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Chelates of β -Diketones. V. Preparation and Properties of Chelates Containing Sterically Hindered Ligands¹

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A number of metal chelates containing the anions of β -diketones as ligands have been prepared. Various synthetic procedures are described and physical characteristics are reported.

In the course of studies of the chemistry of metal chelate compounds in organic solvents we have prepared and characterized a considerable number of chelates containing the anions of β -diketones as ligands. Since we have been particularly interested in substances which are highly soluble in aprotic solvents we have concentrated much of our effort on the preparation of neutral chelates containing the anion of 2,2,6,6-tetramethylheptane-3,5-dione (dipivaloylmethide ion), I, as the ligand. Preparative procedures are, in many cases, routine. On the other hand, the preparation of chelates of Fe^{II} , Co^{II} , and Mn^{II} is very difficult and only the cobaltous compound has been obtained in an adequate state of purity. Tables I and II list the chelates which have been prepared and summarize their properties briefly. Reference also is made to general preparative methods used to obtain the particular compounds. The methods are described in the Experimental section.

Experimental

Dipivaloylmethane was prepared by condensation of phenyl pivalate or methyl pivalate with pinacolone using either sodium hydride or lithium amide as the condensing agent.² The crude product was converted to its copper chelate by treatment with a solution of cupric acetate in hot, aqueous ethanol. The copper chelate was recrystallized from ethanol, dissolved in ether, and decomposed by treatment with 10% hydrochloric acid. The product was distilled under reduced pressure, b.p. 93–94° at 35 mm.

Benzoylpivaloylmethane (4,4-dimethyl-1-phenylpentane-1,3-dione) was prepared by condensation of phenyl benzoate with pinacolone in the presence of lithium amide. The crude product was distilled giving the product, b.p. 151–152° at 13 mm., in 85% yield.

Anal. Calcd. for $\text{C}_{13}\text{H}_{16}\text{O}_2$: C, 76.45; H, 7.88. Found: C, 76.26; H, 7.07.

General Preparative Method A.—An ethanol solution of the β -diketone was added to an aqueous solution containing either the metal chloride or the metal sulfate and an excess of sodium acetate.³ The metal chelate was removed by filtration.

Method B.—A toluene solution of the β -diketone was heated under reflux with the appropriate metal for several days. Residual metal was removed by filtration and the solvent was removed by distillation.

Method C.—The β -diketone was added to an aqueous solution

of the metallic hydroxide and the two-phase system was shaken.³ The solid chelate was removed by filtration and washed carefully with a small amount of cold water.

Method D.—The metallic chloride or acetate was dissolved in aqueous ethanol and the β -diketone was added. Concentrated aqueous ammonia then was added dropwise with stirring. The chelate gradually separated and was removed by filtration.

Method E.—An ethanolic solution of dipivaloylmethanato sodium (or potassium) was added to an ethanolic solution of the metallic halide. The chelate separated and was removed by filtration.

Method F.—The metallic oxide was dissolved in the minimum volume of dilute aqueous hydrochloric acid. Ammonia was added until the hydroxide began to separate; hydrochloric acid then was added to just redissolve the precipitate. An equal volume of ethanol then was added, followed by the β -diketone in excess. Ammonia then was added dropwise to the stirred solution. The chelate separated and was isolated by extraction with petroleum ether. The extract was dried over Drierite and the chelate was recovered by evaporation of the solvent.

All chelates prepared by the general procedures were purified by recrystallization and/or sublimation as indicated in Tables I and II.

Bis-(dipivaloylmethanato)-magnesium was prepared by heating a solution of the β -diketone in 70% aqueous ethanol under reflux in the presence of metallic magnesium.⁴ The chelate crystallized from the reaction mixture on cooling and was purified by sublimation *in vacuo*. Samples melted at 94°, although a sample melting at 134° once was obtained, but not analyzed, during an early stage of the work. The chelate was analyzed for the ratio of metal to ligand. A known amount of chelate was hydrolyzed with concentrated hydrochloric acid and diluted with isopropyl alcohol. The ligand content was determined spectrophotometrically by measurement of the absorbance at the maximum at 2720 Å. The ratio was one magnesium to two ligands. The magnesium was determined by EDTA titration.

