

STUDIES IN THE STEREOCHEMISTRY OF ZINC(II)*

II. DERIVATIVES OF BIS(BENZOYLACETONATO)ZINC(II)

By D. P. GRADDON† and D. G. WEEDEN†

In Part I¹ we described the preparation and properties of a series of base adducts of bis(acetylacetonato)zinc(II) and showed by molecular weight determinations that in these compounds the zinc is preferentially 5-coordinate. This paper describes the analogous compounds formed by bis(benzoylacetonato)zinc(II).

The only reference which we have been able to find to bis(benzoylacetonato)-zinc(II) is to a determination of its diamagnetic susceptibility by Mehta² in 1957; its preparation is not there described in detail, and although it is said to have been purified by repeated crystallization and its purity confirmed by the melting point and analysis, neither of these is quoted.

By reaction between zinc hydroxide and benzoylacetone we have isolated, after crystallization, methanolbis(benzoylacetonato)zinc(II), from which we have obtained anhydrous bis(benzoylacetonato)zinc(II) and a series of adducts with heterocyclic bases and ammonia. We have not succeeded in isolating any hydrated species.

Molecular weight determinations on anhydrous bis(benzoylacetonato)zinc(II) are less accurate than we should like, because of the impurity of our sample, but show that this compound is monomeric in solution in non-donor solvents, and presumably tetrahedral. We have found no evidence for polymerization, in contrast to the corresponding nickel(II) compound, which has been shown³ to be trimeric in a variety of solvents.

Formally 5-coordinated species, obtained by the addition of one molecule of methanol or heterocyclic base, are shown to remain undissociated in benzene solution as observed for the corresponding acetylacetonato compounds. In triphenylmethane solutions, however, dissociation occurred into two species, presumably free base and anhydrous bis(benzoylacetonato)zinc(II); in every case this dissociation was complete in 5% solutions and only with the 4-methylpyridine adduct could a solution be obtained sufficiently concentrated for dissociation to be negligible. In this solvent, therefore, the 5-coordinated benzoylacetonato compounds are less stable than the corresponding acetylacetonato compounds.

The formally 5-coordinate ammine $(C_{10}H_9O_2)_2Zn \cdot NH_3$, was found to be insoluble in non-donor solvents and molecular weights could not be determined; we presume that this compound is polymeric, the coordination number of the zinc atom

* Manuscript received October 25, 1963.

† Inorganic Chemistry Department, University of New South Wales, Kensington, N.S.W.

¹ Graddon, D. P., and Weeden, D. G., *Aust. J. Chem.*, 1963, **16**, 980.

² Mehta, S., and Dessai, D. M., *J. Indian Chem. Soc.*, 1957, **34**, 559.

³ Graddon, D. P., *Nature*, 1962, **195**, 891.

being increased to six. We were unable to obtain a diammine, in contrast to the acetylacetonato series, in which we obtained a diammine but no monoammine.

$(C_{10}H_9O_2)_2Znpy_2$ and $(C_{10}H_9O_2)_2Zn(4\text{-mepy})_2$, two formally 6-coordinate compounds, were found to dissociate completely in benzene solution giving two species, presumably free base and the corresponding 5-coordinate compounds; similar dissociation was observed in triphenylmethane solution at high concentrations, but on dilution further dissociation occurred, presumably to two molecules of free base and anhydrous bis(benzoylacetonato)zinc(II).

In solutions of the base adducts of bis(benzoylacetonato)zinc(II) the coordination numbers of the zinc atoms are thus: 5 in benzene solutions at 5° and in very concentrated solutions in triphenylmethane at 92°, and 4 in more dilute solutions in triphenylmethane.

Experimental

Methanolbis(benzoylacetonato)zinc(II).—3 g of zinc hydroxide (1 mole) and 16 g of benzoylacetonato (3·3 mole) were heated together on a steam-bath until all of the zinc hydroxide had dissolved. The product was dissolved in a hot mixture of methanol and chloroform, and this solution on cooling deposited most of the excess benzoylacetonato as crystals; these were removed and on concentration of the mother liquor crystals of the zinc compound were obtained (Found: C, 60·0; H, 5·4; Zn, 15·5%. Calc. for $(C_{10}H_9O_2)_2Zn(CH_3OH)$: C, 60·1; H, 5·3; Zn, 15·6%). Yield 12 g (80% of theoretical based on zinc hydroxide). White needles, melting at 118° to a yellow liquid.

Bis(benzoylacetonato)zinc(II) (anhydrous).—This compound was obtained by heating the methanol adduct *in vacuo* at 100° over phosphorus pentoxide. The product was a clear, pale yellow glass, which we have been unable to crystallize; on heating it became fluid at about 130° (Found: C, 59·7; H, 4·8; Zn, 16·8%. Calc. for $(C_{10}H_9O_2)_2Zn$: C, 61·9; H, 4·7; Zn, 16·9%).

We have been unable to improve on the purity of this compound. The low carbon analysis suggested that our product might be a hemihydrate (C, 60·5; H, 4·8; Zn, 16·5%) but the infrared spectrum showed no absorption above 3150 cm^{-1} , and we conclude that our product is anhydrous, but contaminated by zinc oxide.

