[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, VANDERBILT UNIVERSITY]

A New Method of Preparing Some Acetylacetonate Complexes

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The reaction between basic solutions of metal complexes and acetylacetone can be used in several cases for the preparation of the corresponding acetylacetone complexes. Successful preparations of this type have been developed for the acetylacetonates of MoO_2^{+2}, Th(IV), Cu(II), Be(II), Al(III) and the diammine of the Ni(II) acetylacetonate. Reactions of this type which resulted in basic complexes include those of the complex ions of Zn(II), Cd(II), La(III), Co(II), Ce(IV) and UO_2^{+2}. Under similar conditions no apparent complex formation occurred with W(VI), Cr(III) or Si(IV).

The customary method for preparing acetylacetonate complexes of metals involves treatment of an acidic solution of the metal ion with an ammonium or sodium acetylacetonate solution. Variations of this procedure commonly involve mixing a solution of a metal salt with acetylacetone and then raising the *p*H of the solution until the complex precipitates.[1] When such a procedure is inconvenient or unsuccessful, the direct reaction of the metal, metal oxide or metal carbonate with boiling acetylacetone[2] may sometimes be used to advantage. Occasionally such procedures involve partial reduction of the starting material. The results presented below indicate that a completely unexpected method may be very satisfactory for some of these compounds, *viz.*, precipitation from a *basic* solution by very carefully acidifying such a basic solution containing the metal (in an anion or complex ion) and acetylacetone. In some cases this provides a very superior method for preparation of such complexes as regards both yields and purity. In other instances it merely provides an alternative route to the desired complex.

For those oxidation states of an element which do not form well-defined and easily obtained cationic species, the preparation of β-diketone derivatives is occasionally quite difficult. An example of such an oxidation state is Mo(VI). The cation MoO_2^{+2} is not present as such even in solutions of MoO_3 in strong acids.[3] The usual method of preparing $MoO_2(C_5H_7O_2)_2$ is to reflux the anhydride with acetylacetone.[4] The complex forms in small amounts and its crystals are separated manually from the unreacted molybdic anhydride. Although the use of molybdate solutions as a starting point would seem unpromising for such a preparation, they can in fact be used to advantage.

Because of the ease with which this reaction proceeded, it was decided to find whether other acetylacetonates could be made by similar or related procedures. It was found that these acetylacetonates could be produced from basic *solutions* (not slurries): Be(II), Th(IV), Al(III) and Cu(II). In the case of nickel, the diammine of Ni(II) bisacetylacetonate was produced from ammoniacal solutions of nickel nitrate. All attempts to produce a tungsten(VI), chromium(III) or silicon(IV) complex ended in the precipitation of a hydrated oxide. Similar reactions with Cd(II), UO_2^{+2}, La(III), Ce(IV), Zn(II) and Co(II) produced basic compounds which were not completely characterized.

Experimental

Bis-(2,4-pentanediono)-dioxomolybdenum (VI).—Molybdic anhydride (25 g.) was dissolved in a slight excess of aqueous ammonia. To this, acetylacetone (40 ml.) was added and the resultant mixture stirred while the solution was acidified by the dropwise addition of 10% HNO_3. The acidification was stopped when the *p*H reached 3.5. After standing overnight, the yellow crystals which had precipitated were collected on a buchner funnel and sucked dry. The product was analyzed. Calcd. for $MoO_2(C_5H_7O_2)_2$: Mo, 29.5; C, 36.8; H, 4.3. Found: Mo, 29.1; C, 36.4; H, 4.4. It was found that when the *p*H was made lower than 3.5, considerable amounts of molybdic acid were present in the precipitate.

An alternative preparation may be used in which the starting material is ammonium "paramolybdate." In this method, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ was used. A yellow precipitate formed immediately and was collected on a buchner funnel and sucked dry. The yield was about 97% of theory. Analysis of this product showed Mo, 29.4%; C, 36.6% and H, 4.34%. The m.p. was 179° compared with the literature[4] value of 175°.

Tetrakis-(2,4-pentanediono)-thorium(IV).—Thorium nitrate tetrahydrate (10 g.) was dissolved in distilled water (100 ml.). This solution was stirred while a solution of K_2CO_3 (13 g.) in distilled water (25 ml.) was added. The precipitate which formed initially dissolved easily in an excess of carbonate solution. With continued stirring, acetylacetone (20 ml.) was added dropwise. A white precipitate formed almost immediately. After the addition of the acetylacetone was complete, the precipitate was collected on a buchner funnel and sucked dry. The yield was 9.45 g. (83% of theory). *Anal.* of the precipitate. Calcd. for $Th(C_5H_7O_2)_4$: Th, 36.90; C, 38.25; H, 4.49. Found: Th, 36.80; C, 38.32; H, 4.47.

