CHEMISTRY LETTERS, pp. 117-120, 1976. Published by the Chemical Society of Japan

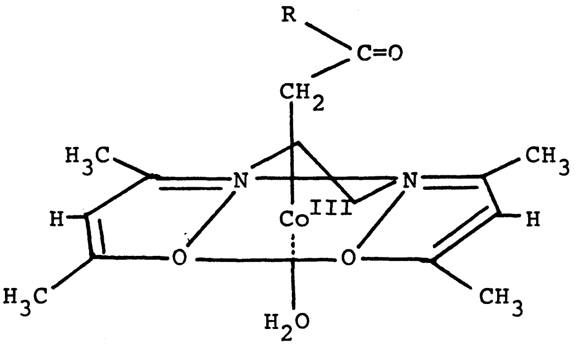
PREPARATION OF ORGANOMETALLIC COBALT(III)-SCHIFF-BASE COMPLEXES CONTAINING KETONE OR NITROMETHANE

Yuki FUJII and Tadashi YOSHIZAWA

Department of Chemistry, Faculty of Science, Ibaraki University,
Bunkyo-cho, Mito, Ibaraki 310

A series of new mixed cobalt(III)-Schiff-base complexes with the general formula of [Co(acac$_2$en)(L)(H$_2$O)], where L = monoanion of acetone, methylethylketone, acetophenone, or nitromethane, have been prepared from [Co(acac$_2$en)] and L by air oxidation. The organic ligand, L, has been found to coordinate to cobalt(III) ion with its active methylene group.

Recently, it has been reported that cobalt(III)-sal$_2$en complex reacts with an active methylene compound to form organometallic cobalt(III) complex, [Co(sal$_2$en)-(L)(X)] (L = monoanion of malonenitrile, acetone, or nitromethane, X = H$_2$O or CH$_3$OH), in which the active methylene compound coordinates to cobalt(III) ion with its active methylene carbanion.[1,2] In this connection, this letter reports a series of new organometallic cobalt(III)-acac$_2$en complexes (acac$_2$en = dianion of N,N'-ethylene-bis(acetylacetonimine)), [Co(acac$_2$en)(L)(H$_2$O)], where L = monoanion of acetone, methylethylketone, acetophenone, or nitromethane.



R = CH$_3$, C$_2$H$_5$, C$_6$H$_5$

The complexes were prepared by dissolving [Co(acac$_2$en)] in ketones or nitromethane and by oxidizing it in air : [Co(acac$_2$en)] (10 g) was partially dissolved in about 200 ml of acetone, methylethylketone, acetophenone, or nitromethane (30% methanol solution) and the mixture was allowed to stand in open air at room temperature for one or two days. By this procedure, the color of the complex solution turned from orange to green and green

Table 1. Characterization Data of $[Co(acac_2en)(L)(H_2O)]$ complex

L	C(%)	(Calcd)	H(%)	(Calcd)	N(%)	(Calcd)	$\nu_{C=O}$ (cm^{-1})	First Absorption Band (cm^{-1})	($\log\varepsilon$)
CH_2COCH_3	50.48	(50.56)	7.08	(7.07)	7.82	(7.86)	1655	14000	(2.40)
$CH_2COC_2H_5$	51.64	(51.89)	7.50	(7.35)	7.56	(7.56)	1647	14000	(2.32)
$CH_2COC_6H_5$	57.58	(57.42)	6.58	(6.51)	6.76	(6.70)	1630	14000	(2.37)
CH_2NO_2	43.28	(43.46)	6.05	(6.17)	11.77	(11.70)		14000	(2.37)

crystals separated out. They were washed with water. Yields, about 30 - 70%. All the complexes were diamagnetic. The anal. data are summarized in Table 1. In this method, air oxidation was indispensable for the formation of the green complexes. The addition of water to the reaction mixtures gave no distinct inhibition for the formation of the green complexes.

The green complexes easily decomposed by light to form $[Co(acac_2en)]$, and the green complexes easily formed their pyridine derivatives, $[Co(acac_2en)(L)(py)]$. Since these behaviors are characteristic for the related organometallic cobalt(III)-Schiff-base complexes, $[Co(sal_2en)(R)(H_2O)]$ (R = CH_3, C_2H_5, C_3H_7),3,4) it is assumed that the ketones or nitromethane coordinate to cobalt(III) ion through Co-C bonding in the green complexes.

