Some Reactions of the Carbonyl Group in Co-ordinated Keto-carboxylates

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Ketocarboxylatopenta-amminecobalt(III) complexes react with hydroxylamine and with semicarbazide to produce the corresponding carboxylato-bonded imino derivatives; some of these new complexes can be isolated.

SEVERAL cobalt(III) complexes containing an α-keto-carboxylate group are known,[1,2] having the general formula $[M\cdot OOC\cdot CO\cdot R]^{2+}$, where $M = Co(NH_3)_5$, and it was shown that, in aqueous solution, the carbonyl group is partly converted to $\cdot C(OH)_2$ by the addition of H_2O. We have studied some other reactions involving the carbonyl group in these complexes, and in the complex[3] containing the γ-keto-carboxylate, levulinate, with the reagents semicarbazide, hydroxylamine, and bisulphite. The products, which are formed without breaking the bond between the cobalt and the carboxylate oxygen, are new complexes, which do not appear to have been reported previously; some of them can be isolated as the perchlorate salts.

EXPERIMENTAL

Analyses are by the Microanalytical Laboratory, Imperial College. Pyruvic acid and glyoxylic acid (as the crystalline hydrate) were obtained from Koch-Light Limited, and levulinic acid from B.D.H. Ltd. Trimethylpyruvic acid and phenylglyoxylic acid were prepared by permanganate oxidation of pinacolone[4] and mandelic acid[5] respectively.

Ketocarboxylatopenta-amminecobalt(III) *Complexes*.—*Phenylglyoxylatopenta-amminecobalt*(III) *diperchlorate*, $[M\cdot OOC\cdot CO\cdot Ph](ClO_4)_2$. Phenylglyoxylic acid (20 g, 0·13 mol) in 15 ml water, was partly neutralised with sodium hydroxide (4·7 g in 18 ml water). Aquopenta-amminecobalt(III) triperchlorate (12 g, 0·026 mol) was added, and the solution heated for 16 h at 40—45 °C. It was then acidified with concentrated perchloric acid, and cooled in ice. The red *crystals* which separated were filtered off, washed with ice-cold water, and recrystallised from dilute perchloric acid. After filtering, the crystals were washed with ice-cold dilute perchloric acid, ethanol and ether, and dried *in vacuo* (10·3 g, 80%) (Found: C, 19·4; H, 4·1; N, 14·2. $C_8H_{20}Cl_2CoN_5O_{11}$ requires C, 19·5; H, 4·1; N, 14·2%). The corresponding glyoxylato,[1] pyruvato,[2] trimethylpyruvato,[2] and levulinato[3] complexes were prepared following the given methods; satisfactory analyses were obtained.

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[1] H. J. Price and H. Taube, *J. Amer. Chem. Soc.*, 1967, **89**, 269.

[2] H. J. Price and H. Taube, *Inorg. Chem.*, 1968, **7**, 1.

[3] E. S. Gould and H. Taube, *J. Amer. Chem. Soc.*, 1964, **86**, 1318.

[4] C. Glücksmann, *Monatsh.*, 1889, **10**, 770.

[5] B. B. Corson, R. A. Dodge, S. A. Harris, and R. K. Hazen, *Org. Synth., Coll. Vol. I* (*2nd edn.*), 1941, p. 244; see also *ibid.*, footnote 11, p. 244, by C. D. Hurd and R. W. McNamee.

Imino-derivatives.—Semicarbazone derivatives of the keto-carboxylato-complexes were prepared as follows: semicarbazide hydrochloride was dissolved in the minimum volume of water at room temperature, and neutralised by adding solid sodium carbonate. An equimolar amount of the solid complex was added gradually to the solution, whose pH was kept in the range 4—5. The solution finally obtained was left in a vacuum desiccator over concentrated sulphuric acid until the volume had been reduced to about one fifth, when red *crystals* had separated. The solution was cooled to 0 °C, the crystals filtered off, washed with small amounts of ice-cold water, and dried *in vacuo*. The products are fairly soluble; recrystallisation was difficult and did not lead to improved analyses, which are given for the initial products.

Semicarbazonoacetatopenta-amminecobalt(III) *Diperchlorate*, [M·OOC·CH:N·NH·CONH$_2$](ClO$_4$)$_2$, yield 26% (Found: C, 7·7; H, 4·0; N, 23·45. $C_3H_{19}Cl_2CoN_8O_{11}$ requires C, 7·6; H, 4·0; N, 23·7%).

2-*Semicarbazonopropionatopenta-amminecobalt*(III) *Diperchlorate*, [M·OOC·C(:N·NH·CONH$_2$)·CH$_3$](ClO$_4$)$_2$, yield 35% (Found: C, 9·9; H, 4·3; N, 22·9. $C_4H_{21}Cl_2CoN_8O_{11}$ requires C, 9·9; H, 4·35; N, 23·0%).