Anal. Calcd. for $\text{C}_{22}\text{H}_{38}\text{O}_4\text{Mg}$: Mg, 6.24. Found: Mg, 6.18.

Bis-(dipivaloylmethanato)-mercury(II) was prepared by the reaction of mercuric acetate and dipivaloylmethane in aqueous ethanol. The yield was 63% of a white product (I) which melted at 225–227° after recrystallization from 95% ethanol. An earlier preparation using mercuric chloride and excess sodium acetate gave a white product having a wide melting range; repeated recrystallization of this compound gave a product (II) melting at 192°. Compound I will not sublime readily and 1 mole of the compound consumes 2 moles of iodine (1 g. of the compound consumed 0.00358 mole of iodine) when titrated with a standard solution of iodine. Compound II will sublime readily; 1 g. of the material consumes 0.00186 mole of iodine. It is clear that I has the composition of a mercury(II) dipivaloylmethide and that II does not.

Anal. Calcd. for $\text{HgC}_{22}\text{H}_{38}\text{O}_4$: C, 46.59; H, 6.75. Found for I: C, 46.41; H, 6.51. Found for II: C, 32.15; H, 3.47.

(1) Part IV is G. S. Hammond, A. W. Moschel, and W. G. Bordin, *J. Chem. Phys.*, **64**, 1782 (1960).

(2) K. R. Kopecky, D. C. Nonhebel, G. Morris, and G. S. Hammond, *J. Org. Chem.*, **27**, 1036 (1962).

(3) G. T. Morgan and H. W. Moss, *J. Chem. Soc.*, 196 (1914).

(4) L. F. Hatch and G. Sutherland, *J. Org. Chem.*, **13**, 251 (1948).

TABLE I
 METAL CHELATES OF DIPIVALOYLMETHANE

Metal chelate	Method of preparation ^a	Method of purification	Physical characteristics	M.p., °C.
Li(DPM)	B	Sublimation	White powder	dec.
Na(DPM)	C	Sublimation	White powder	dec.
K(DPM)	C	Sublimation	White powder	dec.
Be(DPM) ₂	D	Recryst. from methanol	White needles	93-97
Mg(DPM) ₂	B(E)	Recryst. from petrol. ether	White needles	94 (134?)
Ca(DPM) ₂	D	Recryst. from aq. ethanol	White needles	224
Sr(DPM) ₂	D	Recryst. from aq. ethanol	White needles	200
Ba(DPM) ₂	C	Recryst. from aq. ethanol	White needles	172
Co(DPM) ₂ ^c	D	Sublimation	Purple crystals	143
Ni(DPM) ₂ ^b	A, D	Sublimation	Pink needles	225
Cu(DPM) ₂	A	Recryst. from <i>n</i> -heptane	Deep blue prisms	198
Zn(DPM) ₂	D	Sublimation	White needles	144
Hg(DPM) ₂	— ^a	Recryst. from methanol	White needles	225
Al(DPM) ₃	A	Recryst. from ethanol	White needles	264-265
Cr(DPM) ₃	— ^a	Sublimation	Purple crystals	229
Mn(DPM) ₃	— ^a	Sublimation	Black crystals	165
Fe(DPM) ₃	A	Recryst. from DMF or sublimation	Red needles	163
Co(DPM) ₃	— ^a	Sublimation	Dark green crystals	245
La(DPM) ₃	E	Recryst. from DMF	White needles	148-149
Sm(DPM) ₃	F	Recryst. from DMF	White needles	143-144
Ho(DPM) ₃	E	Recryst. from DMF	White needles	154-155
Er(DPM) ₃	F	Recryst. from DMF	Pink needles	153-154

^a See Experimental section. ^b The nickel chelate was isolated from the reaction as its green dihydrate. On drying it loses its water of crystallization and becomes pinkish red in color. ^c A beige colored hydrate or ammoniate is obtained first; drying over P₂O₅ produces anhydrous purple chelate.