Fig. 1 shows representative PMR spectra of the green complexes. The complexes show C=CH signal at about 5.2 ppm, CH_2CH_2 signal at about 3.5 ppm, two methyl signals at about 2.2 and 2.1 ppm for the coordinated $acac_2en$. This PMR spectral pattern for $acac_2en$ signals corresponds to trans structure.6) It was found that methylene signals of the coordinated ketones or nitromethane shift to lower field as compared with the corresponding methyl signals of the free ketones or nitromethane (Fig. 2). This low field shift is due to the inductive effect of highly charged cobalt(III) ion.5)

It is well known that cobalt(III)-Schiff-base complexes containing Co-C bonding exhibit the first absorption band at about 15000 cm^{-1} ($\log\varepsilon$ = 2 - 2.5).1,6) The energy of the first absorption band is much lower than that of the usual cobalt(III) complexes and is characteristic for organometallic cobalt(III)-Schiff-base complexes. Since the green complexes obtained here also show their first absorption bands at low energy site (Table 1), the existence of Co-C bonding in these complexes is supported.

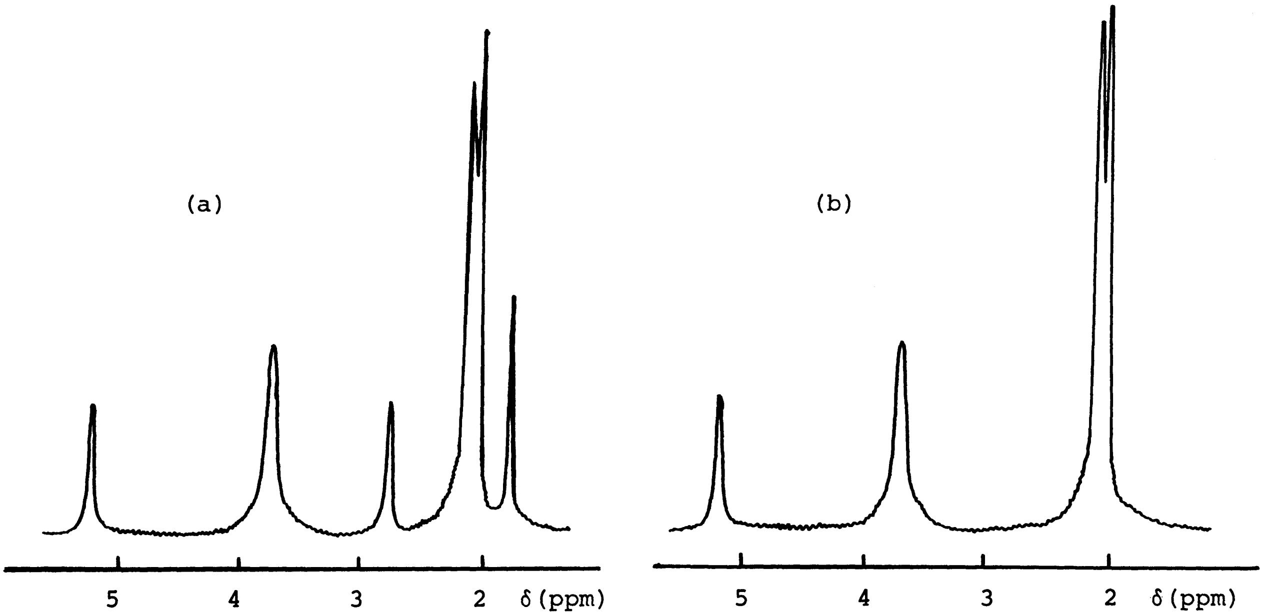


Fig. 1. Representative PMR Spectra of Complexes in $CDCl_3$.

(a) = $[Co(acac_2en)(CH_2COCH_3)(H_2O)]$, (b) = $[Co(acac_2en)(CD_2COCD_3)(H_2O)]$