Bis-(2,4-pentanediono)-copper(II).—Copper(II) nitrate trihydrate (10 g.) was dissolved in distilled water (100 ml.) and concentrated aqueous ammonia (15 ml.) added. To the resulting solution of $Cu(NH_3)_4^{+2}$, acetylacetone (11 ml.) was added dropwise with stirring. A light blue precipitate was obtained; yield about 10.6 g. or 98% of theory. This material was recrystallized from chloroform prior to analysis. *Anal.* Calcd. for $Cu(C_5H_7O_2)_2$: Cu, 24.3; C, 45.88; H, 5.39. Found: Cu, 24.4; C, 46.03; H, 5.42.

Bis-(2,4-pentanediono)-beryllium(II).—Beryllium(II) sulfate tetrahydrate (10 g.) was dissolved in distilled water (100 ml.) and 3 *M* NaOH (100 ml.) added to obtain a clear strongly basic solution. Acetylacetone (30 ml.) was added, dropwise and with stirring, and a white precipitate formed. The yield was 5.1 g. (43% of theory). *Anal.* Calcd. for $Be(C_5H_7O_2)_2$: Be, 4.35; C, 57.96; H, 6.81. Found: Be, 4.23; C, 57.59; H, 6.69.

Tris-(2,4-pentanediono)-aluminum(III).—Aluminum nitrate-9 hydrate (10 g.) was dissolved in distilled water (100 ml.) and 3 *M* NaOH (30 ml.) added. The precipitate of $Al(OH)_3$ which formed initially redissolved completely. Acetylacetone (20 ml.) was added slowly with stirring and a slightly off-white crystalline precipitate was obtained. The yield was 6.9 g. (80% of theory). *Anal.* Calcd. for $Al(C_5H_7O_2)_3$: Al, 8.32; C, 55.55; H, 6.53. Found: Al, 8.28; C, 55.64; H, 6.36.

Bis-(2,4-pentanediono)-diamminenickel(II).—In the reaction between an ammoniacal solution of a nickel salt and acetylacetone, it was noted that if sufficient acetylacetone were added, a blue precipitate formed and the supernatant

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(1) L. E. Marchi, "Inorganic Syntheses," Vol. II, ed. W. C. Fernelius, McGraw-Hill Book Co., New York, N. Y., 1946, p. 10 ff.

(2) W. C. Fernelius and B. E. Bryant, ref. 1, Vol. V, ed. T. Moeller, 1957, p. 105 ff.

(3) M. M. Jones, THIS JOURNAL, **76**, 4233 (1954).

(4) G. T. Morgan and R. A. S. Castell, *J. Chem. Soc.*, 3252 (1928).

solution was *colorless*. Because the resultant precipitate contained ammonia which was lost easily, an attempt was made to determine how nearly quantitative this reaction was. Nickel(II) nitrate "6" hydrate (15.2902 g.), which had lost a small portion of its water of crystallization, was dissolved in distilled water (100 ml.) and then treated with concentrated aqueous ammonia (40 ml.). To the resulting dark blue solution, acetylacetone (20 ml.) was added slowly and a light blue precipitate formed leaving a colorless solution. After drying in an atmosphere of ammonia, the weight of the precipitate was 15.4481 g. If the nickel nitrate-6 hydrate had been of stoichiometric composition, the amount of $Ni(C_5H_7O_2)_2 \cdot 2NH_3$ for quantitative precipitation of the nickel would be 15.2996 g. *Anal.* Calcd. for $Ni(C_5H_7O_2)_2 \cdot 2NH_3$: Ni, 20.17; C, 41.27; H, 6.93; N, 9.63. Found: Ni, 20.03; C, 41.13; H, 6.77; N, 8.64. This compound loses ammonia on standing and is converted into the well-characterized green compound, $Ni(C_5H_7O_2)_2$.

Other Reactions.—Attempts to carry out similar reactions with tungstate, chromite and silicate solutions failed completely. The solid reaction products in these cases were the hydrous oxides or hydroxides.

Reactions in basic conditions were examined with $Cd(NH_3)_4{}^{+2}$, $Zn(NH_3)_4{}^{+2}$, $La(CO_3)_x{}^{+3-2x}$, $UO_2(CO_3)_y{}^{-2-2y}$ and $Co(NH_3)_6{}^{+2}$. The reaction between $Ce(NO_3)_6{}^{-2}$ and acetylacetone in acidic solution was also investigated. In all of these instances the products obtained contained varying amounts of basic materials. The conditions and products of these reactions are summarized in Table I.