 TABLE II
 METAL CHELATES OF BENZOYLPIVALOYLMETHANE

Metal chelate	Method of preparation	Method of purification	Physical characteristics	M.p., °C.
Li(BPM)	B	Recryst. from acetone	White powder	dec.
K(BPM)	C	Recryst. from acetone	White needles	dec.
Ca(BPM) ₂	B	Recryst. from methanol	White needles	dec.
Ba(BPM) ₂	C	Recryst. from ethanol	White needles	dec.
Cu(BPM) ₂	A	Recryst. from petrol. ether	Gray-green needles	202
Ni(BPM) ₂	A	Recryst. from petrol. ether		243

Tris-(dipivaloylmethanato)-cobalt(III) was prepared by the procedure used for the synthesis of the acetylacetonate.⁵ A mixture of cobaltous carbonate (0.0126 mole) and dipivaloylmethane (0.0542 mole) was heated to 90° and 30 ml. of 10% aqueous hydrogen peroxide was added to the solution over a 50-min. period. The mixture then was maintained at 90° for one additional hour. The organic layer was separated and chilled to -5°. One g. of precipitate (13% yield) was collected and sublimed at 100° and 1 mm. pressure. The dark green crystals melted at 243-245°.

Anal. Calcd. for CoC₃₃H₅₇O₉: C, 65.11; H, 9.45. Found: C, 64.93; H, 9.42.

Tris-(dipivaloylmethanato)-chromium(III) was prepared by a modification of the procedure used in the preparation of the acetylacetonate.⁶ A solution of 3 g. of chromium(III) chloride hexahydrate, 20 g. of urea, and 5 g. of dipivaloylmethane in a solvent consisting of 25 ml. of water and 65 ml. of ethanol was heated at 90° for 20 hr. The solution was cooled to room temperature and 100 ml. of water was added. The precipitate was filtered, dried, and sublimed *in vacuo*; yield, 3.5 g.; 60%. The dark purple crystals melted at 229-229.5°.

Anal. Calcd. for CrC₃₃H₅₇O₉: C, 65.86; H, 9.77. Found: C, 66.05; H, 9.56.

Bis-(acetylacetonato)-manganese(II).—Preparation of the

(5) B. Bryant and W. C. Fernelius, *Inorg. Sym.*, **5**, 188 (1937).

(6) W. C. Fernelius and J. E. Blanch, *ibid.*, **5**, 130 (1937).

TABLE III

Compound		Calcd.			Found		
		C	H	Metal	C	H	Metal
LiDPM	LiC ₁₁ H ₁₉ O ₂	69.46	10.07	3.65	67.61	9.89	3.57
NaDPM	NaC ₁₁ H ₁₉ O ₂	64.05	9.29	11.15	57.53	9.26	10.75
Be(DPM) ₂	BeC ₂₂ H ₃₈ O ₄	70.36	10.20	2.40	70.91	9.84	2.32
Ca(DPM) ₂	CaC ₂₂ H ₃₈ O ₄	64.98	9.42	9.86	61.29	9.07	10.32
Co(DPM) ₂	CoC ₂₂ H ₃₈ O ₄	62.10	9.00	13.85	62.09	8.93	13.87
Ni(DPM) ₂	NiC ₂₂ H ₃₈ O ₄	61.84	8.96	13.81	61.92	8.99	13.57
Cu(DPM) ₂	CuC ₂₂ H ₃₈ O ₄	61.44	8.91	14.77	61.41	9.00	14.63
Zn(DPM) ₂	ZnC ₂₂ H ₃₈ O ₄	60.89	8.82	15.17	61.18	8.77	15.45
Hg(DPM) ₂	HgC ₂₂ H ₃₈ O ₄	46.59	6.75	35.37	46.41	6.51	34.6
Al(DPM) ₃	AlC ₃₃ H ₅₇ O ₆	68.72	9.96	4.68	68.27	10.08	4.68
Cr(DPM) ₃	CrC ₃₃ H ₅₇ O ₆	65.86	9.77	8.47	66.05	9.56	8.49
Mn(DPM) ₃	MnC ₃₃ H ₅₇ O ₆	65.54	9.50	9.08	65.48	9.44	9.25
Fe(DPM) ₃	FeC ₃₃ H ₅₇ O ₆	65.44	9.48	9.22	65.10	9.25	9.31
Co(DPM) ₃	CoC ₃₃ H ₅₇ O ₆	65.11	9.45	9.68	64.93	9.42	9.14
Er(DPM) ₃	ErC ₃₃ H ₅₇ O ₆	55.27	8.01		55.26	8.21	

