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Synthesis and PMR Study of Mixed Ligand Cobalt(III) Complexes with Aliphatic α-Hydroxyimino Ketone and Pyridine

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Cobalt(III) complexes with a series of aliphatic α-hydroxyimino ketone (moH) and pyridine (py) were obtained as fine crystals. The aliphatic α-hydroxyimino ketones used are R–C(=O)–C(=NOH)–R′ where R=CH_3 or C_2H_5 and R′=CH_3, C_2H_5, *i*-C_3H_7, *n*-C_3H_7 or $COCH_3$. These complexes are formulated as $[Co(mo)_2(py)_2]ClO_4$. The PMR spectral investigation shows that the proton resonances of the alkyl group bound to the hydroxyimino group are shifted toward higher fields upon complex formation. This unusual upfield shift is accounted for by consideration of the specific configuration and ring-current of the pyridine in the complex.

The α-hydroxyimino ketones, R–C(=O)–C(=NOH)–R′, abbreviated as moH, are known to react with transition metal ions.[1] The specific cobalt complexes studied have been reported as having the formula $Co^{III}(mo)_3$. In the case where R and/or R′ are saturated alkyl groups, the α-hydroxyimino ketones appear to produce less stable complexes than aromatic α-hydroxyimino ketones with phenyl or 2-furyl groups. Thus, in respect to the aliphatic α-hydroxyimino ketone complexes, their synthesis and characterization appear to remain equivocal.

In the present paper, the method of preparation of the crystalline cobalt(III) complexes of aliphatic α-hydroxyimino ketones having the formula $[Co(mo)_2(py)_2]ClO_4$, where py is pyridine, is described. The PMR spectral behavior is discussed in terms of a specific steric configuration of alkyl groups of the complexes in solution.

Experimental

Preparation. The α-hydroxyimino ketones were prepared by the hydroxyimination reaction of the methylene group of the corresponding ketone with isopentyl nitrite.[2]

Cobalt(III) complexes were obtained by the following general procedure: to 50 ml of a tetrahydrofuran solution of 0.01 mol of α-hydroxyimino ketone and 0.005 mol of $Co(ClO_4)_2 6H_2O$ was added 0.01 mol of pyridine. The mixture was stirred in air at room temperature for 2 h. The precipitate separated was collected on a glass filter, and then recrystallized from ethanol. Table 1 shows the analytical data for the complexes thus obtained. The same procedure using ammonia or aniline as a base resulted in no precipitation of any similar complex.

Measurement. PMR spectra were recorded with a Japan Electron Optics Model JNM-PS-100 spectrometer at a frequency of 100 MHz and/or a JNM-3H spectrometer at 60 MHz, at an ambient probe temperature of 20 °C. The chemical shifts were determined in ppm using TMS as an internal standard.

Results and Discussion

The results of elemental analysis, as listed in Table 1, show that the composition of the complexes corresponds closely to the formula, $[Co\{R-C(=O)-C(=NO)-R'\}_2(py)_2]ClO_4$. These complexes are diamagnetic, which suggests that cobalt(III) complexes were obtained.

The PMR spectra of free biacetyl monoxime (R=R′=CH_3) and its complex are given in Fig. 1. The free ligand exhibits three singlet signals at 2.00, 2.39, and 9.83 ppm; these are readily assigned to the CH_3^α, CH_3^a, and NOH protons on the basis of published data,[3] respectively. The complex has two signals for the CH_3^α singlet and the CH_3^a singlet (at 1.95 and 2.53 ppm, respectively) and no signal for the NOH proton, which indicates that the two biacetyl monoximato ligands are equivalent. It should be noted that upon complex formation, the resonances of the H^α and H^a protons are shifted in opposite directions, that is, the H^α signal is shifted toward higher fields, whereas the H^a signal is shifted toward lower fields.

In general, it is considered that the coordination of the functional group as $\rangle C=NO^-$ or $\rangle C=O$ bound to an alkyl group accompanies either no appreciable or only a small downfield shift of the alkyl proton resonance. This PMR spectral characteristic has been shown in the case of $Co^{III}(2,4\text{-pentanedionato})_3$[4] and *trans*-$[Co^{III}(dimethylglyoximato)_2(py)X]$ (X=NO_2^- or halide ions).[5] The downfield shift of the alkyl proton

Table 1. Analytical data of the complexes, $[Co\{R-C(=O)-C(=NO)-R'\}_2(py)_2]ClO_4$[a]

Complex		Found %			Calcd %		
R	R′	C	H	N	C	H	N
CH_3	CH_3	41.71	4.34	10.76	41.85	4.26	10.84
CH_3	CH_2CH_3	44.29	4.85	9.94	44.10	4.77	10.28
CH_3	$CH_2CH_2CH_3$	46.11	5.28	9.80	45.97	5.24	9.77
CH_3	$CH(CH_3)_2$	46.11	5.82	9.46	45.97	5.24	9.77
CH_3	$COCH_3$	41.75	4.06	9.31	41.95	3.84	9.78
CH_3CH_2	CH_3	43.37	4.79	10.17	44.10	4.77	10.28

a) py=pyridine.

