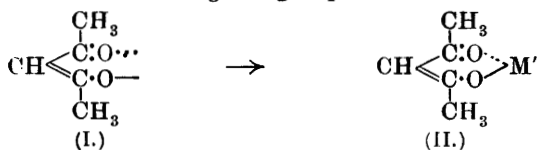


XXIV.—*Researches on Residual Affinity and Co-ordination. Part I. Metallic Acetylacetonates and their Absorption Spectra.*

By GILBERT T. MORGAN and HENRY WEBSTER MOSS.

THE remarkable properties exhibited by many metallic acetylacetonates, their non-ionisable character, their solubility in anhydrous organic solvents, their stability on heating, and, in certain instances, their anomalous colours, have led to the view that in these compounds the metallic atoms are combined with the unsaturated organic complex, not only through their principal valencies, but also by means of their residual affinity or auxiliary valency. Moreover, as the univalent organic complex (formula I) consists of an open-chain of five atoms, its intimate association with the metal is assumed to arise from the general tendency to form six-membered rings (formula II), the metallic atom serving as the connecting link between the ends of the organic group:



Influence of Symmetry on the Stability of Metallic Acetylacetonates.

The acetylacetonate radicle (I) being univalent, the number of these groups combining with a metallic atom will depend primarily on the principal valency of this atom, and as each acetylacetonate group is equivalent to two associating units it follows that the acetylacetonates of univalent, bivalent, trivalent, and quadrivalent metals will be characterised respectively by a molecular arrange-

ment of two, four, six, and eight points on the sphere of influence of the metallic atom.

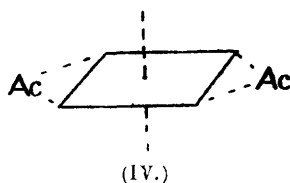
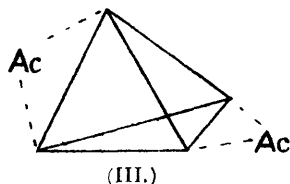
Of these arrangements the last two will probably correspond with the octahedron and the cube. The second case may correspond with the tetrahedron, or alternately the molecule may have the less symmetrical plane configuration. The first case, that of two points on the sphere, cannot in the circumstances be a symmetrical arrangement. In an earlier communication (T., 1913, **103**, 81) the authors advocated the view that co-ordination is due not only to the residual affinity of the central atom, but also to the mutual attractions of the associating units, and, this hypothesis being accepted, the most stable systems will be those in which the forces interacting between the associating units are symmetrically distributed, a condition which is satisfied by arranging these units symmetrically round the sphere of influence of the central atom.

Acetylacetonates of Univalent Metals (Formula II).—On the foregoing assumption, these compounds should manifest their want of symmetry by their instability. Lithium and thallos acetylacetonate are the most stable members of this series, and both are decomposed on heating, the latter at 160° (Kurovski, *Ber.*, 1910, **63**, 1078). The sodium, potassium, and caesium acetylacetonates char on heating, and are unstable in solution or in a moist condition. They are decomposed by hot water into acetone and alkali acetate (Combes, *Compt. rend.*, 1887, **105**, 871). Silver acetylacetonate decomposes spontaneously at the ordinary temperature, with the liberation of silver.

This summary of the properties of the acetylacetonates of univalent metals justifies the contention that dissymmetry leads to instability.

Acetylacetonates of Bivalent Metals.—The compounds of this series, which may possess either a tetrahedral (formula III) or a plane (formula IV) configuration, are on either alternative more symmetrical than the acetylacetonates of univalent metals. They also display a higher degree of stability.

The acetylacetonates of the metals of the second periodic series have all been prepared; those of the alkaline earth metals are



decidedly more stable than the corresponding compounds of the alkali metals (Tanatar and Kurovski, *J. Russ. Phys. Chem. Soc.*,

1906, **40**, 580). Glucinum and zinc acetylacetonates can be distilled without decomposition, the former under atmospheric, and the latter under reduced pressure (Combes, *Compt. rend.*, 1894, **119**, 1222; Tanatar and Kurovski, *loc. cit.*):

The following metals functioning as diads have also yielded stable acetylacetonates: copper, lead, iron, cobalt, nickel, and platinum (Combes, *Compt. rend.*, 1887, **105**, 868; Gach, *Monatsh.*, 1900, **21**, 98; Werner, *Ber.*, 1901, **34**, 2584).

