liberation of black mercury from these compounds by hydrazine hydrate or phenyl hydrazine shows further the weakness of the carbon-mercury bond in these compounds.

From the foregoing evidences and as supported by
analytical data the compounds are represented as:

\[
\begin{align*}
\text{CH}_3\text{COOHg} & \quad \text{C} \quad \text{COR} \\
\text{CH}_3\text{COOHg} & \quad \text{COCH}_3
\end{align*}
\]

<table>
<thead>
<tr>
<th>No.</th>
<th>R</th>
<th>Compound</th>
<th>Decomp. point °C</th>
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<tbody>
<tr>
<td>1</td>
<td>CH₃</td>
<td>Diacetoxymercuri acetylacetone</td>
<td>215</td>
</tr>
<tr>
<td>2</td>
<td>CF₃</td>
<td>Diacetoxymercuri trifluoroacetylacetone</td>
<td>230</td>
</tr>
<tr>
<td>3</td>
<td>OC₂H₅</td>
<td>Diacetoxymercuri ethylacetoacetate</td>
<td>245</td>
</tr>
<tr>
<td>4</td>
<td>NH.C₆H₅</td>
<td>Diacetoxymercuri acetoacetanilide</td>
<td>205</td>
</tr>
<tr>
<td>5</td>
<td>NH.C₆H₅.Cl</td>
<td>Diacetoxymercuri acetoacet.orthochloroanilide</td>
<td>208</td>
</tr>
</tbody>
</table>

All these compounds share the common property of being insoluble in all common organic solvents. They have poor thermal stability above 200°C.

Robust cobalt and chromium compounds did not react with mercuric acetate even on prolonged contact. This suggests the possibility that in the labile chelates, mercuration occurs in the ligand anions formed through dissociation of the metal chelates under the conditions of preparation.
Attempts to prepare monoacetoxymercuri derivatives using restricted quantities of mercuric acetate were not successful; in all cases only diacetoxymercuri derivatives were formed, almost quantitatively. This is another indication that dissociation might be a prior step to mercuration. The ligand anions formed by the slow dissociation of the metal chelate, will have all the mercuric acetate to react with. Consequently, only the diacetoxymercuri derivatives are formed.

Mercuration of the aromatic nucleus (compounds 4 and 5) did not occur under the experimental conditions. From analytical data and decomposition points, compounds 3 and 4 are found to be the same as prepared by Patel and Mankad and by Naik and Patel, from the respective ligands.

Experimental

Copper trifluoroacetylacetone, copper ethylacetoacetate and copper acetoacetanilide were prepared by reported methods.

**Copper trifluoroacetylacetone**
- **Found:** Cu, 17.26%.
- **Calcd.:** Cu, 17.19%.

**Copper ethylacetoacetate**
- **Found:** C, 45.01; H, 5.76%.
- **Calcd.:** C, 44.70; H, 5.60%.

**Copper acetoacetanilide**
- **Found:** C, 57.50; H, 5.01%.
- **Calcd.:** C, 57.77; H, 4.81%.
Copper acetooacet.o.rthochloroanilide was prepared by the same method as used for copper acetooacetanilide\textsuperscript{44}. Recrystallized from chloroform; m.p., 200\degree C (decomp.). Found: C, 60.01; H, 4.04; N, 4.82; Cu, 13.01%. \( \text{C}_{20}\text{H}_{18}\text{Cl}_{2}\text{N}_{2}\text{O}_{4}\text{Cu} \) requires: C, 49.56; H, 3.72; N, 5.78; Cu, 13.11%.

\textbf{Diacetoxymercuri acetylacetone}

In the initial attempts of mercuration copper acetylacetonate and mercuric acetate were mixed in the 1:2 mole ratio. About 50\% of the copper chelate remained unaffected in such cases. Hence the ratio used in all cases was 1:4.