Semicarbazonophenylacetatopenta-amminecobalt(III) *Diperchlorate*, [M·OOC·C(:N·NH·CONH$_2$)C$_6$H$_5$] (ClO$_4$)$_2$, yield 12% (Found: C, 20·0; H, 4·3; N, 20·2. $C_9H_{23}Cl_2CoN_8O_{11}$ requires C, 19·7; H, 4·2; N, 20·4%).

4-*Semicarbazonovaleratopenta-amminecobalt*(III) *Diperchlorate Monohydrate*, [M·OOC·(CH$_2$)$_2$·C(:N·NH·CONH$_2$)-CH$_3$](ClO$_4$)$_2$,H$_2$O, yield 50% (Found: C, 13·3; H, 5·3; N, 20·9. $C_6H_{27}Cl_2CoN_8O_{12}$ requires C, 13·5; H, 5·1; N, 21·0). The trimethylpyruvato-derivative was obtained only in small yield and poor analyses were obtained.

The oxime derivatives were prepared similarly by adding the solid keto-complex to a concentrated aqueous solution of freshly neutralised hydroxylamine hydrochloride in three-fold excess. 2-*Oximinopropionatopenta-amminecobalt*(III) *diperchlorate*, [M·OOC·C(:NOH)CH$_3$](ClO$_4$)$_2$, yield 25% (Found: C, 8·6; H, 4·75; N, 19·9. $C_3H_{19}Cl_2CoN_6O_{11}$ requires C, 8·1; H, 4·7; N, 18·9%). 2-*Oximinovaleratopenta-amminecobalt*(III) *diperchlorate*, [M·OOC·(CH$_2$)$_2$·C(:NOH)-CH$_3$](ClO$_4$)$_2$; yield 30% (Found: C, 12·4; H, 5·1; N, 17·6. $C_5H_{23}Cl_2CoN_6O_{11}$ requires C, 12·7; H, 4·9; N, 17·8%). Attempts to isolate the other oximes, which are very soluble, gave solids with very poor analyses.

Oximes and semicarbazones of the free ketoacids were prepared by standard methods; their m.p.s agreed closely with the reported values.

^{1}H *Nuclear Magnetic Resonance Spectra.*—These were recorded in solution in H$_2$O or D$_2$O, at 100 MHz and a temperature of 35 °C on a Perkin-Elmer R14 spectrometer; t-butyl alcohol, whose methyl protons have τ = 8·77,[6] was used as internal reference. The line positions for the CH and the ammine protons are given in the Table; as expected, no separate lines from protons in OH, NH, or NH$_2$ groups were observed.

N.m.r. line positions [a] for CH and NH$_3$ protons in keto-carboxylate derivatives

(*i*) CH protons

X	Y	Glyoxylic HCX·COOY	Pyruvic CH$_3$CX·COOY	Trimethyl-pyruvic Me$_3$C·CX·-COOY	Phenyl-glyoxylic C$_6$H$_5$·CX·COOY [b]	Levulinic CH$_3$·CX·(CH$_2$)$_2$·COOY CH$_3$	(CH$_2$)$_2$
=O	Na [c]		7·62	8·58	2·2 [d]	7·78	7·42 [e]
=NOH	Na	2·40	8·00	8·84	2·35	7·76; [f] 8·12 [g]	7·24; [e,f] 7·56 [g]
=N·NH·CONH$_2$	Na	2·62	7·98	8·82	2·3	7·78; [f] 8·12 [g]	7·38; [e,f] 7·49 [g]
(OH)$_2$	Na	4·88	8·62	8·81	2·2 [d]		
(OH)(SO$_3$Na)	Na	5·13	8·35	8·87	2·1	8·54	7·64 [e]
=O	Co(NH$_3$)$_5$		7·63	8·60	1·9(2); 2·2(3) [d]	7·78	7·35 [e]
=NOH	Co(NH$_3$)$_5$	2·44	8·04	8·90	2·45(3); 2·6(2) [d]	7·79; [f] 8·12 [g]	7·32; [e,f] 7·55 [g]
=N·NH·CONH$_2$	Co(NH$_3$)$_5$	2·64	8·06	8·87	2·4	7·78; [f] 8·12 [g]	7·38; [e,f] 7·49 [g]
(OH)$_2$	Co(NH$_3$)$_5$	4·86	8·55	8·83	1·9(2); 2·2(3)		
(OH)(SO$_3$Na)	Co(NH$_3$)$_5$	4·97	8·36	8·92	2·05(2); 2·4(3)	8·56	7·75 [e]