TABLE 2. PMR DATA FOR FREE- AND COORDINATED-HYDROXYIMINO KETONES

R	R′	Solvent	Chemical shift, ppm									
			R-C(=O)-C(=NOH)-R′					[Co{R-C(=O)-C(=NO)-R′}$_2$(py)$_2$]ClO$_4$				
			H^a	H^b	H$^\alpha$	H$^\beta$	H$^\gamma$	H^a	H^b	H$^\alpha$	H$^\beta$	H$^\gamma$
CH_3^a	CH_3^α	$CDCl_3$	2.39 s		2.00 s			2.53 s		1.95 s		
		d_6-DMSO	2.32 s		1.83 s			2.52 s		1.68 s		
		Py	2.45 s		2.15 s			2.54 s		1.90 s		
		$H_2O$$^{a)}$	2.35 s		1.86 s			2.42 s$^{b)}$		1.84 s$^{b)}$		
CH_3^a	$CH_2^\alpha CH_3^\beta$	$CDCl_3$	2.38 s		2.55 q	1.05 t		2.55 s		2.38 q	0.66 t	
		d_6-DMSO	2.29 s		—$^{c)}$	0.91 t		2.55 s		2.29 q	0.54 t	
CH_3^a	$CH_2^\alpha CH_2^\beta CH_3^\gamma$	$CDCl_3$	2.39 s		2.54 t	1.50 m	0.93 t	2.54 s		2.34 t	1.13 m	0.46 t
		d_6-DMSO	2.29 s		2.40 t	1.38 m	0.82 t	2.55 s		2.31 t	1.05 m	0.35 t
CH_3^a	$CH^\alpha(CH_3^\beta)_2$	$CDCl_3$	2.38 s		3.45 m	1.24 d		2.55 s		—$^{d)}$	0.93 d	
		d_6-DMSO	2.26 s		3.31 m	1.13 d		2.56 s		3.30 m	0.83 d	
CH_3^a	$COCH_3^\beta$	$CDCl_3$	2.43 s$^{e)}$			2.43 s$^{e)}$		2.90 s			2.33 s	
$CH_3^bCH_2^a$	CH_3^α	d_6-DMSO	—	1.15 t	1.98 s			2.83 q	1.17 t	1.89 s		

s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet.

a) Sodium 3-trimethylsilylpropanesulfonate is used as an external reference. b) Obtained for the sodium salt. c) Obscured by the solvent signal. d) An accurate value is not obtained due to low solubility. e) H^a and H$^\beta$ are observed as one signal.

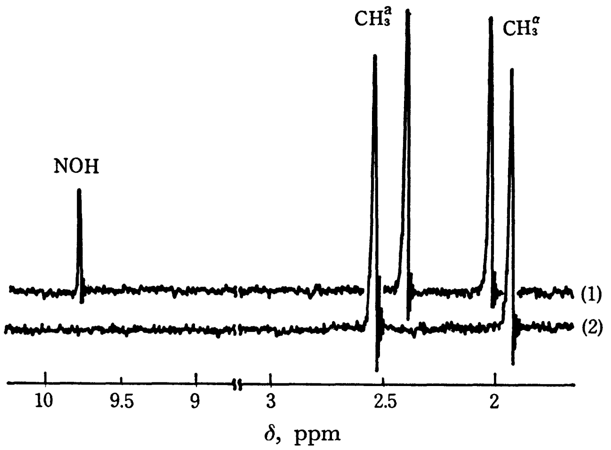

Fig. 1. PMR spectra in $CDCl_3$.
(1): CH_3^a-C(=O)-C(=NOH)-CH_3^α.
(2): [Co{CH_3^a-C(=O)-C(=NO)-CH_3^α}$_2$(py)$_2$]ClO$_4$.

resonance may be interpreted as follows. The electron density on the coordinated atom decreases, which causes a decrease in the shielding of the alkyl protons. The observed downfield shift of the H^a signal by coordination is consistent with the above interpretation. On the other hand, the upfield shift for the H$^\alpha$ signal is unexpected. There is no appreciable difference between the H$^\alpha$ chemical shift values of biacetyl monoximato anion and the neutral biacetyl monoxime, as shown in Table 2. This fact implies that it is improbable that the unusual upfield shift is caused by the negative charge on the functional group.

