The Base-Catalysed Methyl Hydrogen Exchange in β-Diketonato-cobalt(III) Complexes [1]

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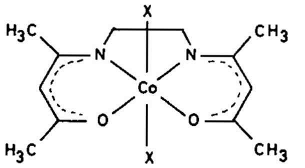
The activation of methyl groups of ligands in coordination compounds is not so common as in organometallic compounds. Previously, we reported [2] that one of the methyl groups of the Schiff base chelate (I),


(1)

undergoes a base-catalysed hydrogen exchange reaction, where X = NH_3, NO_2^-, CH_3NH_2, and pyridine. The methyl group that is exchanged in I is later assigned to the methyl group adjacent to the diimine bridge [3]. Likewise, the methyl hydrogens of the bis(dimethylglyoximato)cobalt(III) complexes, $[Co(dgH)_2(X)_2]^{+/-}$ with X = NH_3, CH_3NH_2, CN^-, or NO_2^-, are deuterated in 2% $NaOD/D_2O$ solution [4]. Recently, Golding *et al.* [5] reported that the methyl group of the pyruvilidene-imine chelate complex of tetraamminecobalt(III) undergoes a facile hydrogen exchange reaction. Thus, the methyl groups reported to be exchanged so far are all imine methyls.

We report here that the methyl hydrogens of the β-diketonato chelates of cobalt(III) ions, $[Co(N)_4(RC(=O)CHC(O)CH_3)]^{2+}$, undergo base-catalysed deuteration in deuterium oxide, where $(N)_4$ = $(NH_3)_4$, $(en)_2$, $(tn)_2$, $(bpy)_2$ and R = CH_3 or CF_3*.

The complexes examined in this work were $[Co(NH_3)_4(acac)]I_2$, $[Co(en)_2(acac)]I_2$, $[Co(tn)_2(acac)]I_2$, $[Co(bpy)_2(acac)]Br_2$, $[Co(phen)_2(acac)]Br_2$, $[Co(en)_2(tfac)]I_2$, $[Co(tn)_2(tfac)]I_2$, $[Co(en)_2(Me\text{-}acac)]I_2$, and $[[Co(en)_2(Et\text{-}acac)]I_2$. They were prepared by the literature methods [6] and $[Co(bpy)_2(acac)]Br_2$ and $[Co(phen)_2(acac)]Br_2$ were recrystallized from methanol. The sample complexes were dissolved in deuterium oxide containing an appropriate amount of sodium carbonate to adjust the solution pH and the intensity of the methyl proton resonance was followed at suitable time intervals**. The deuteration at methyl groups was base-catalysed and the observed pseudo-first-order rate constant, k_{obs}, was converted to the second-order rate constant, k, by the equation $k = k_{obs}/[OD^-]$.**

Table I summarizes the rate constants obtained at 36.4 °C. It is noteworthy that the rate of $[Co(bpy)_2(acac)]Br_2$ is about three orders of magnitude larger than the rates of the $(NH_3)_4$, $(en)_2$, and $(tn)_2$ complexes and is also much larger than even the rate of alpha-hydrogen exchange in $[Co(en)_2(gly)]^{2+}$ [7]. Since the ligand-field strengths of bpy, NH_3, en, and tn ligands are not so different and the overall charge on the complex is the same for all these complexes, the remarkable acidity of $[Co(bpy)_2(acac)]^{2+}$ might be correlated to the hydrophobic nature of this complex cation. The rate constants for the acetylacetonato chelates of $(NH_3)_4$, $(en)_2$, and $(tn)_2$ complexes are roughly an order smaller than those for the exchange of alpha-hydrogens of the alaninato or valinato chelates of bis(ethylenediamine)cobalt(III) [8]. Likewise, the values obtained here are much larger than those for the imine methyls of the Schiff base chelates (I).

The trifluoroacetylacetonato chelates of bis(ethylenediamine)- and bis(trimethylenediamine)cobalt(III) undergo base-hydrolysis, as well as the methyl hydrogen exchange, to *cis*-$[Co(en)_2(OH)_2]^+$ and

TABLE I. The Rate of Methyl Hydrogen Exchange at 36.4 °C.

Complex	k (mol^{-1} dm^3 sec^{-1})
$[Co(NH_3)_4(acac)]I_2$	2.9×10^{-3}
$[Co(en)_2(acac)]I_2$	3.7×10^{-3}
$[Co(tn)_2(acac)]I_2$	5.0×10^{-3}
$[Co(bpy)_2(acac)]Br_2$	1.9
$[Co(phen)_2(acac)]Br_2$	a)
$[Co(en)_2(tfac)]I_2$	5.5×10 b)
$[Co(tn)_2(tfac)]I_2$	5.5×10 b)
$[Co(en)_2(Me\text{-}acac)]I_2$	no exchange
$[Co(tn)_2(Et\text{-}acac)]I_2$	no exchange

a)Decomposition. b)See text.

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*Abbreviations; en = ethylenediamine, tn = 1,3-propanediamine, bpy = 2,2′-bipyridine, phen = 1,10-phenantroline, acac = 2,4-pentanedionate, tfac = trifluoroacetylacetonate, Me-acac = methylacetoacetonate, Et-acac = ethylacetoacetonate, gly = glycinate, ala = alaninate, val = valinate, and mal = malonate.