Mercuric acetate (12.75 g.; 0.04 mole) was dissolved in water (100 ml.) containing a drop of acetic acid, for clarity. Powdered copper acetylacetonate (2.62 g.; 0.01 mole) was added and the mixture stirred while being warmed over a hot plate. The reaction was complete in an hour. Filtered and the white residue was washed repeatedly with water. Sucked dry. The dry product was washed repeatedly with warm chloroform in order to remove any trace of the copper chelate that might be present. The solvent was removed from the product in vacuum. Yield, 11.5 g. (93%). Found: Hg, 64.19; C-methyl, 3.32\%. Required for \( \text{C}_{9}\text{H}_{12}\text{O}_{5}\text{Hg}_{2} \): Hg, 64.98; C-methyl, 3.72\%.

The method was the same in all preparations; almost theoretical yield was obtained in all cases.
Diacetoxymercuri trifluoroacetylacetone: Found: Hg, 58.92%. Required for C$_{10}$H$_{14}$F$_{3}$O$_{6}$Hg$_{2}$: Hg, 59.77%.

Diacetoxymercuri ethylacetoacetate: Found: Hg, 61.01%; C-methyl, 9.30%. Required for C$_{10}$H$_{14}$O$_{7}$Hg$_{2}$: Hg, 61.97%; C-methyl, 9.27%.

Diacetoxymercuri acetoacetanilide: Found: Hg, 57.50%; C-methyl, 6.51%. Required for C$_{14}$H$_{15}$NO$_{6}$Hg$_{2}$: Hg, 57.79%; C-methyl, 6.48%.

Diacetoxymercuri acetoacet.orthochloroanilide: Found: Hg, 54.34%; C-methyl, 7.32%. Required for C$_{14}$H$_{14}$ClNO$_{6}$Hg$_{2}$: Hg, 55.06%; C-methyl, 7.23%.

Metal was determined in these organometallic compounds as mercuric sulphide. A known weight of the substance was suspended in dilute hydrochloric acid and stirred vigorously. Decomposition was facilitated by warming. The solid ligands deposited during decomposition were filtered off.

A slow stream of hydrogen sulphide was then passed until the colour of the precipitate turned completely black, and the precipitate settled down. Filtered through a tared sintered glass crucible, washed successively with water, alcohol and carbon disulphide and dried at 105-110°C.

Alkali liberated on treatment with potassium iodide was
determined using standard hydrochloric acid. The acid was standardized against 'AnalaR' mercuric oxide. Methyl orange was used as indicator. The presence of the ligands was found not to affect the end point. Alkali liberated from one mole of each organo-metallic compound was found to be 2 moles ± 0.01 mole.

The microanalytical section of this laboratory does not undertake carbon and hydrogen micro analysis of organomercury compounds. Hence the C-methyl estimations.
CHAPTER 5

ADDUCT FORMATION

Uranyl complexes of acetoacetanilide and acetoacet.orthochloroanilide
ADDUCT FORMATION

Uranyl complexes of acetoacetanilide and acetoac.orthochloranilide

The factors which lead to a high coordination number for a given metal atom has not been well established for molecular species. It was once assumed that the first-row elements could not surpass a coordination number of four, but there are now many examples of five and six coordination, especially for boron\(^{46,47}\). Eight coordination for third-row elements has been reported, for instance, in the diarsine chelate of titanium(IV)\(^{48,49}\). Bivalent metals, particularly those of the first transition series, are found in their normal chelates to increase the coordination sphere by forming adducts of the Lewis acid-base type with oxygen, nitrogen, sulphur and phosphorus donors\(^{50-53}\). Recently, it has been demonstrated that tropolone\(^{54}\) forms compounds with many metals in which the metal atoms exhibit high coordination numbers. These reports call for a reappraisal of the characteristic coordination numbers of elements.

Uranyl ion (UO\(_2^{++}\)) is one of the most prolific in complex formation; in the complexes formed, uranium shows variability of coordination number. Well-defined crystalline
compounds which are formed with it and \( \beta \)-dicarbonyl compounds\(^5\) conform to the general formula \( \text{U} \text{O}_2 \text{A}_2 \), where A stands for the anion of the dicarbonyl compound HA. In these hexacovalent compounds, however, uranium is coordinatively unsaturated and shows proclivity to increase the coordination number further. This tendency manifests itself in solvation or adduct formation. Indeed, the best solvents for these chelates are oxygen-donors like alcohol, acetone and ether, from which they crystallize with a molecule or more of the solvent\(^5\). When formed from aqueous medium, these chelates contain from 1 to 2.8 moles of water, which are eliminated only with difficulty. Stable 1:1 adducts are formed by the chelates with ammonia, amines and heterocyclic bases\(^5\).

