A Ketonic Complex of Acetylacetone with Cobalt(II) Bromide

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A NOVEL ketonic complex of acetylacetone with cobalt(II) bromide was prepared by two methods, and transformed to the usual enolate-chelate by the action of a base.

If 2·5 moles of bromine is added to 1 mole of tris(acetylacetonato)cobalt(III) in dichloromethane at 0°, the reaction represented by equation (1) proceeds to completion,

$$\mathrm{Co(HA)_3} + 2{\cdot}5\mathrm{Br_2} = \mathrm{CoBr_2} + 3\mathrm{HABr} \qquad (1)$$

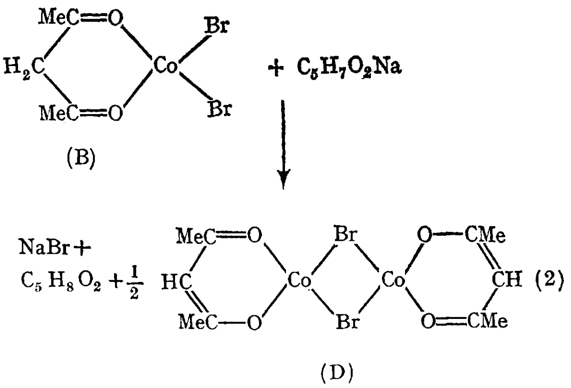
(H_2A denotes acetylacetone). No precipitate appears until the amount of bromine exceeds 1 mole. An intermediate (A) is stable and soluble in this cold solvent. When the solution was concentrated by evaporation at 0°, a light blue precipitate (B), insoluble in dichloromethane and different from (A), separated out.

Elemental analysis of (B) is consistent with an adduct of acetylacetone and cobalt(II) bromide. The effective magnetic moment of 4·25 B.M. confirms that this is a $\mathrm{Co^{II}}$ compound. The i.r. spectrum shows the characteristic carbonyl band at 1705 cm.$^{-1}$ together with a shoulder at 1720 cm.$^{-1}$, coinciding with that reported for the ketonic form of acetylacetone.[1] No bands attributable to the enolic molecule or the chelated enolate anion were observed, indicating unequivocally that a ketonic molecule of acetylacetone is coordinated to the cobalt atom. The absorption spectrum of the solid (Nujol mull) resembles that observed for $\mathrm{CoBr_2(acetone)_2}$,[2] suggesting a tetrahedral structure for (B).

The compound (B) was also prepared directly by the reaction of anhydrous cobalt(II) bromide with acetylacetone. An ampoule containing anhydrous cobalt bromide was evacuated and acetylacetone was distilled in. Green cobalt bromide dissolved gradually and purple crystals (C) appeared. These were isolated and dried *in vacuo* at room temperature. Analysis indicated the formula $\mathrm{CoBr_2(C_5H_8O_2)_2}$. The purple compound (C) was further evacuated at 60° for about 5 hr., resulting in a light-blue powder which was identified as (B) from the elemental analysis and electronic and i.r. spectra.

The compound (C) is much less soluble than (B) in acetylacetone. If a concentrated solution of (B) in this solvent is kept standing at room temperature, (C) is soon precipitated. The electronic and i.r. spectra of these two compounds are quite similar. An excess molecule of acetylacetone in (C) might be contained as the solvent of crystallisation, $\mathrm{[CoBr_2(C_5H_8O_2)](C_5H_8O_2)}$.

The ketonic complex of acetylacetone (B), much more acidic than free acetylacetone, was treated with an equimolar amount of sodium acetylacetonate in acetylacetone. After the solvent was evaporated *in vacuo*, dichloromethane was distilled into the reaction vessel and sodium bromide was filtered off. The filtrate was evaporated and a blue solid (D) was obtained. All these procedures were performed at 0°. The analytical data of this compound (D) correspond to values calculated for CoBr(HA). The i.r. spectrum ($\nu_{\mathrm{C=O}}$: 1570, 1525 cm.$^{-1}$) indicates that (D) is an enolate chelate of acetylacetone; the electronic spectrum suggests a tetrahedral $\mathrm{Co(O)_2Br_2}$ configuration. The compound (D) was also obtained in the reaction of bis(acetylacetonato)cobalt(II) with bromine (1 : 1) in dichloromethane at 0°, and assumed to have a dimeric structure containing a bromine double bridge.[3] Thus the reaction of B to D could be represented by:



(B)

(D)

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