The similar spectral behavior of the upfield shift for the R′ proton is also observed in the case of 3-hydroxyimino-2,4-pentanedione (R = CH_3^a and R′ = $COCH_3^\beta$). The free 3-hydroxyimino-2,4-pentanedione in $CDCl_3$ has one singlet at 2.43 ppm, as shown in Fig. 2. Patel and Haldar[6] have reported that the signal near 2.43 ppm is split into two peaks in dioxane.

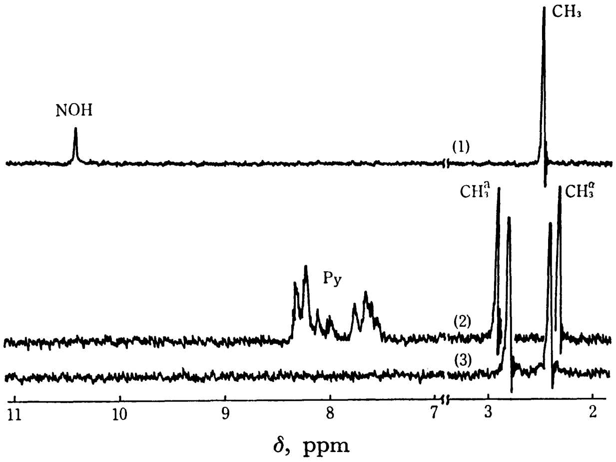

Fig. 2. PMR spectra in $CDCl_3$.
(1): CH_3^a-C(=O)-C(=NOH)-C(=O)-CH_3^{α}.
(2): [Co{CH_3^a-C(=O)-C(=NO)-C(=O)-CH_3^{α}}$_2$-(py)$_2$]ClO$_4$.
(3): Co{CH_3^a-C(=O)-C(=NO)-C(=O)-CH_3}$_3$.

Both phenomena stated above can be explained by the rate of bond switching in hydrogen bonding between hydroxyimino-hydrogen and two carbonyl-oxygens. In the solution of $CDCl_3$, the bond switching time is shorter than the measurement time. One resonace signal is then obtained in the present case. The tris-complex, Co^{III}(3-hydroxyimino-2,4-pentanedionato)$_3$, exhibits two singlets at 2.40 and 2.79 ppm and the bis-complex, [Co^{III}(3-hydroxyimino-2,4-pentanedionato)$_2$(py)$_2$]ClO$_4$, also gives rise to two singlets at 2.33 and 2.90 ppm. The singlet at 2.33 ppm for the bis-complex is shifted toward higher fields by 0.1 ppm than that of the free ligand and is assigned to the $COCH_3$ protons considering its similarity to the upfield shift of the H$^\alpha$ proton signal in biacetyl monoxime.

The upfield shift of the R′ proton resonance is also confirmed in the PMR spectra of a series of α-hydroxyimino ketones with such R′ groups as C_2H_5, *i*-C_3H_7, and *n*-C_3H_7. From the PMR data presented in Tables 2 and 3, it is found that upon complex formation, the amount of the upfield shift for the R′ proton resonances increases in the following order: $H^\alpha < H^\beta < H^\gamma$. On the other hand, the H^b proton signal in R=$CH_3^bCH_2^a$ is shifted to lower fields upon coordination, as expected.

In order to interpret the above upfield shift for the R′ proton resonances, it is proposed that the R′ group in the complex is situated so as to experience a strong shielding effect due to the magnetic anisotropy—the pyridine ring-current. A similar shielding effect has been pointed out for the methylene proton resonance of 1,4-polymethylenebenzene analogues, where the methylene groups are above the phenyl ring.⁽⁷⁾ Hill and Morallee⁽⁸⁾ have reported that the resonances of the bridging methylene protons are shifted toward higher fields by the axial coordination of pyridine with RCo(bae), where R=an alkyl group and bae=a bis(acetylacetone)ethylenediiminato anion. This upfield shift is attributed to the ring-current effect of the coordinated pyridine. Abott and Martel⁽⁹⁾ have shown that the 2-CH_3 signal of the bis(pyridoxylideneserinato)Al(III) complex is found to be as much as 100 Hz higher than that of the 2-CH_3 of the free Schiff base.

It is beyond the aim of this study to describe the conclusive structure of [Co(mo)$_2$(py)$_2$]ClO$_4$.⁽¹⁰⁾ Figure 3 shows the limiting structure for R′=*n*-C_3H_7, where the alkyl group experiences most strongly the shielding effect of the pyridine. The framework molecular model suggests that the free rotation of the R′ group is not restricted sterically. For the 1,2-dioximato chelates, it has been suggested that the d_π-orbitals of the metal interact with both p_π-orbitals of the chelate ligand and the pyridine which perpendicularly coordinates with the metal-chelate plane.⁽¹¹⁾ It is also possible to expect a similar interaction of the p_π(pyridine)-, d_π(cobalt)-, and p_π(hydroxyiminato nitrogen)-orbitals for the pyridine conformation in [Co(mo)$_2$(py)$_2$]ClO$_4$ given in Fig. 3. Consequently, the pyridine occupies the position in which the pyridine plane is perpendicular to the Co–N(hydroxyiminato nitrogen) bonding. The pyridine plane then faces the R′ group and an upfield shift of the R′ proton resonances is obtained. Because the carbon atom of the hydroxyimino group is sp^2-hybridized, the CH_2^α carbon atom is drawn on the xy-plane.