Occasionally the urge for increased coordination number finds expression in polymerisation as is the case of the eight-coordinate, uranyl benzoylnicotinoylmethane polymer\(^5\). In a few other cases, an extra molecule of the ligand itself is held with the chelates. This occurs when the acetylacetonate chelate of uranyl is crystallized from acetylacetone\(^5\) or when uranyl is extracted with a solution of dibenzoylmethane\(^5\). A similar case has also been detected in solution with thenoyltrifluoroacetone\(^5\). Perhaps,
the most well-defined of such cases is the 8-hydroxyquinolinate of uranyl. When prepared, it invariably contains an excess molecule of the ligand held tenaciously. This reaction which forms the basis for the quantitative determination of uranyl has been extensively studied.

Acetoacetanilide and acetoacet.orthochloroanilide complexes of uranyl which are reported here furnish two other instances where an extra molecule of the ligand is strongly associated with the chelate.

Aqueous solution of uranyl nitrate hexahydrate on treatment with an alcoholic solution of acetoacetanilide or acetoacet.orthochloroanilide, does not yield any solid product even after brief warming and subsequent cooling. However, well-defined crystals are obtained if the above mixed solution is carefully neutralized with alcoholic potash. The products, after recrystallization from alcohol or acetone and drying at 80°C in vacuum, got analysed for complexes containing three moles of the ligand per uranyl.

The same products are obtained without the neutralization step and in a much purer state when an aqueous solution of uranyl acetate dihydrate is treated with an alcoholic solution of acetoacetanilide or acetoacet.orthochloroanilide and stirred for a short while.
It was found subsequently that the two compounds are best prepared when an aqueous solution of the uranyl acetate and alcoholic solution of the ligand are mixed in the 1:3 ratio; in the earlier attempts, the ratio used was 1:2.

Even after several crystallizations the compounds did not undergo any change in composition. A thermogravimetric analysis was, therefore, attempted. The acetoacetanilide complex of uranyl lost one mole of the ligand quickly in a single sharp step between 180° and 230°C. The decomposition continued thereafter at a much slower rate. The acetoacet.orthochloroanilide complex of uranyl behaved very similarly. In this case, the removal of one mole of the ligand occurred between 220° and 265°C. Same results were obtained when the thermogravimetric analyses were repeated. In Fig.13 the thermogravimetric data have been presented on an absolute weight loss basis, in keeping with the widespread practice of reporting the results of thermogravimetric analysis of inorganic and coordination compounds.63

Evidence for the structure of the compounds comes from their infrared spectra, which have been compared with those of the ligands and copper and chromium chelates of the ligands.
The vibrations of the uranyl group are characterized by three frequencies $\nu_2, 210 \text{ cm}^{-1}; \nu_1, 860 \text{ cm}^{-1}; \nu_3, 330 \text{ cm}^{-1}$. If the uranyl group is not linear, all the three frequencies should be active both in the Raman and in the infrared spectra, but if it is linear, only $\nu_1$ should be Raman active and $\nu_2$ and $\nu_3$ only infrared active. Conn and Wu examined the Raman spectra of uranyl nitrate, chloride and sulphate and found the frequencies $\nu_1$ and $\nu_2$, while in the infrared spectrum of the chloride and the acetate, $\nu_3$ and $\nu_1$ were observed; the latter was not always established with certainty because it is weak and overlaps the very intense $\nu_3$ band. The frequency $\nu_2$ is outside the range of observation in the infrared region. Lecomte and Freyman examined the infrared spectra of a number of uranyl salts and found always an intense band between 307 and 340 cm$^{-1}$ and in many of these salts, a weak band at about 860 cm$^{-1}$. Sevchenko and Stepanov examined the infrared spectra of uranyl sulphate, the potassium double sulphate, the nitrate and the acetate. They did not always find the fundamental vibration at 860 cm$^{-1}$. In the infrared spectra of uranyl chelates of $\alpha$-diketones a strong band is observed at about 310 cm$^{-1}$. This has been attributed to $\nu_3$. The presence of the $\nu_1$ band was not generally ascertained.