compound has been reported previously,⁷ but physical properties were not recorded. To an aqueous solution of manganous chloride (0.05 mole in 10 ml. of water) were added 200 ml. of 6 *N* aqueous ammonium chloride and 20 ml. of 15 *N* ammonium hydroxide. Acetylacetone (10 g. in an equal volume of methyl alcohol) was added dropwise to the buffered solution over a period of about 5 min. A yellowish precipitate was formed and was separated by filtration, washed with water, and dried *in vacuo* over phosphorus pentoxide for 12 hr. at room temperature and for 6 hr. at 57°. The crude yield was 90%. The product was purified by vacuum sublimation first at 140° to remove the remaining ammonium chloride, then at 200° giving light yellow crystals, m.p. 246° (sealed tube).

Anal. Calcd. for MnC₁₀H₁₄O₄: Mn, 21.70. Found: Mn, 21.23.

Attempts to Prepare Bis-(dipivaloylmethanato)-manganese(II).

—Various procedures were used to prepare the compound in the absence of oxygen. In the most nearly successful attempt an all-glass apparatus bearing several side arms was used. Reagents were placed in different side arms and degassed by pumping during repeated freeze-thaw cycles. The reagents (an aqueous buffer prepared from 40 ml. of 6 *N* ammonium chloride and 4 ml. of 15 *N* ammonium hydroxide, 0.01 mole of manganous chloride tetrahydrate in 40 ml. of methyl alcohol, and 0.02 mole of dipivaloylmethane in 50 ml. of methyl alcohol) were mixed and stirred with a magnetic stirrer. A yellow precipitate formed and was removed by forcing the mixture out of the reaction vessel and through a buchner funnel which was joined to the rest of the system by ground glass joints. The transfer was accomplished by admitting nitrogen and application of suction. The precipitate was washed with a solution consisting of 60 ml. of methyl alcohol and 20 ml. of water which had been degassed and retained in one of the reservoirs. The buchner funnel which contained the product was removed from the assembly and transferred rapidly to a vacuum desiccator which had been pre-filled with nitrogen. The desiccator, which contained phosphorus pentoxide, was evacuated quickly to less than 1 mm. pressure. The product was yellow when introduced into the desiccator but had become dark gray by the end of 6 hr. The desiccator was opened and the product charred immediately on contact with the air; the surface actually became hot and the interior of the sample turned to a soft black tar. Other attempts to prepare the manganous chelate with less rigorous exclusion of air gave only the manganese(III) chelate as a product.

Tris-(dipivaloylmethanato)-manganese(III) was prepared by minor modification of the method used by Cartledge for the preparation of the acetylacetonate.⁸ To a solution of 0.008 mole of manganous chloride in 50 ml. of methanol and 10 ml. of water were added 0.002 mole of potassium permanganate and 5 ml. of 2.5 *N* ammonium hydroxide. The solution registered a

reading of 6 on the scale of a pH meter. Dipivaloylmethane (0.03 mole) was added dropwise along with sufficient ammonium hydroxide to maintain the pH meter reading between 6 and 7. The reaction mixture then was stirred at room temperature for 10 hr. The black precipitate was collected, washed with 50% aqueous methanol, and dried *in vacuo* over phosphorus pentoxide; yield 78%. The crude product was sublimed at 140° at 1 mm. pressure, giving black crystals, m.p. 164–165°.