The bivalent radicles, vanadyl, VO^{II} , and uranyl, UO_2^{II} , have furnished stable acetylacetonates, which may be of this type (T., 1913, **103**, 86; Biltz, *Zeitsch. anorg. Chem.*, 1904, **40**, 221).

From the ease with which the acetylacetonates of bivalent metals form stable additive compounds (Biltz, *loc. cit.*; Werner, *loc. cit.*) of the type $\text{R}^{\text{II}}\text{Ac}_2\cdot 2\text{X}$ having the co-ordination number 6, and consequently an octahedral symmetry, it is probable, although it does not necessarily follow, that these acetylacetonates themselves have the plane configuration (formula IV).

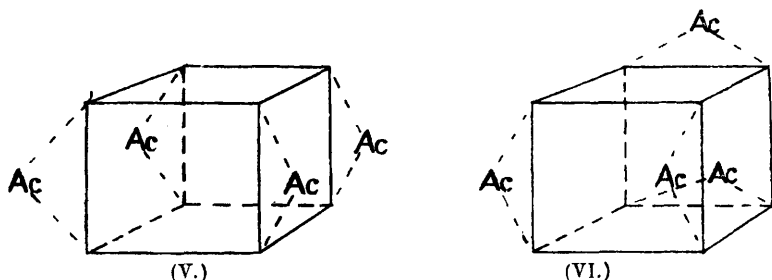
Acetylacetonates of Tervalent Elements.—The case of boron is of great interest; this element resembles carbon in having a very small atomic volume, and probably on this account it also resembles carbon in having a maximum co-ordination number 4, as exhibited by fluoboric acid, $\text{H}(\text{BF}_4)$, and its salts. Boron accordingly associates only with two acetylacetonate radicles, and the products have the general formula $[\text{BAC}_2]\text{X}$, where X is an ionisable radicle (Dilthey, *Annalen*, 1905, **344**, 326).

The acetylacetonates of the trivalent metals, which are the most stable examples of this class, undoubtedly possess the octahedral symmetry, although they have not yet been resolved into their enantiomorphous components (compare T., 1913, **103**, 84). Aluminium and indium acetylacetonates can be distilled (Combes, *Compt. rend.*, 1889, **108**, 405; Chabrié and Rengade, *ibid.*, 1900, **131**, 1300), and vaporisable acetylacetonates of trivalent vanadium, chromium, manganese, iron, and cobalt have also been prepared (T., 1913, **133**, 85; Urbain and Debiere, *Compt. rend.*, 1899, **129**, 302). Many members of the rare earth metals (lanthanum, samarium, neodymium, praseodymium, and trivalent cerium) have yielded fairly stable acetylacetonates (Hantzsch and Desch, *ibid.*, 1902, **323**, 26; Biltz, *Annalen*, 1904, **331**, 334), and the scandium compound can be distilled without decomposition.

The behaviour on heating of this group of acetylacetonates justifies the contention that a symmetrical arrangement of associating units conduces to stability.

Acetylacetonates of Quadrivalent Metals.—These compounds, which correspond with an arrangement of eight associating units round

the central atom, have in all probability a cubic symmetry, and should be resolvable into two stereoisomeric non-enantiomorphous components (V and VI):



Four of these compounds are now known, namely, thorium, zirconium, ceric and uranous acetylacetonates (Urbain, *Bull. Soc. chim.*, 1896, [iii], **15**, 338, 347; Biltz, *Zeitsch. anorg. Chem.*, 1904, **40**, 219; Job and Goissedet, *Compt. rend.*, 1913, **157**, 51).

Residual Affinity of Metallic Acetylacetonates: Additive Compounds.