The strong absorption band observed for the acetoacetanilide and acetoacet.orthochloroanilide complexes...
of uranyl in the region 896-912 cm\(^{-1}\), is undoubtedly due to the asymmetric stretching of the uranyl. Even when this band is excluded, the 850-1600 cm\(^{-1}\) region of the spectra of these uranyl compounds show more complex a band pattern than the corresponding chromium and copper compounds. This should be expected in view of the presence in the uranium compounds of a molecule of the ligand, bonded somewhat differently from the remaining two molecules as has been brought out by their thermograms.

In the spectra of acetoacetanilide and acetoacet. orthochloroanilide (ligands), there are two strong bands in the 1660-1730 cm\(^{-1}\) region, which can be assigned to the acetyl and anilide carbonyls. There is no absorption in this region in the copper and chromium chelates, since the perturbed carbonyl frequency (through chelation to the metal) is shifted to longer wave-lengths. In the uranyl complexes, however, a medium intensity band is observed at about 1700 cm\(^{-1}\). From its position it is attributable to the free acetyl carbonyl of the third molecule of the ligand. Since the free anilide carbonyl band is not observed, its entry into bonding with uranium is inferred. The N-H stretching frequency is observed at the same region in the copper and
chromium compounds as well as in the uranyl complexes. This is indicative of the non-involvement of nitrogen in bonding with uranium. The higher frequency regions were also examined in hexachlorobutadiene. No additional band was observed.

Infrared spectral evidence thus leads to a coordination number seven for uranium in these compounds. It is this coordination number that uranium attains when the normal β-dicarbonyl chelates of uranyl form 1:1 adducts with ammonia, amines and heterocyclic bases. In uranyl acetylacetonate monohydrate and potassium pentafluoro-dioxo-uranium(VI), coordination number seven of the central atom has been established. Infrared spectra of the two uranyl complexes and of copper(II) and chromium(III) acetoset.orthochloroanilide chelates are shown in Figs. 14, 15, 16 and 17.

Attempts to obtain the normal type of chelate, by thermal removal of the third molecule at ideal conditions selected from the thermograms were, however, frustrating since removal of one molecule of the ligand was found to cause instability on the remainder of the complex. In all attempts, the product obtained was found to be partly decomposed. Efforts to extract the chelate from the decomposed product, using alcohol or acetone, always ended up with the original complex (1:3 ratio).
Experimental

Uranyl acetoacetanilide complex: Acetoacetanilide (5.31 g; 0.03 mole) was dissolved in absolute alcohol (70 ml.) and then added slowly with stirring to an aqueous solution (55 ml.) of uranyl acetate dihydrate (4.24 g; 0.01 mole). The deep red, clear solution obtained was stirred for 3 hr. The reddish brown crystalline precipitate formed was filtered, washed with water and sucked dry. Crystallized twice from alcohol. The solvent was removed from the crystals at 80°C in vacuum. Yield: 3.9 g (60%); m.p., 164°C. Found: C, 44.36; H, 4.01; N, 6.41; U, 29.63%. Required for C₂₃H₂₁N₂O₈U: C, 46.06; H, 3.83; N, 6.90%.

Uranyl acetoacet.ortho chloroanilide complex: Prepared similarly. Orange red crystals; yield, 45%; m.p., 210°C. Found: C, 39.71; H, 3.24; N, 4.03; Cl, 26.50%. C₃₀H₂₈Cl₃N₃O₈U requires: C, 39.90; H, 3.10; N, 4.65; U, 26.37%.

Chromium chelate of acetoacetanilide: Prepared from chromic chloride, acetoacetanilide and urea as in the preparation of chromium acetylacetonate. Found: C, 62.06; H, 5.29; N, 7.35; Cr, 9.02%. Required for C₃₀H₃₀N₆Cr: C, 62.06; H, 5.17; N, 7.24; Cr, 8.96%.