(*ii*) *Ammine* NH$_3$ *protons*; (values given in order *cis, trans*). Glyoxylato-series: oximino, 5·99; 7·00; semicarbazono, 6·02, 7·05; dihydroxo, 6·03, 7·05; bisulphito, 6·07, 7·00. Pyruvato-series: keto (including dihydroxo), 5·99, 6·99; oximino, 6·01, 7·11; semicarbazono, 6·04, 7·07; bisulphito, 6·07, 7·09. Trimethylpyruvato: keto (including dihydroxo), 5·99, 7·04; oximino, 6·00, 7·03; semicarbazono, 5·98, 7·02; bisulphito, 6·07, 7·11. Phenylglyoxylato series: keto (including dihydroxo), 5·91, 6·91; oximino, 6·04, 7·08; semicarbazono, 5·97, 7·02; bisulphito, 6·07, 7·10. Levulinato series: keto, 6·15, 7·12; oximino, 6·12, 7·10; semicarbazono, 6·14, 7·12; bisulphito, 6·15, 7·15.

[a] Measured relative to the methyl line of the internal reference, t-butyl alcohol, which was taken to have τ = 8·77 [6] in converting the measured positions to the quoted τ values. [b] Values indicate centres of bands; where more than one band was seen, the relative areas are given in brackets. [c] Values for Na salts recorded at pH *ca.* 7. [d] Keto- and dihydroxo-species not distinguished. [e] Centre of an A$_2$B$_2$ pattern. [f,g] Bands from first and from second of two species.

The formation of the oximes and semicarbazones in H$_2$O solutions was followed by observing the decrease in intensity of the spectrum of the reactant free acid or complex, accompanied by the growth of the spectrum of the product. The latter spectra, which were identical with those found when the solid products were redissolved (in D$_2$O), were usually clearly separate from those of the parent complexes, and also different from those of the corresponding oxime and semicarbazone derivatives of the free acids, whose lines can be distinguished since their positions change with pH.

It was also possible to show the formation of the bisulphite addition derivatives, when the keto-acids or complexes were treated with an excess of sodium bisulphite solution at pH 5—6; these derivatives were not isolated as solids.

Infrared Spectra.—These were recorded, for the solid complexes, in mulls (Nujol and hexachlorobutadiene) using Perkin-Elmer Infracord and 457 spectrometers.

RESULTS AND DISCUSSION

The structures of the imino-derivatives are indicated by their ^{1}H n.m.r. spectra, and, in some cases, by the

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[6] R. J. Abraham and W. A. Thomas, *J. Chem. Soc.*, 1964, 3739.

analyses of the solid complexes. Since the free oximes and semicarbazones each contain several atoms which could bond to the single site on the penta-ammine cobalt group, each could give rise to several isomeric monodentate complexes; the present procedure may be useful in that it gives only the carboxylato-bonded isomers. *syn*- and *anti*-isomers are possible, but only one set of lines was observed with each compound in the α series; however, the levulinates, both free and co-ordinated, each gave two sets of lines. The equilibrium proportions of the dihydroxo-compounds, formed by the addition of H_2O to the keto-complexes, were found to be 30% for the pyruvato and about 100% for the glyoxylato, in agreement with the earlier estimates;[1,2] the levulinato shows none.

The spectra of all the complexes show two additional broad lines, of relative intensities 12 : 3, from the NH_3 groups respectively *cis* and *trans* to the co-ordinated carboxylate;[7] the origin of this separation has been discussed.[8] The broadness of these lines is probably the result of partial averaging, by quadrupole relaxation, of the spin coupling from the nitrogen-14[9] and cobalt-59[10] nuclei. The widths (at half height) are *ca.* 20—25 Hz, except for the bisulphito-complexes, for which they are *ca.* 10 Hz; possibly the presence of the anionic SO_3 group increases the electric field gradients at the two nuclei, giving more extensive relaxation.[10]

If the bond between cobalt and the carboxylate oxygen had broken during the reactions, a likely product would be the aquopenta-amminecobalt(III) complex, whose *cis* and *trans* NH_3 lines, which occur at slightly lower values than in the carboxylates (5·90 and 6·96 respectively), have markedly greater widths (*ca.* 45 Hz); these were not observed during the reactions. The aquo-complex is produced, however, if the imino-complexes are left in solution at low pH (below 1) for several hours.

The i.r. spectra gave little information about the structures of the solids, since there are several groups in the complexes whose bands lie close together. However, the band for the free C=O group, which could be seen clearly in potassium pyruvate (1700 cm^{-1}) and in the pyruvatopenta-ammine complex (1720 cm^{-1}), had disappeared in the corresponding oximino-derivatives.

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[8] D. N. Hendrickson and W. L. Jolly, *Inorg. Chem.*, 1970, **9**, 1197.

[9] R. L. Lichter and J. D. Roberts, *Spectrochim. Acta*, 1970, **26A**, 1813.

[10] J. K. Beattie, *Inorg. Chem.*, 1971, **10**, 426.