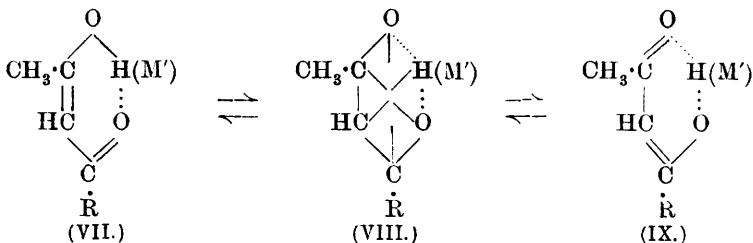
The additive compounds of metallic acetylacetonates with water, alcohol, ammonia, or organic bases may be divided into two classes: the more stable additive compounds in which addition is accompanied by an increase of symmetry, and an unstable class, in which the addition decreases the symmetry. The acetylacetonates of bivalent metals furnish the best examples of the first class, for they combine additively with two molecular proportions of alcohol, ammonia, or organic amine, yielding in general compounds having the general formulæ, $M^{II}Ac_2 \cdot 2X$, where X may be water, alcohol, ammonia, pyridine, or aniline (Tanatar and Kurovski, *loc. cit.*; Biltz, *Zeitsch. anorg. Chem.*, *loc. cit.*). Whether the acetylacetonates, $M^{II}Ac_2$, have the tetrahedral or the plane configuration (formulæ III and IV), there can be little doubt that the additive compounds have the octahedral symmetry.

The unstable additive compounds are formed by the combination of ammonia or an organic amine with acetylacetonates of the metals of the rare earths, including thorium; the products have the general formulæ $2M^{III}Ac_3 \cdot NH_3$, $3M^{III}Ac_3 \cdot 2NH_3$, and $2ThAc_4 \cdot NH_3$ (Biltz, *Annalen*, *loc. cit.*). It is noteworthy that the acetylacetonates which combine in this way with ammonia also manifest their residual affinity by forming complex molecules, $(M^{III}Ac_3)_2$, in solution.

Scandium acetylacetonate, the most stable compound of the series, neither combines with ammonia nor exhibits association in organic solvents, in this respect resembling aluminium acetylacetonate.

The Structure of the Organic Complex in the Metallic Acetylacetonates.

Compounds resembling the metallic acetylacetonates have been obtained with benzoylacetone, acetylacetylacetone, ethyl acetoacetate, acetyl mesityl oxide, and numerous other β -diketones and β -keto-esters. These substances and their metallic derivatives may be represented by either of the formulæ VII and IX, from which it will be seen that structural isomerism is possible if the arrangement is regarded as static in either case, but inasmuch as at present there is no experimental evidence that isomerism of this kind exists among these compounds, it is much more likely that these two formulæ are analogous to the two phases of Kekulé's benzene formula. The configuration of the metallic acetylacetonates and their analogues may oscillate between these two extreme positions, or a rearrangement may lead to an intermediate centric distribution of the chemical affinities corresponding with the Armstrong-Baeyer centric formula for benzene and its homologues. This arrangement is indicated by the formula VIII:



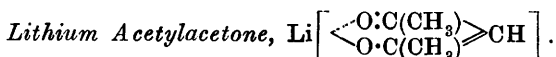
When $\text{R} = \text{CH}_3$, as in acetylacetonate and its metallic derivatives, the organic complex in formula VIII becomes symmetrical on either side of the metallic radicle M^{I} , and, if this symmetry exists in the molecule, the acetylacetonates of bivalent metals would not be resolvable into enantiomorphs, even although possessing the tetrahedral configuration indicated by formula III.

An examination of the absorption spectra of fourteen acetylacetonates shows that, with the exception of the chromium compound, which has two bands, they all exhibit one absorption band like the parent diketone itself. The character of the absorption is not materially altered by substituting the benzoylacetone for the acetylacetonate complex (T., 1913, 103, 89). Neither is any change effected by substituting methyl for the hydrogen attached to the α -carbon atom in formula VII, VIII, or IX, as is done by the use of acetylacetylacetone instead of acetylacetonate. The absorption band, which characterises this whole series of β -diketones and their metallic derivatives, is certainly not due to any oscillatory migration of

labile hydrogen from its carbon attachment to an enolic combination with oxygen, for in the case of vanadyl bisacetylmethylacetone the band persists even when both labile hydrogens have been substituted, one by methyl and the other by vanadyl (T., 1913, 103, 90).

EXPERIMENTAL.

Acetylacetones of Univalent Metals.



Lithium carbonate does not react to any appreciable extent with acetylacetone in dilute alcohol, even after prolonged boiling. Lithium oxide, prepared by igniting lithium nitrate, was boiled in a reflux apparatus for two hours with acetylacetone in 60 per cent. alcohol. The filtered solution on concentration yielded acicular crystals of lithium acetylacetone, but the yield was not good, as much of the oxide remained undissolved. A solution of lithium hydroxide, prepared by boiling aqueous lithium carbonate with fresh lime (from calcite) in a nickel basin for two hours, was filtered through asbestos, and treated whilst warm with excess of acetylacetone, when, after concentrating, several crops of crystalline lithium acetylacetone were obtained:

0.3508 gave 0.1724 Li_2SO_4 . $\text{Li} = 6.27$.