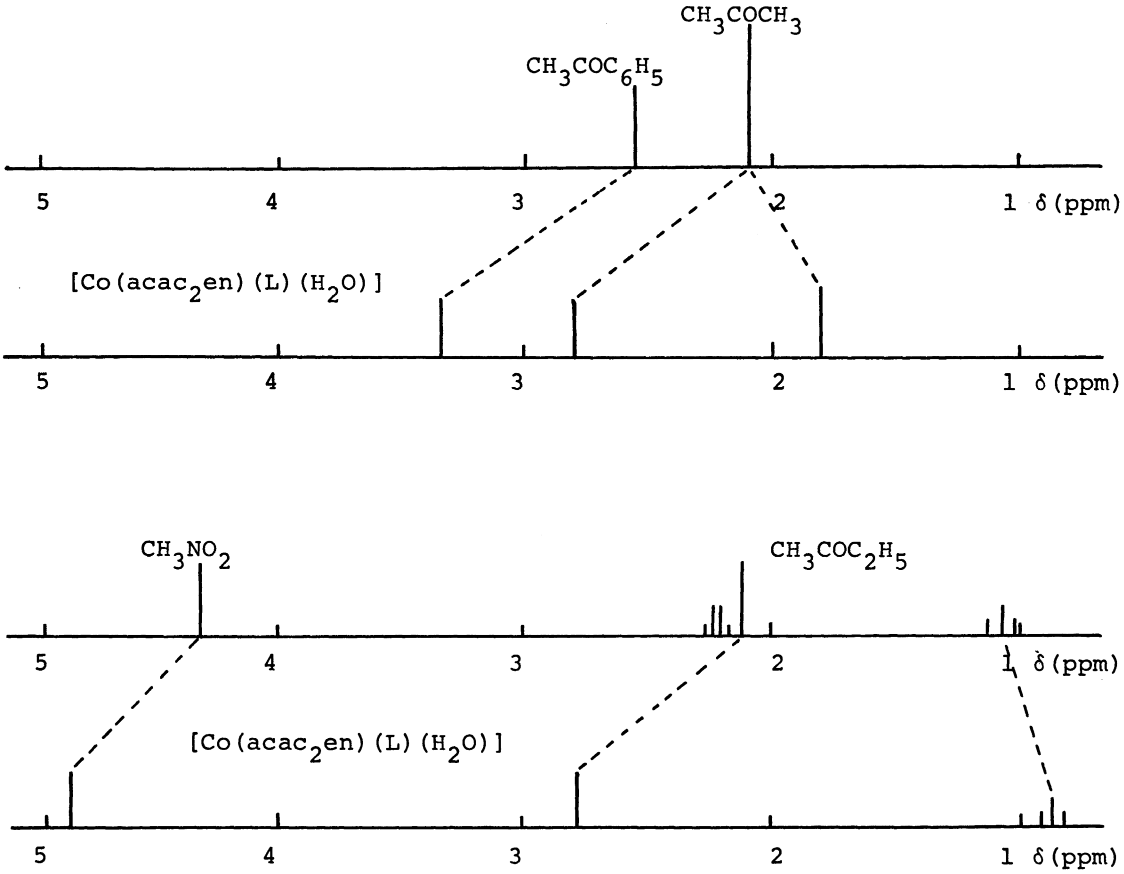


Fig. 2. Relative Position of PMR Signal of Free and Coordinated L.

References

1) A. Bigotto, et al., Inorg. Chim. Acta Reviews, 4, 41 (1970).

2) M. Cesari, et al., Chem. Comm., 276 (1970), N. A. Bailey, B. M. Higson, and E. D. Mckenzie, Inorg. Nucl. Chem. Lett., 7, 591 (1971), D. Cummins, B. M. Higson, and E. D. Mckenzie, J. Chem. Soc., Dalton, 414 and 1359 (1973), and references therein.

3) H. Tanaka, A. Nakahara, and S. Fukui, "Bioinorganic Chemistry", The special number of Kagaku, Kagaku Dojin, Kyoto, 1974, p. 69, A. Nakahara, "Boundary between Coordination Chemistry and Biochemistry", The special number of Kagaku no Ryoiki, Nankodo, Tokyo, 1967, p. 240, H. Ogino and K. Ogino, "Coordination Chemistry of Metalloenzymes", Kagaku no Ryoiki Sensho 7, Nankodo, Tokyo, 1974, p. 217, G. Costa, Coord. Chem. Rev., 8, 63 (1972), and references therein.

4) G. Costa, G. Mestroni, and L. Stefani, J. Organometal. Chem., 7, 493 (1967).

5) G. Costa, et al., ibid., 6, 181 (1966), C. Floriani, M. Puppis, and F. Calderazzo, ibid., 12, 209 (1968), A. Bergen, K. S. Murray, and B. O. West, ibid., 33, 89 (1971), M. Maumberg, K. Duong, and A. Gandemer, ibid., 25, 231 (1970).

6) Y. Fujii, et al., Bull. Chem. Soc. Jap., 45, 2459 (1972).

7) G. Costa, G. Mestroni, and G. Pellizer, J. Organometal. Chem., 11, 333 (1968), J. P. Fox, et al., Inorg. Chem., 11, 2379 (1972).

(Received November 26, 1975)