**Proton magnetic resonance spectra were run on a Varian T-60 spectrometer at 36.4 °C. The solution pH was adjusted by sodium carbonate. The OD^- concentration was calculated from direct pH meter readings by the empirical formula, pD = pH (meter readings) + 0.42 (at 20 °C) and $K_w(D_2O) = 0.15 \times 10^{-14}$. See; (a) T. H. Fife and T. C. Bruice, *J. Phys. Chem.*, *65*, 1079 (1961); (b) P. K. Glasoe and F. A. Long, *J. Phys. Chem.*, *64*, 188 (1960).

cis-$[Co(tn)_2(OH)_2]^+$,[*] respectively, which then become equilibrium mixtures with the corresponding *trans* isomers. The base-hydrolysis and subsequent isomerization of the ethylenediamine complex was studied spectrophotometrically under pseudo-first-order conditions; $[OH^-] \gg [Co]$, ionic strength = 1.0 mol dm^{-3} with sodium perchlorate. The base-hydrolysis of $[Co(en)_2(tfac)]^{2+}$ was found to follow the rate law, rate = $k[Co][OH^-]$ with $k \cong 1.6 \times 10^{-2}$ mol^{-1} dm^3 sec^{-1} at 27 °C. This rate is unexpectedly large when compared to the very stable nature of $[Co(en)_2(acac)]^{2+}$ and is comparable to the rates of base-hydrolysis of $[Co(en)_2(mal)]^+$ [9] and $[Co(en)_2(CO_3)]^+$ [10]. The rate data for the isomerization of $[Co(en)_2(OH)_2]^+$ and the relevant spectroscopic data were in agreement with those given in the literature [11]. The rate of base-hydrolysis of $[Co(en)_2(tfac)]^{2+}$ is much smaller than the rate for the methyl hydrogen exchange. Therefore, the hydrogen exchange is assumed to take place while retaining the chelate structure of the tfac group. The larger rates of the tfac complexes might result from the electron-withdrawing effect of the CF_3 group and this is contrasted with the methyl- and ethyl-acetoacetonato complexes, where no hydrogen exchange at the methyl groups was observed, possibly due to the electron-releasing methoxy and ethoxy groups.

For all the complexes, since the methine hydrogens of uncoordinated β-diketones are exchanged with deuterium instantaneously, it is quite easy to confirm whether the methyl hydrogen exchange takes place in coordinated or free ligands.

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[*] Thus, the trifluoroacetylacetonato complexes gave, upon treating with concentrated aqueous solutions of sodium carbonate, the corresponding carbonato complexes. *Anal.* Found: C, 17.77; H, 4.78; N, 16.56% for the compound isolated from the reaction $[Co(en)_2(tfac)](ClO_4)_2 + Na_2CO_3$. Calcd for $[Co(en)_2(CO_3)]ClO_4$: C, 17.74; H, 4.76; N, 16.55%; Found: C, 15.11; H, 5.13; N, 13.83% for the compound obtained from the reaction $[Co(en)_2(tfac)I_2 + Na_2CO_3$. Calcd for $[Co(en)_2(CO_3)]I \cdot 2H_2O$: C, 14.94; H, 5.01; N, 13.93%. Found: C, 20.52; H. 5.44; N, 13.49% for the compound isolated from the reaction $[Co(tn)_2(tfac)]I_2 + Na_2CO_3$. Calcd for $[Co(tn)_2(CO_3)]I \cdot H_2O$: C, 20.40; H, 5.38; N, 13.60%.

References

1 Part 20 of 'Proton Magnetic Resonance Spectra of Metal Ammine Complexes'. Part 18; A. Miyanaga, U. Sakaguchi, Y. Morimoto, Y. Kushi and H. Yoneda, *Inorg. Chem.*, to be published.

2 H. Yoneda, I. Takagi and Y. Morimoto, *Bull. Chem. Soc. Jpn., 44*, 3493 (1971).

3 U. Sakaguchi and H. Yoneda, *Chem. Lett.*, 831 (1975).

4 I. Takagi and H. Yoneda, *Bull. Chem. Soc. Jpn., 46*, 3593 (1973).

5 B. T. Golding, J. M. Harrowfield, G. B. Robertson, A. M. Sargeson and P. O. Whimp, *J. Amer. Chem. Soc., 96*, 3691 (1974).

6 (a)L. J. Boucher, E. J. Battis and N. G. Paez, *J. Inorg. Nucl. Chem., 33*, 1373 (1971); (b)L. J. Boucher, *Inorg. Chim. Acta, 6*, 29 (1972); (c)L. J. Boucher and J. C. Bailar, Jr., *Inorg. Chem., 3*, 589 (1964); (d)K. Kashiwabara, K. Igi and B. E. Douglas, *Bull. Chem. Soc. Jpn., 49*, 1573 (1976).

7 T. Ama, H. Kawaguchi, M. Kanekiyo and T. Yasui, *Bull. Chem. Soc. Jpn., 53*, 956 (1980).

8 D. A. Buckingham, L. G. Marzilli and A. M. Sargeson, *J. Amer. Chem. Soc., 89*, 5133 (1967).

9 M. E. Farago and I. M. Keefe, *Inorg. Chim. Acta, 15*, 5 (1975).

10 D. J. Francis and R. B. Jordan, *J. Amer. Chem. Soc., 91*, 6626 (1969).

11 (a)J. Bjerrum and S. E. Rasmussen, *Acta Chem. Scand., 6*, 1265 (1952); (b)J. Y. Tong and P. E. Yankewich, *J. Amer. Chem. Soc., 80*, 2664 (1958); (c)W. Kruse and H. Taube, *J. Amer. Chem. Soc., 83*, 1280 (1961); (d)M. E. Farago, B. A. Page and C. F. V. Mason, *Inorg. Chem., 8*, 2270 (1969).