Chromium chelate of acetoacet.ortho chloroanilide: Prepared as in the above preparation. Recrystallized from chloroform. Found: C, 52.31; H, 4.08; N, 6.32; Cr, 7.71%. Required for C₃₀H₂₇Cl₃N₃O₈Cr: C, 52.27; H, 3.35; N, 6.14; Cr, 7.61%.
The thermal behaviour of the uranyl complexes in a stream of nitrogen was determined in a thermogravimetric balance using a McBain-Baker type quartz spring. This had a sensitivity of 2.5 mg./mm. extension and required only about 25 mg. of the sample for investigation. The temperature of the furnace was raised at a constant rate of about 2°C/min. by means of a programming system. The extension of the spring was measured with a travelling microscope every 2 minutes.

Uranium in the uranyl complexes was estimated by ignition at 900°C to U₃O₈.
CHAPTER 6

LIGAND REPLACEMENT IN METAL ACETYLACETONATES
BY ETHYLENEDIAMINETETRAACETIC ACID
LIGAND REPLACEMENT IN METAL ACETYLACetonates
BY ETHYLENEDIAMINETETRAACETIC ACID

During the past several years Schwarzenbach and his associates have published a series of papers dealing with complexing agents of extraordinary potency. To these aminocarboxylic acids they gave the name 'complexones'. The most familiar of these and possibly the most useful is ethylenediaminetetraacetic acid*, EDTA.

EDTA was first made available by the I.C.Farbenindustrie in 1936 and has since found ever increasing use as a complexing agent for metal ions. Its sodium salts are referred to in the literature by several trade names; Versene, Sequestrene, Trilon B and Complexone II, III or IV.

The acid itself is sparingly soluble in water and, therefore, has been of limited interest. The sodium salts have been generally used for studies involving EDTA. The chemistry of EDTA is characterized by the large number of metals for which it possesses an affinity rather than the quality of specificity.

* (ethylenedinitrilo)tetraacetic acid.
The peculiar ability of EDTA to form very stable complexes results from the availability of four carboxyl and two tertiary amine groups to enter into strainless, five-membered rings, each ring including the metal ion. This system of rings is further stabilized by the ethylenic linkage between the two nitrogen atoms. The formation of more than four such rings is, however, difficult due to steric effects, leaving in the coordination sphere at least one molecule of water, which is replaceable by such groups as $\text{OH}^-$, $\text{NH}_3^+$, $\text{SCN}^-$, etc.

Though question has been raised as to the ability of an EDTA anion to occupy six coordination positions in the coordination sphere, a number of types of evidences for its hexadentate nature have been cited.

Solid EDTA chelates of metals have been prepared in many instances using simple metal salts and alkali or ammonium salts of EDTA. Possibilities of anion penetration leaves in doubt the exact composition of the products obtained. It was, therefore, of interest to synthesize metal-EDTA chelates by ligand replacement.

Several metal acetylacetonates were found in this investigation to react with EDTA in aqueous suspension.
From the resulting solution well-defined crystals of metal-EDTA chelates have been obtained.

When equivalent quantities are used the reaction proceeds to completion. The solution so obtained does not contain any other crystallizable substance, nor anions which can penetrate, so that almost theoretical yield of the pure substance is possible.

The EDTA chelates prepared by ligand replacement are of copper(II), nickel(II), cerium(III), lanthanum(III), neodymium(III), zirconium(IV) and thorium(IV). These compounds are represented as:

\[
\begin{align*}
\text{CuH}_2Y.\text{H}_2O & \quad \text{CeHY}.\text{H}_2O & \quad \text{ThY}.2\text{H}_2O \\
\text{NiH}_2Y.\text{H}_2O & \quad \text{LaHY}.\text{H}_2O & \quad \text{ZrY}.2\text{H}_2O \\
& \quad \text{NdHY}.\text{H}_2O
\end{align*}
\]

where \( Y \) stands for the ethylenediaminotetraacetate anion.

The best use of this method, however, has been in the preparation of manganese(III) chelate of EDTA. A very well defined and stable non-ionic compound showing the unusual oxidation state of three for manganese is its acetylacetonate. This has been used for the preparation of the EDTA chelate. However, the corresponding acid...
(MnX.nH₂O) was found to decompose on standing in solution. Hence the stable potassium salt(KMnX·PH₂O) was prepared using the acetylacetonate, EDTA and potassium hydroxide in the right proportion.