$\text{C}_5\text{H}_7\text{O}_2\text{Li}$ requires $\text{Li} = 6.55$ per cent.

Lithium acetylacetone chars on heating, without exhibiting any definite melting point. When pure the compound is colourless, but its alcoholic and aqueous solutions soon become yellow, owing to the decomposition of the organic complex by the alkali set free by hydrolysis. It dissolves readily in water, sparingly in cold, more freely in hot alcohol, and is insoluble in benzene or chloroform.

Caesium acetylacetone, a colourless, crystalline substance, was produced by the interaction of caesium hydroxide and acetylacetone in alcoholic solution, the filtered solution being concentrated under diminished pressure at the ordinary temperature until the product separated. (Found, $\text{Cs} = 59.81$. $\text{C}_5\text{H}_7\text{O}_2\text{Cs}$ requires $\text{Cs} = 57.33$ per cent.) The compound is very soluble in water or alcohol, and attempts to purify it by repeated crystallisation led to decomposition. It charred on heating, and had no definite melting point.

Silver Acetylacetone.—Interaction between silver nitrate and acetylacetone in aqueous or aqueous-alcoholic solution generally led to the production of a silver mirror. The compound was obtained as a white, granular mass by shaking freshly prepared moist silver oxide in the cold with excess of acetylacetone. The product rapidly blackened on exposure; it was sparingly soluble in water,

but the solution was unstable, generally depositing the silver as a mirror.

Thallos acetylacetonate (compare E. Kurovski, *Ber.*, 1910, **43**, 1078).—Interaction between thallos hydroxide and acetylacetonate in aqueous solution gave rise to a basic product crystallising from alcohol, which even after recrystallisation contained approximately one molecular proportion of thallos hydroxide combined with the normal acetylacetonate. The normal compound was prepared by isolating thallos hydroxide, obtained by the double decomposition of thallos sulphate, and crystallised barium hydroxide; the yellow, acicular crystals were dissolved in alcohol containing acetylacetonate, and the solution concentrated at the ordinary temperature under diminished pressure. Thallos acetylacetonate separated in well-defined, colourless, flattened needles and flakes, very soluble in warm alcohol; it melted sharply, and decomposed at 153°.

Acetylacetonates of Bivalent Metals (compare Tanatar and Kurovski, *J. Russ. Phys. Chem. Soc.*, 1908, **40**, 580).

Calcium acetylacetonate, $\text{Ca} \left[\begin{array}{c} \text{O}:\text{C}(\text{CH}_3) \\ \text{O}:\text{C}(\text{CH}_3) \end{array} \right]_2 \text{CH}$, prepared by the interaction of aqueous calcium hydroxide and alcoholic acetylacetonate, crystallised in needles, and was freed from water of crystallisation by drying in a vacuum desiccator over sulphuric acid at 60°:

0.4134 gave 0.2442 CaSO_4 . $\text{Ca} = 17.37$.

$\text{C}_{10}\text{H}_{14}\text{O}_4\text{Ca}$ requires $\text{Ca} = 16.80$ per cent.

The calcium compound had no definite melting point, but charred on heating.

Barium acetylacetonate, $\text{Ba} \left[\begin{array}{c} \text{O}:\text{C}(\text{CH}_3) \\ \text{O}:\text{C}(\text{CH}_3) \end{array} \right]_2 \text{CH}$, prepared by dissolving crystallised barium hydroxide in warm water and boiling with alcoholic acetylacetonate for a few minutes; the filtrate yielded the compound in nacreous flakes and plates, the yield being practically quantitative. The dihydrated acetylacetonate (Found, $\text{Ba} = 36.47$. Calc., $\text{Ba} = 36.92$ per cent.) was dehydrated in a vacuum over sulphuric acid at 60°:

0.7350 gave 0.5053 BaSO_4 . $\text{Ba} = 40.46$.

$\text{C}_{10}\text{H}_{14}\text{O}_4\text{Ba}$ requires $\text{Ba} = 40.89$ per cent.

The compound charred on heating.