Bis(pyridine)bis(benzoylacetonato)zinc(II).—This was obtained when 1 g of the methanol adduct was dissolved in 3 ml of pyridine and the solution cooled to 0°. The product was dried *in vacuo* for 1 hr (Found: C, 66·0; H, 5·0; N, 5·4; Zn, 11·9%. Calc. for $(C_{10}H_9O_2)_2Zn(C_5H_5N)_2$: C, 66·0; H, 5·2; N, 5·1; Zn, 12·0%). Yield 1·26 g (97%).

White needles, m.p. 102–106°. Soluble in organic solvents, slowly loses pyridine in air.

Pyridinebis(benzoylacetonato)zinc(II).—This was obtained when the bispyridine adduct was crystallized from absolute ethanol. The product was washed with ethanol and air-dried (Found: C, 64·3; H, 4·9; N, 3·1; Zn, 13·8%. Calc. for $(C_{10}H_9O_2)_2Zn(C_5H_5N)$: C, 64·3; H, 5·0; N, 3·0; Zn, 14·0%). Yield 85%.

White needles, m.p. 125–127°. Soluble in organic solvents.

Bis(4-methylpyridine)bis(benzoylacetonato)zinc(II).—This was prepared by dissolving 2 g of the methanol adduct in 5 ml of 4-methylpyridine and cooling to 0°; it was washed with hexane and dried at the pump (Found: C, 67·1; H, 5·8; N, 5·1; Zn, 11·4%. Calc. for $(C_{10}H_9O_2)_2Zn(C_6H_7N)_2$: C, 66·9; H, 5·6; N, 4·9; Zn, 11·4%). Yield 1·4 g (50%).

White needles, m.p. 78–79°. Soluble in organic solvents, slowly loses 4-methylpyridine in air.

4-Methylpyridinebis(benzoylacetonato)zinc(II).—Obtained by crystallization of the bis-(4-methylpyridine) compound from 95% ethanol; washed with hexane and dried *in vacuo* (Found: C, 64·7; H, 5·0; N, 2·6; Zn, 13·5%. Calc. for $(C_{10}H_9O_2)_2Zn(C_6H_7N)$: C, 65·0; H, 5·2; N, 2·9; Zn, 13·6%). Yield 67%.

White needles, m.p. 106–108°. Soluble in organic solvents.

2-Methylpyridinebis(benzoylacetato)zinc(II).—Obtained by dissolving 1.3 g of the methanol adduct in 5 ml of 2-methylpyridine and cooling the solution to 0°. It was washed with hexane, and air-dried (Found: C, 64.8; H, 5.1; N, 3.1; Zn, 13.5%. Calc. for $(C_{10}H_9O_2)_2Zn(C_6H_7N)$: C, 65.0; H, 5.2; N, 2.9; Zn, 13.6%). Yield 0.7 g (47%).

White needles, m.p. 116–118° (decomp.). Soluble in organic solvents.

TABLE 1
MOLECULAR WEIGHTS

Compound	Formula Wt.	In Triphenylmethane			In Benzene		
		Conc.	Mol. Wt.	Complexity	Conc.	Mol. Wt.	Complexity
$C_{20}H_{18}O_4Zn$	388	20.0	353	0.9	1.22	410	1.1
		4.9	267	0.7	0.59	455	1.2
$C_{20}H_{18}O_4Zn(CH_3OH)$	420	10.6	262	0.6	1.00	330	0.8
		7.7	247	0.6	0.57	340	0.8
		6.3	188	0.5			
$C_{20}H_{18}O_4Zn(C_5H_5N)$	467	20.0	359	0.8	1.10	458	1.0
		9.5	299	0.6	0.49	462	1.0
		6.0	218	0.5			
$C_{20}H_{18}O_4Zn(4\text{-mepy})$	481	23.0	470	1.0	1.80	442	0.9
		10.0	297	0.6	1.40	418	0.9
		5.0	240	0.5	0.47	394	0.8
$C_{20}H_{18}O_4Zn(2\text{-mepy})$	481	9.4	259	0.5	0.92	426	0.9
		5.1	244	0.5	0.45	417	0.9
$C_{20}H_{18}O_4Zn(C_5H_5N)_2$	546	10.0	276	0.5	0.99	300	0.5
		5.5	270	0.5	0.49	300	0.5
		2.8	210	0.4			
$C_{20}H_{18}O_4Zn(4\text{-mepy})_2$	574	10.3	281	0.5			
		7.7	247	0.4	0.60	281	0.5
		5.1	188	0.3			

Amminebis(benzoylacetato)zinc(II).—Obtained by exposing the methanol adduct in an atmosphere saturated with water vapour and ammonia at 20° for 3 days. Loss of weight occurred equivalent to replacement of methanol by ammonia; no further change in weight occurred on exposure in the open laboratory for several weeks (Found: C, 59.3; H, 5.5; N, 3.7; Zn, 16.1%. Calc. for $(C_{10}H_9O_2)_2Zn \cdot NH_3$: C, 59.3; H, 5.2; N, 3.5; Zn, 16.1%). Quantitative yield.

Small white cubes, m.p. 198–200° (decomp. to yellow solid). Insoluble in water and organic solvents.

Molecular Weight Determinations.—Molecular weights were determined cryoscopically in benzene over a range of about 0.5–2% solute by weight and in triphenylmethane over a range of about 3–20% solute by weight. Table 1 gives the formula weight, concentration (g solute per 100 g solvent), observed molecular weight, and complexity (as the ratio of observed molecular weight to formula weight) for each compound.