EDTA chelate of titanium(IV) was also prepared. However, in this preparation the starting material used was dichloro-bis(acetylacetonato)titanium(IV) and hence the disodium salt of EDTA was employed in place of EDTA. Due to the presence of sodium chloride in solution, only a small first crop was obtained pure (TiY·H₂O).

Infrared spectra of the compounds have been found to be similar to those reported. A comparison of the spectra of these compounds is instructive.

All the EDTA chelates show a medium intensity band at about 1110 cm⁻¹. The occurrence of this band in anhydrous and hydrated metal EDTA chelates has been cited as an evidence of the nitrogen atoms being bonded to the metal in either type. It is necessary that the nitrogens be coordinated to the metal, as otherwise, the ring structures formed will be unusually large.

The copper EDTA chelate showed two absorption bands of almost equal intensity at 1720 and 1606 cm⁻¹. The
spectrum of the nickel compound is similar, but for the broadening of the 1600 cm\(^{-1}\) band. In the rare-earth metal chelates, a medium intensity band at 1670 cm\(^{-1}\) and a strong band at 1600 cm\(^{-1}\) were observed. The absorption at the higher frequency is due to the carboxylate group(s) of the ligand protected from coordination to the metal by being bonded to proton(s); the lower frequency band being due to the carboxylate groups bonded to the metal.

The relative intensities of the two bands are in agreement with the number of coordinated and uncoordinated carboxylate groups present. The EDTA residue, therefore, occupies four coordination positions of copper and nickel, and five coordination positions of the rare-earth metals.

For the cobalt(III) EDTA chelate, which is considered to be covalently bonded, the band due to the metal-bonded carboxylate groups occurs\(^\text{86}\) at 1650 cm\(^{-1}\). An increase in this frequency corresponds to an increase in the covalent character\(^\text{83}\). The occurrence of the band in these compounds near 1600 cm\(^{-1}\) shows the ionic nature of the carboxylate-metal bonds.

In the EDTA chelates of manganese(III), titanium(IV), thorium(IV) and zirconium(IV), the two bands were found to merge in the 1600-1700 cm\(^{-1}\) region, forming a single broad
band. In thorium and manganese compounds, the broad band also showed fine structure. From the merging of the two bands, it is inferred that in these compounds all the four carboxylate groups are bonded to the metal. The broadness and fine structure might be due to small differences in the strengths of the metal-carboxylate bonds. Strain resulting from six-coordination of the ligand might lead to difference in bond lengths.

**Experimental**

Acetylacetonates of nickel(II), cerium(II), lanthanum(III), neodymium(III), zirconium(IV), thorium(IV) and titanium(V) were prepared and purified by reported methods\(^1\)\(^2\)\(^3\)\(^4\)\(^5\).

\[\text{Ni(acac)}_2 \quad \text{Found: C, 47.10; H, 5.62%. Calcd.: C, 46.76; H, 5.45%}.\]

\[\text{Ce(acac)}_3 \quad \text{Found: C, 41.32; H, 4.35%. Calcd.: C, 41.18; H, 4.20%}.\]

\[\text{La(acac)}_3 \quad \text{Found: C, 41.63; H, 4.97%. Calcd.: C, 41.30; H, 4.82%}.\]

\[\text{Nd(acac)}_3 \quad \text{Found: C, 41.10; H, 4.71%. Calcd.: C, 40.80; H, 4.76%}.\]

\[\text{Zr(acac)}_4 \quad \text{Found: C, 43.47; H, 5.38%. Calcd.: C, 43.26; H, 5.76%}.\]

\[\text{Th(acac)}_4 \quad \text{Found: C, 38.51; H, 4.64%. Calcd.: C, 38.21; H, 4.46%}.\]

\[\text{TlCl}_2(\text{acac})_2 \quad \text{Found: C, 37.49; H, 4.61%. Calcd.: C, 37.87; H, 4.42%}.\]

\[\text{CuHgY.H}_2\text{O} \quad \text{Powdered copper acetylacetonate}(3.9 \text{ g}; 0.015 \text{ mole}) \text{ was added to a suspension of Analar EDTA}\]
In water (60 ml.) and stirred briskly. Warmed over a hot plate. The deep blue solution obtained was filtered and concentrated over a water bath. When crystals started appearing, it was allowed to cool slowly. When cold, it was further cooled in ice water, filtered, washed with ice-cold water and sucked dry. Another crop was obtained similarly. The bluish-green glistening crystals were powdered and further dried in a desiccator over concentrated sulphuric acid for a week. Yield: 4.1 g. (75%). Found: C, 32.62; H, 4.05; N, 7.70; Cu, 17.23%. Required for \( C_{10}H_{16}N_2O_3Cu \):

32.29; H, 4.30; N, 7.54; Cu, 17.09%.