Zinc acetylacetonate, $\text{Zn} \left[\begin{array}{c} \text{O}:\text{C}(\text{CH}_3) \\ \text{O}:\text{C}(\text{CH}_3) \end{array} \right]_2 \text{CH}$, formerly described as a yellow compound (Tanatar and Kurovski, *loc. cit.*), was obtained in well-defined, colourless needles by boiling zinc hydroxide with aqueous acetylacetonate, and allowing the filtrate to cool:

0.1385 gave 0.0435 ZnO. Zn = 25.20.

$C_{10}H_{14}O_4Zn$ requires Zn = 24.81 per cent.

Zinc acetylacetonone melted to an opaque, white liquid at 138°.

Cadmium acetylacetonone, which is much less soluble than its zinc analogue, was prepared by digesting cadmium hydroxide with excess of aqueous acetylacetonone, and also by double decomposition from cadmium acetate and sodium acetylacetonone :

0.5084 gave 0.3402 $CdSO_4$. Cd = 36.08.

$C_{10}H_{14}O_4Cd$ requires Cd = 36.21 per cent.

Mercuric acetylacetonone was obtained by mixing equivalent amounts of mercuric chloride and sodium acetylacetonone in aqueous solution ; it separated at once as a sparingly soluble, granular, white precipitate.

When mercurous nitrate was employed in this reaction, partial reduction occurred, the precipitate containing mercury and mercuric acetylacetonone. Copper acetylacetonone was prepared by the interaction of cupric chloride, acetylacetonone, and aqueous sodium acetate, the powdery, pale blue precipitate crystallising from chloroform in deep violet-blue needles. This compound dissolved in quinoline, and the solution on cooling deposited green crystals of an additive compound.

Acetylacetonones of Tervalent Metals.

Scandium Acetylacetonone, $Sc \left[\begin{array}{c} \text{O} \cdot \text{C}(\text{CH}_3) \\ \text{O} \cdot \text{C}(\text{CH}_3) \end{array} \right] \text{CH}]_3$, (compare R. J. Meyer and Winter, *Zeitsch. anorg. Chem.*, 1910, **67**, 398).

For the scandia employed in the following experiments, the authors are indebted to Sir William Crookes, and tender their best thanks. The oxide (1.0164 grams) was covered with pure concentrated nitric acid, and digested for about four hours on the steam-bath. The product was syrupy scandium nitrate with about 6 per cent. of undissolved oxide. After dilution with water and filtration, the solution was digested in a reflux apparatus with a moderate excess of acetylacetonone and ammonia in the presence of benzene. The organic solvent removed quantitatively the scandium acetylacetonone from the aqueous solution, and after concentration deposited colourless plates of scandium acetylacetonone. The substance was purified by dissolving in benzene, in which it was readily soluble, and precipitating with light petroleum, when it separated in colourless needles. From chloroform, scandium acetylacetonone crystallised in colourless, square plates, and it also separated from alcohol in similar, colourless, acicular prisms. The mother liquors from these

crystallisations become yellow, and on warming evolved an odour resembling that of *p*-benzoquinone:

0·1985 gave 0·0402 Sc₂O₃. Sc=13·14.

0·2520 „ 0·0525 Sc₂O₃. Sc=13·15.

(a) 0·1186 gave 0·2264 CO₂ and 0·0755 H₂O. C=52·14; H=7·08.

(b) 0·1228 „ 0·2340 CO₂ „ 0·0728 H₂O. C=51·95; H=6·58.

C₁₅H₂₁O₆Sc requires Sc=12·90; C=52·78; H=6·15 per cent.

The preparations used in the foregoing analyses were purified by crystallisation (*a*) from benzene and light petroleum, (*b*) from alcohol. When dried at the ordinary temperature these preparations melted somewhat indefinitely from 177° to 187°. The indefiniteness of the melting points of acetylacetonates of other metals of the rare earths was previously commented on by Biltz (*Annalen, loc. cit.*, p. 349). Comparative experiments on the distillation of the acetylacetonates of scandium and thorium showed that scandium acetylacetonate was the more stable at temperatures near its melting point.

Volatility of Scandium Acetylacetonate.—Recrystallised specimens of this compound dried at 80° were heated in small tubes placed in a metal bath, the pressure being reduced to 8—10 mm. At 157° the substance began to sublime appreciably, and condensed on the cooler parts of the tubes in small, well-defined, brilliant, colourless crystals of cubical form. The sublimation proceeded smoothly until the melting point (187°) was reached, when the distillation was rapidly completed. The purified specimens, as prepared for analysis, sublimed completely below the melting point, and left no non-volatile residue. There was no charring, and the sublimed contents of the tubes had no odour of acetylacetonate or other organic material.