TABLE I

REACTIONS OF ACETYLACETONE WITH SOME COMPLEX IONS

Ion	Soln, expected product		Anal., %
$Cd(NH_3)_4{}^{+2}$	Basic	$Cd(C_5H_7O_2)_2$	
			Calcd. Cd, 36.2; C, 38.7; H, 4.54
			Found Cd, 33.9; C, 32.65; H, 5.22
$Zn(NH_3)_4{}^{+2}$	Basic	$Zn(C_5H_7O_2)_2$	
			Calcd. Zn, 24.8; C, 45.6; H, 5.35
			Found Zn, 39.2; C, 41.71; N, 5.70
$La(CO_3)^{+3-2x}$	Basic	$La(C_5H_7O_2)_3$	
			Calcd. La, 31.8
			Found La, 39.9
$UO_2(CO_3)_y{}^{+2-2y}$	Basic	$UO_2(C_5H_7O_2)_2{}^a$	
			Calcd. U, 48.9
			Found U, 43.2 to 50.8
$Co(NH_3)_6{}^{+2}$	Basic	$Co(C_5H_7O_2)_2$	
			Calcd. Co, 22.9; C, 46.7; H, 5.48
			Found Co, 19.2; C, 38.57; H, 6.93
$Ce(NO_3)_5{}^{-2}$	Acidic	$Ce(C_5H_7O_2)_3{}^b$	
			Calcd. Ce, 32.8
			Found Ce, 30.8 to 33.8

[a] Acetylacetone dissolves in a solution of the uranyl carbonate complex without causing any precipitation. Only after a considerable amount of acid has been added to this solution does a precipitate begin to form. The final precipitate was obtained from a solution that was still slightly basic, however. [b] When acetylacetone is added to a solution of ammonium hexanitratocerate(IV), an initial reaction produces the dark blood-red tetrakis-(2,4-pentanediono)-cerium(IV). The reduction of the cerium(IV) by the acetylacetone soon occurs, however, to give a very pale yellow solution. When the *p*H of this solution is raised by the slow addition of aqueous ammonia, a light yellow precipitate is obtained and it is this latter material to which the table entries refer.

The precipitate formed with uranium was recrystallized from chloroform and analyzed. It was found to contain 46.7% U and consisted predominantly of bis-(2,4-pentanediono)-dioxouranium(VI) and a small amount of impurity. Since practically the whole of this material was readily soluble in chloroform, the separation of the complex from the basic materials could be assured.

The oxidation products obtained with the Ce(IV) reaction accompanied the complex when it was recrystallized from chloroform. Although the material was very dark in color, its analysis corresponded closely with that expected for the Ce(III) complex rather than the Ce(IV) complex. This material contained 32.9% Ce and the theoretical value for $Ce(C_5H_7O_2)_3$ is 32.0% Ce.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CLARK UNIVERSITY]

Inner Complex Chelates. II. Analogs and Polar Substituted Analogs of Bisacetylacetoneëthylenediimine and its Metal Chelates[1,2]

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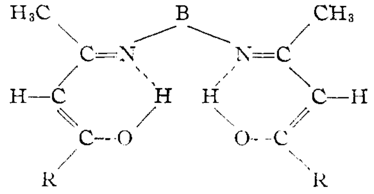
The syntheses of tetradentate chelating agents of the Schiff base type containing such polar groups as *p*-bromophenyl, *m*-nitrophenyl and trifluoromethyl, and the preparation of some of the corresponding metal chelates of Cu(II), Co(II), Ni(II) and V(IV) are described. The tendency of the imino groups in the ligands to be hydrolytically cleaved is decreased by the presence of phenyl or substituted phenyl groups and by chelation of the ligands with metal ions. Benzene complexes of bisdibenzoylmethaneoxovanadium(IV) and of bisbenzoylacetonepropylenediiminoöxovanadium(IV) are described.

The first paper[3] in this series described the syntheses and properties of several analogs of bisacetylacetone-ethylenediimine and their metal chelates. This work has now been extended and includes many derivatives of the parent compound containing highly polar groups such as *p*-bromophenyl, *m*-nitrophenyl and trifluoromethyl. In subsequent investigations the dipole moments of these ligands and metal chelates will be studied in the light of the information already available on the simpler unsubstituted Schiff bases and their metal chelates.[4]

Results

The compounds which have been synthesized are listed in Table I and may be represented by formula I. In the formula B is the alkyl (or aryl) radical of the diamine and R stands for various polar and non-polar groups. As far as it is known none of the metal chelates listed in Table I has been reported previously; the preparation of three ligands listed in the table, *i.e.*, the propylenediamine Schiff bases



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[2] Abstracted in part from a dissertation submitted by Richard J. Hovey to the Faculty of Clark University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[3] P. J. McCarthy, R. J. Hovey, K. Ueno and A. E. Martell, THIS JOURNAL, **77**, 5820 (1955).

[4] P. J. McCarthy and A. E. Martell, *ibid.*, **78**, 264, 2106 (1956).