Other EDTA chelates except those of manganese and titanium were prepared similarly. Shining crystals were obtained in all cases. Yield: 75-85%.

\( MgY.H_2O \) - Found: C, 32.37; H, 4.73; N, 7.66; Mg, 16.23%. Required for \( C_{10}H_{16}N_2O_3Mg \) : C, 32.73; H, 4.36; N, 7.64; Mg, 16.01%.

\( CeHY.H_2O \) - Found: C, 27.01; H, 3.85; N, 6.42; Ce, 31.12%.

\( C_{10}H_{16}N_2O_3Ce \) Requires: C, 26.84; H, 3.35; N, 6.26; Ce, 31.31%.
LaHY₂⁺₂O⁻ : Found: C, 26.58; H, 3.22; N, 6.13; La, 31.41%.  
\( C_{10}H_{16}N_2O_3La \) required: C, 26.91; H, 3.36; N, 6.28; La, 31.16%.  
NdHY₂⁺₂O⁻ : Found: C, 26.33; H, 3.56; N, 6.04; Nd, 32.23%.  
\( C_{10}H_{16}N_2O_3Nd \) requires: C, 26.53; H, 3.32; N, 6.20; Nd, 31.98%.  
ZrHY₂⁺₂O⁻ : Found: C, 28.87; H, 4.01; N, 5.61; Zr, 21.33%.  
\( C_{10}H_{16}N_2O_2Zr \) requires: C, 28.91; H, 3.95; N, 6.75; Zr, 21.99%.  
ThHY₂⁺₂O⁻ : Found: C, 21.70; H, 2.71; N, 5.31; Th, 42.11%.  
\( C_{10}H_{16}N_2O_2Th \) requires: C, 21.58; H, 2.87; N, 5.04; Th, 41.73%.  

KMnHY₂⁺₂O⁻ : Powdered manganese(III) acetylacetonate (3.52 g.; 0.01 mole) was added to a thoroughly stirred mixture of potassium hydroxide (0.56 g.; 0.01 mole) and EDTA (3.73 g.; 0.01 mole) in cold water (16 ml.). A deep red solution was obtained, which was filtered. Cold alcohol (20 ml.) was added and the mixture kept in a refrigerator for 2 days. Well-defined deep red crystals were obtained. Another crop was obtained by adding more alcohol (10 ml.) and cooling again. Washed with alcohol and sucked dry.  
Yield: 2.5 g. (60%).  
Found: C, 28.33; H, 3.61; N, 6.75; Mn, 13.26%.  
\( C_{10}H_{16}N_2O_2K\text{Mn} \) requires: C, 28.71; H, 3.93; N, 6.70; Mn, 13.14%.  

TiHY₂⁺₂O⁻ : Powdered dichloro-bis(acetylacetonato)titanium(IV) complex (3.17 g.; 0.01 mole) was added to a solution of
disodium salt of EDTA (3.72 g.; 0.01 mole) in water (100 ml.). After stirring briskly, it was filtered. To the clear filtrate alcohol was added with stirring until turbidity appeared. At this stage it was allowed to crystallize slowly. Uniform white crystals. Washed with alcohol and sucked dry. Yield: 1.2 g. (35%). Another crop obtained was found to be contaminated. Found: C, 33.98; H, 4.21; N, 8.06; Ti, 13.81%. Required for C_{10}H_{14}N_0Ti: C, 33.90; H, 3.96; N, 7.91; Ti, 13.53%.

Copper and manganese were estimated iodometrically. Other metals were determined by direct ignition to oxide. Nitrogen was estimated by Kjeldahl's method.