Sublimed scandium acetylacetonate melted sharply at 187—187·5°. Under atmospheric pressure very little scandium acetylacetonate distilled below 190°; colourless crystals sublimed from 210° to 250°. At 260° the sublimate showed a yellow tinge, but even at 360° very little decomposition was noticed.

Thorium acetylacetonate, purified by crystallisation and through its ammonia additive compound (Biltz, *loc. cit.*), melted at 168—169° (Urbain gives 171—172°, *Bull. Soc. chim.*, 1896, [iii], 15, 338). When heated under 8—10 mm. pressure it began to sublime at 160° in colourless crystals, closely resembling those of the scandium compound. Very little volatilisation occurred below the melting point; the compound boiled at about 260—270°, and the condensed solid showed a faint yellow tinge.

Under the atmospheric pressure very little thorium acetylacetonate sublimed below 210°. At 250° the distillate was yellow, and only

partly solid. At 260° further decomposition occurred, and a brown, charred residue remained.

These comparative experiments showed that scandium acetylacetonone could be distilled under atmospheric pressure without decomposition, whereas in similar circumstances the thorium compound underwent considerable decomposition.

Molecular-weight determinations by the ebullioscopic method showed that scandium acetylacetonone did not undergo association in boiling chloroform or benzene:

0.074 in 20.00 CHCl_3 gave $\Delta t = 0.039$. M.W. = 347.

0.1016 ,, 12.40 C_6H_6 ,, $\Delta t = 0.060$. M.W. = 312.

$\text{Sc}(\text{C}_5\text{H}_7\text{O}_2)_3$ requires M.W. = 341.

The acetylacetonones of trivalent chromium, iron and cobalt were prepared by the general method (Urbain and Debierne, *Compt. rend.*, 1899, **129**, 302), and for the purpose of comparison the corresponding compound of bivalent cobalt was also obtained (Gach, *Monatsh.*, 1900, **21**, 98).

Ultra-violet Absorption Spectra of Metallic Acetylacetonone.

The compounds were dissolved in absolute alcohol to $M/5000$ -solutions, and examined in thicknesses of 1.6, 2.5, 4.0, 6.3, 10.0, 20.0, 31.6, 50.1, and 100.0 mm. with a one-prism Hilger spectrometer and an iron arc. In Fig. 1a the absorption curve of lithium acetylacetonone (unbroken line) is compared with that of acetylacetonone itself (dot and dash line). The two curves are closely coincident, but the band of the lithium compound is less persistent than that of the parent β -diketonone. This comparison is of interest because next to hydrogen, lithium is the element of least atomic weight available for the purpose of these comparative experiments.

On Fig. 2a the absorption curve for thallos acetylacetonone is shown by the broken line (dash and two dots). The metal in this compound has the high atomic weight of 204, and functions as a univalent element. The absorption band is as persistent as that of the lithium compound, but is decidedly narrower.

The third curve on Fig. 1a (dotted line) representing the absorption band of copper acetylacetonone is remarkably like the absorption of vanadyl bisacetylacetonone (T., 1913, **103**, 89), the band being equally persistent, but shifted towards the more refrangible end of the spectrum.

The five curves of Fig. 1b are those of certain bivalent metals of the second vertical series of the periodic classification. The calcium acetylacetonone curve (unbroken line) has an absorption band with its head at $1/\lambda$ 3500; the barium acetylacetonone curve (dash

and two dots) has a wider, shallower absorption band, with its head at $1/\lambda$ 3650. The zinc acetylaceton curve (dotted line) and the

FIG. 1a.

Oscillation Frequencies.