Anal. Calcd. for MnC₃₃H₅₇O₆: C, 65.54; H, 9.50. Found: C, 65.48; H, 9.44.

Attempts to Prepare Bis-(dipivaloylmethanato)-iron(II).—The procedures used were modifications of the method of Emmert and Jarczyński⁹ for the preparation of acetylacetonatoiron(II). As a pilot procedure we repeated the preparation of the latter compound. The product was obtained in 75% yield as a brown powder (sealed *in vacuo*), m.p. 166–195° with charring at 170° (lit.⁵ chars at 170°). The crude product gave a negative test for iron(III) when decomposed with aqueous acid and treated with thiocyanate; however, attempts to purify the compound by sublimation always gave material which gave a positive test for the presence of Fe^{III}. Various modifications of the procedure were used in the attempts to prepare ferrous dipivaloylmethide. Piperidine, sodium acetate, and diisopropylamine were used as bases to precipitate solid products from 50% ethanol-water solutions containing dipivaloylmethane and ferrous sulfate. Brown products which gave positive tests for both Fe^{III} and Fe^{II} were obtained. Samples rich in Fe^{II} usually melted in the range 100–125°. Sublimation always gave ferric dipivaloylmethide and an infusible residue. In a number of experiments attempts were made to ensure oxygen-free conditions by carrying out all operations in a nitrogen-filled drybox. Preparation of the desired product by vacuum line techniques has not yet been attempted.

Analyses for the chelates are reported in Table III.

Discussion

Dipivaloylmethanato¹⁰ chelates (I) are remarkably soluble in a wide range of organic solvents including benzene and petroleum ether; even the alkali derivatives show significant solubility in such media. Benzoylpivaloylmethides (II) are less soluble in hydrocarbons but are still sufficiently soluble to make them of interest as reactants in homogeneous,

(9) B. Emmert and R. Jarczyński, *Ber.*, **64**, 1074 (1931).

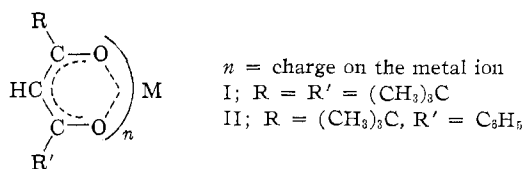
(10) We suggest the retention of the name dipivaloylmethanato for this ligand. The practice would be consistent with the use of the name acetylacetonato¹¹ and is much more manageable than the systematic name, 2,2,6,6-tetramethyl-3,5-heptanedionato.

(11) W. C. Fernelius, "Chemical Nomenclature," *Advances in Chemistry VIII*, Am. Chem. Soc. Special Publication, 1953, p. 9.

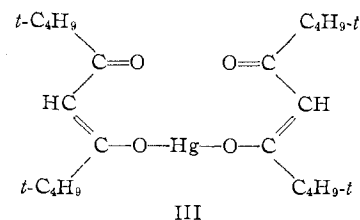
(7) B. Emmert, H. Gsottschneider, and H. Stanger, *Ber.*, **69**, 1319 (1936).