It is scarcely possible to evaluate the exact distance between the pyridine and the alkyl group of the complex in solution. The vertical distance of the alkyl carbon from the xy-plane is, therefore, estimated using the molecular model framework and is tentatively plotted versus the amount of upfield shift of the R′=$CH_2^\alpha CH_2^\beta CH_3^\gamma$ proton resonance caused by coordination (Fig. 4). Figure 4 suggests that the shielding effect by the pyridine increases in the order: $H^\alpha < H^\beta < H^\gamma$. The distance between the CH_3 carbon atom and the center of the pyridine ring is about 2.8 Å at its distance of closest approach, as shown in Fig. 3. In the case of 1,4-polymethylenebenzene analogues,⁽⁷⁾ it is seen from the molecular model that the methylene carbons are vertically situated at about 2 Å above the phenyl ring.

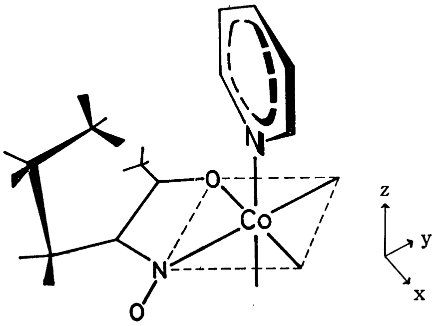

Fig. 3. Proposed limiting structure for [Co{CH_3^a-C(=O)-C(=NO)-$CH_2^\alpha CH_2^\beta CH_3^\gamma$}$_2(py)_2$]ClO$_4$.

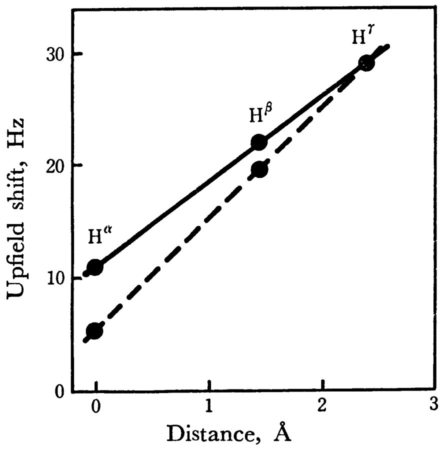

Fig. 4. Amount of the upfield shift caused by coordination and vertical distance of the alkyl carbon atom from the metal-chelate plane for [Co{CH_3^a-C(=O)-C(=NO)-$CH_2^\alpha CH_2^\beta CH_3^\gamma$}$_2(py)_2$]ClO$_4$.
——: in CDCl$_3$, - - -: in d_6-DMSO.

Table 3. Upfield shift of the R′ proton signal from free ligands caused by complex formation

R	R′$^{a)}$	Amount of upfield shift in CDCl$_3$, Hz$^{b)}$		
		H^α	H^β	H^γ
CH_3^a	CH_3^α	4		
CH_3^a	$CH_2^\alpha CH_3^\beta$	12	24	
CH_3^a	$CH_2^\alpha CH_2^\beta CH_3^\gamma$	11	22	29
CH_3^a	$CH^\alpha(CH_3^\beta)_2$		19	
CH_3^a	$COCH_3^\beta$		6	

a) For the general formula, refer to Table 1.
b) The data were obtained at 60 MHz.

As summarized in Table 3, upon complex formation, the upfield shift of the H^α or H^β signal for R′=$CH_2^\alpha CH_3^\beta$ is nearly equal to that of the corresponding signal for R′=$CH_2^\alpha CH_2^\beta CH_3^\gamma$. On the other hand, the upfield shift of the H^β signal for R′=$COCH_3^\beta$ (6 Hz) is smaller than that of the H^β signal for R′=C_2H_5 or *n*-C_3H_7 (22 to 24 Hz). This result is interpreted as follows. The H^β protons in $COCH_3^\beta$ are farther from the pyridine than in C_2H_5 and *n*-C_3H_7, because the CH_3^β group is bound to the sp^2-carbonyl carbon atom. The small upfield shift of 6 Hz is obtained as a result of the decrease in the shielding effect by the pyridine. Compared with the upfield shift of the H^α signal for $R'=C_2H_5$ or n-C_3H_7, that of the H^α signal for $R'=CH_3^\alpha$ is rather small.

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