Lithium acetylaceton —————
Copper " - - - - -
Acetylaceton " - · - · -

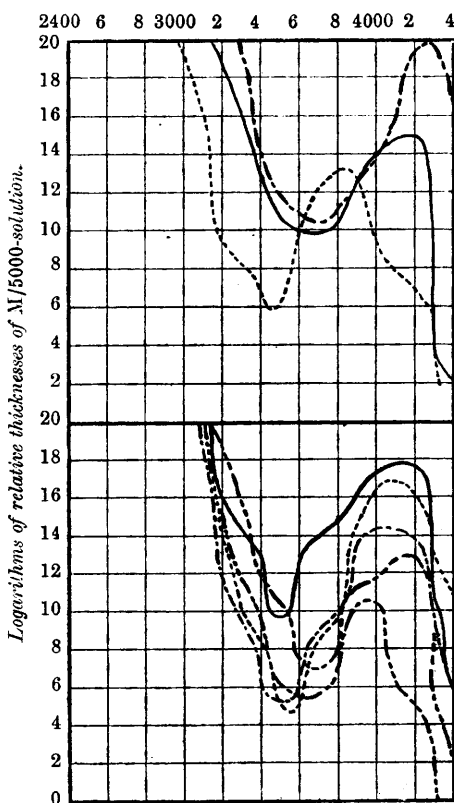


FIG. 1b.

Calcium acetylaceton —————
Zinc " - - - - -
Cadmium " · · · · ·
Barium " - - - - -
Mercuric " - · - · -

cadmium acetylaceton curve (dot and dash) are closely coincident, but the former has the deeper band. The mercuric acetylaceton curve (dash and three dots) shows a shallower band than those due

to zinc and cadmium, with a decided shift towards the more refrangible end, the bands being situated as follows: Zn $1/\lambda$ 3550, Cd $1/\lambda$ 3500, and Hg^{II} $1/\lambda$ 3700.

FIG. 2a.

Oscillation frequencies.

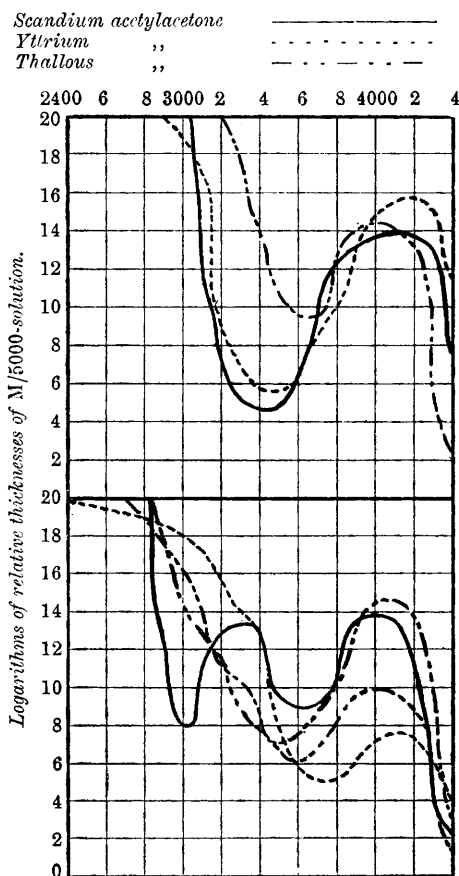


FIG. 2b.

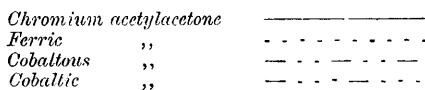


Fig. 2b shows the absorption curves of the acetylacetonates of chromium (unbroken line), iron (dotted line), trivalent cobalt (dash and three dots), and bivalent cobalt (dash and two dots). The curve

for the chromium compound is exceptional in showing two bands, the more refrangible being undoubtedly the acetylacetone band, whereas that towards the red end is probably due to the metallic radicle.

The curve for ferric acetylacetone shows a shallow band with head at $1/\lambda$ 3750. The curve for cobaltic acetylacetone, like the preceding curve, exhibits a somewhat shallow band, the band for cobaltous acetylacetone being much deeper.

The change from cobaltous to cobaltic acetylacetone involves a shifting of the band towards the more refrangible end, similar to the change observed in passing from vanadyl bisacetylacetone to vanadium teracetylacetone (T., 1913, **103**, 89), the heads of the bands being situated as follows:

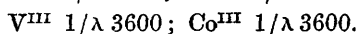
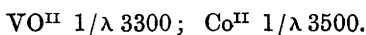


Fig. 2a shows the absorption curves for scandium acetylacetone (unbroken line) and yttrium acetylacetone (dotted line); the two curves are almost superposable, each exhibiting a strong band at $1/\lambda$ 3450. The absorption spectrum of thorium acetylacetone, which was previously examined by Baly and Desch (T., 1904, **85**, 1029; 1905, **87**, 766), exhibited a strong band at $1/\lambda$ 3600.

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