(8) G. H. Cartledge, *J. Am. Chem. Soc.*, **73**, 4416 (1951).

organic reactions. Such properties would be expected as an extension of those of acetylacetonates.¹²



The hydrocarbon-like properties of the latter group are greatly increased; probably because the polar, metal-oxygen bonds are buried under a thicker skin of hydrocarbon. The dipivaloylmethides of strontium, barium, and the alkali metals do not melt without decomposition, although the compounds can be purified by conventional procedures of recrystallization and sublimation. The other dipivaloylmethides have well defined melting points and might even be suggested as suitable derivatives for characterization of the various metal ions. Infrared spectra of all of the compounds listed in Tables I and II have been measured but are not recorded in detail because they are, in most cases, similar to spectra reported by Holtzclaw and Collman.¹³ Absorption in the region between 6.3 and 7.4 μ , the "chelate carbonyl" region,¹⁴ is especially characteristic. Absorption is very intense and shows a great deal of fine structure. The spectrum of the mercury(II) derivative of dipivaloylmethane is exceptional in that it shows strong absorption between 5.96 and 6.15 μ . The mercuric derivative of acetylacetonate shows the same feature. Furthermore, the mercury derivative of dipivaloylmethane is much less soluble in organic solvents than are the chelates of other divalent metal ions. The ultraviolet spectrum of mercuric dipivaloylmethide has two maxima at 2050 Å. (ϵ 11,500) and 2750 Å. (ϵ 11,200). Such absorption is entirely incompatible with the view that the compound has the structure of a diketone. If the mercury atom were bound to carbon, one would expect that the compound would exist in the diketonic form; a substituent such as a methyl group on the central carbon atom is bulky enough to force a relatively unhindered system such as acetylacetonate into the dicarbonyl form.¹⁵ Furthermore, the n.m.r. spectrum of the compound shows a resonance 295 c.p.s. downfield from the tetramethylsilane resonance in chloroform solution. This peak, which is attributed to a vinyl proton, has an area equal to about one eighteenth of that of the methyl resonance signal. These data seem to show unequivocally that the compound has an open form with mercury bound to oxygen (structure III)



Bis-(dipivaloylmethanato)-nickel(II) normally is obtained as the green dihydrate but can be converted to the anhydrous, pink chelate either by heating with an infrared lamp or by drying in a vacuum desiccator over phosphorus pentoxide. We also found that the anhydrous compound is diamagnetic, a fact which has been shown by Cotton and Fackler¹⁶ to be associated with the monomeric state of the compound in solution. Cursory examination of some of the chelates by n.m.r. showed that tris-(acetylacetonato)-iron(III), tris-(dipivaloylmethanato)-iron(III), tris-(dipivaloylmethanato)-chromium(III), and bis-(dipivaloylmethanato)-cobalt(II) gave no detectable proton resonance in carbon tetrachloride solution; the resonance of tetramethylsilane which was included as a reference also was totally collapsed. The result clearly shows the effect of the paramagnetic species in decreasing transverse relaxation times. In contrast, tris-(dipivaloylmethanato)-aluminum, tris-(dipivaloylmethanato)-cobalt(III), and bis-(dipivaloylmethanato)-zinc show sharp resonances due to CH and CH₃ protons of the ligand. A solution containing 2.5% by weight of bis-(dipivaloylmethanato)-nickel in dry carbon tetrachloride also gave distinct resonance peaks due to the CH and CH₃ protons of the ligand; however, if moisture is present all peaks, including that of tetramethylsilane, are collapsed, indicating that the hydrate of the nickel chelate is paramagnetic. The n.m.r. spectrum of a chloroform solution of mercury(II) dipivaloylmethide showed a sharp CH₃ resonance but the CH resonance is broadened and occurs at higher field by 30 c.p.s. (60 Mc.) than the CH resonances of the chelates.

Bis-(dipivaloylmethanato)-cobalt(II) was prepared without great difficulty but hydrocarbon solutions of the compound are oxidized rather rapidly on exposure to air. The analogous iron(II) and manganese(II) compounds are so susceptible to oxidation that they have not been obtained yet in pure form. Results to be reported elsewhere¹⁷ show that acetylacetonate and dipivaloylmethane may have specific catalytic effects on the rate of oxidation of Fe^{II} to Fe^{III} in alcoholic solutions. Similar effects of other oxy ligands have been reported recently.¹⁸

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 (13) H. F. Holtzclaw, Jr., and J. P. Collman, *J. Am. Chem. Soc.*, **79**, 3318 (1957).
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