SYNTHESES OF SOME NEW LIGANDS CONTAINING IMIDAZOLES AND REVERSIBLE OXYGENATION OF THE COBALT(II) COMPLEXES

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Tri, tetra, and pentadentate ligands containing imidazole groups were prepared and the oxygenation of their cobalt(II) complexes was briefly investigated.

Imidazole moiety is of special interest in biological systems in view of its multiple functions to act as acid-base, nucleophile, and ligand, etc. at the active site of many enzymes.¹⁾ Recently, Breslow et al. have reported the preparation of bis- and tris-imidazole compounds as the models of metal binding sites of carboxypeptidase and carbonic anhydrase.²⁾

In this paper, we wish to report the preparation of a new family of imidazole derivatives[tridentate(1), tetradentate(2), and pentadentate(3)], and also to describe the oxygenation of cobalt(II) complexes of these ligands. The CPK molecular models of 2 and 3 indicate that the four nitrogen atoms of imidazole groups can be arranged at square planar positions so as to hold a metal ion at the center.



Furthermore, the models indicate that one of the axial positions of the square planar complex is blocked by the hydrogen of phenyl ring in 2, while the pyridine nitrogen occupies an axial position as the fifth ligand atom in 3.

The compounds (1, 2, and 3) were prepared from N-methylimidazole and the corresponding ethyl carboxylates according to the essentially similar procedures described by Breslow et al.²⁾ The results are shown in Table 1.

Compound		Mp/°C	Found (Calcd)/%		
	Yield/%		c	Н	N
1	65	127-9 ^{a)}	62,00	5,68	26,06
			(62,46)	(5.57)	(26.02) ^{b)}
2 ~	60	162-3 ^{C)}	60.57	5,76	23.39
			(60.48)	(5,92)	(23.52) ^{d)}
3 ~	54	$184-6^{e}$	57.72	5,55	26.67
			(57.85)	(5.70)	(26.41) ^{f)}
^{3−CH} 3 ^{CO} 2 ^C 2 ^H 5	-	134-5 ^{g)}	59.81	5.66	25.85
			(59.65)	(5.76)	(25.65) ^{h)}

Table 1. Yields, melting points and elemental analyses

a) From ethyl acetate b) Calcd for $C_{14}H_{15}N_50$ c) From methanol-hexane d) Calcd for $C_{24}H_{26}N_8O_2 \cdot H_2O$ e) From chloroform-hexane f) Calcd for $C_{23}H_{25}N_9O_2 \cdot H_2O$ g) From methanol-ethyl acetate

h) Calcd for 2:1 complex; $C_{23}H_{25}N_9O_2 \cdot \frac{1}{2} CH_3CO_2C_2H_5$

The table indicates that 3 was obtained as the two kinds of crystals depending on the recrystallization solvent. When crude 3 was recrystallized from chloroform-hexane, a crystal of 1:1 composition of 3 and water of mp 184-6°C was obtained. Another crystal of mp 134-5°C was obtained when recrystallized from methanol-ethyl acetate. This crystal was found by IR (C=0, 1720 cm⁻¹) and ¹H NMR spectra to contain 1/2 mol of ethyl acetate per mol of 3. Furthermore, this ethyl acetate was found to be lost as a gas on melting the crystal (>134°C) to give a solid of mp 186-7°C which appeared to be the same as that obtained from chloroform-hexane. Thus, the latter crystal of lower mp must be an inclusion compound. The following esters were further examined for the formation of such inclusion compounds.

 $CH_{3}CO_{2}R [R = CH_{3}, C_{2}H_{5}, C_{3}H_{7}, CH(CH_{3})_{2}, C(CH_{3})_{3}]; C_{2}H_{5}CO_{2}CH_{3};$ $C_{2}H_{5}CO_{2}C_{2}H_{5}; C_{3}H_{7}CO_{2}C_{2}H_{5}$

Among them, only ethyl acetate and methyl propionate were successful³⁾. It may be interesting to note that these two esters have the same chain length.

The cobalt(II) complexes of 1, 2 and 3 were then examined for oxygenation with molecular oxygen. In a Thunberg cuvette, 30 μ l of cobalt(II) nitrate (0.1 M in EtOH) was placed in the upper compartment and the ligand 3 (1x10⁻³M) in CH₃CN (3 ml) in the lower cell. Each solution was bubbled for 30 min with nitrogen. The cobalt(II) complex was then prepared by mixing them. Reversible oxygenation was carried out by alternate introduction of oxygen and nitrogen gas into the solution by bubbling. Admission of oxygen to the solution yielded a red-brown solution.⁴⁾ The absorption spectra are shown in Fig. 1. The figure indicates that the absorption at 500 nm appeared rapidly by bubbling of oxygen and disappeared by nitrogen bubbling through the solution.⁵⁾ This process could be repeated many times, but the absorption intensity obtained by oxygen bubbling decreased gradually to give Co(III) complex.⁶⁾ This spectral change was found to be completely inhibited by the addition of pyridine (10 μ 1), while 2,6-lutidine did not disturb it. Furthermore, such spectral changes as shown in Fig. 1 could not be observed for the ligands 1 and 2 in both CH₃CN and water.



a) After mixing

- b) O₂ bubbling(20 s)
- c) N₂ bubbling(20 min)
- d) O₂ bubbling(20 s)
- e) N₂ bubbling(15 min)
- f) O₂ bubbling(l min)
- g) After 24 h

Fig. 1. Spectral change of cobalt(II) complex of 3

These observations indicate that the oxygenation occurs at the penta-coordinated Co(II).⁴⁾

The stability of the oxygenated Co(II) complex was examined by following the decrease of the absorption at 500 nm. The first-order rate constants at 25°C were $8.3 \times 10^{-2} \text{min}^{-1}$ in CH₃CN, and $2.8 \pm 0.3 \times 10^{-2} \text{min}^{-1}$ in aqueous buffer solutions (pH 4.0-9.4, 0.1 M buffer, [=0.1). The latter rates in water were independent of pH employed. The ratio of oxygen: cobalt(II) complex was also determined by a modified gas-volumetric measurement described by Calvin and his co-worker.⁷⁾ The ratio was found to be 1:2 (O₂: Co(II) complex). This suggests that the oxygenated complex is a binuclear oxygen bridged chelate.⁴⁾

The present study demonstrated that newly synthesized pentadentate imidazolecontaining ligand 3-Co(II) complex was able to take up oxygen reversibly. Further works are in progress in these laboratories such as on the complexes of other metal ions.

References

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