Inorganica Chimica acta, 44 (1980) L169–L170

Electron Transfer Reaction from TMPD to Dioxygen through some Square Planar Cobalt(II) Complexes

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Received October 26, 1979

In the preceding paper [1] we reported that strong new absorption bands (*cf.* Table I) were observed in the 12 ~ 14 × 10^3 cm^{-1} region, when TMPD(N,N,N′,N′-tetramethyl-*p*-phenylenediamine) and a square planar cobalt(II) complex such as [Co(amben)] and [Co(A-14)] (for the abbreviations of ligands, see Fig. 1) were mixed in a solution; whereas no such new bands were observed for the mixed solution of TMPD and the nickel(II) or copper(II) complexes. Thus, it was supposed that the new bands should be due to the charge transfer transition from TMPD to the unfilled d_π orbital of cobalt.

In the present study, however, we have found that in an anaerobic condition no such new bands appear in the mixed solution of TMPD and the cobalt(II) complex. This solution changes its color immediately when it is exposed to the air, and the new bands begin to be observed. Therefore, it is obvious that the new bands emerge only in the presence of O_2.

As shown in Fig. 2, when [Co(aaen)] and $TMPD^+$-(ClO_4) [2] are mixed in a solution under a nitrogen atmosphere, a spectrum quite different from either of the starting components is observed. This spectrum very much resembles the spectrum observed for the mixed solution of [Co(aaen)] and TMPD in an aerobic condition. These facts clearly indicate that the origin of the new bands observed for the mixed solution of [Co(aaen)] and TMPD in the open atmosphere is not the one as supposed in the preceding paper, but is electronic transition in a molecular complex, [Co(aaen)]·$TMPD^+$. This result implies that TMPD is readily oxidized by O_2 in the presence of square planar cobalt(II) complex such as [Co(aaen)] and [Co(A-14)]. In connection with the above facts it is to be noted that cobalt(II) complexes of tetraazamacrocyclic ligands with electron-withdrawing group, such as [Co(B-14)] and [Co(C-14)] display no new bands upon mixing with TMPD in the open atmosphere.

TABLE I. New Absorption Band Data.

Complex	New Band, kK (ε)	Solvent
[Co(A-14)]	12.0(5040)	a
[Co(amben)]	13.7(4000)	b
[Co(aaen)]	14.1(3200)	b
[Co(aben)]	13.4(4020)	b

[a] 1,2-dichloroethane. [b] DMF.

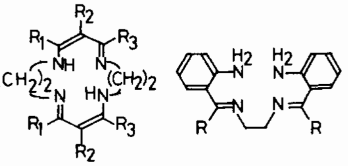

Fig. 1. The ligands used in this study. Abbreviations of the ligands are: N_4-macrocyclic ligands (left); H_2(A-14), R_1 = R_3 = H, R_2 = *p*-tolyl; H_2(B-14), R_1 = H, R_2 = $COCH_3$, R_3 = CH_3; H_2(C-14), R_1 = H, R_2 = $COOC_2H_5$, R_3 = CH_3. Schiff bases (right); H_2(amben), R = H; H_2(aaen), R = CH_3; H_2(aben), R = C_6H_5.

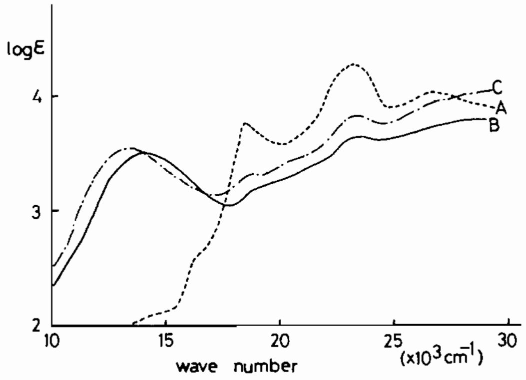

Fig. 2. Absorption spectra of the complexes in DMF (5 × 10^{-4} mol/l). A(---------), [Co(aaen)]; B (———), [Co(aaen)] + TMPD in aerobic condition (25 °C); C (–·–·–), [Co(aaen)] + $TMPD^+(ClO_4)$ in anaerobic condition (25 °C).

Although it is known that TMPD forms a weak molecular complex with O_2 [3], the oxidation reaction proceeds very little in the ambient condition. This was verified by the fact that a DMF solution of TMPD did not exhibit the 16 ~ 18 × 10^3 cm^{-1} band [4] of $TMPD^+$ after in the open atmosphere at room temperature. Also, no evidence [5] has been reported for the formation of O_2 adducts of [Co(amben)] and [Co(A-14)] or the reaction of them with O_2. Thus, the electron transfer reaction proceeds only when TMPD, cobalt(II) complex and O_2 are put together in a solution. Accordingly, this reaction may be called a 'concerted electron transfer reaction' which is often observed in various oxidase and oxygenase in biological system [6].

According to Tamaru *et al.* the reduction of methylene blue by ascorbic acid is catalyzed by the planar molecule DMA(1,3-dimethylalloxazine) [7]. We have found that this reaction also proceeds smoothly in the presence of square planar cobalt(II) complex such as [Co(aaen)] and [Co(A-14)] instead of DMA. These facts suggest that the electron transfer from TMPD (or ascorbic acid) to O_2 (or methylene blue) takes place through the cobalt ion in forming a three-molecule complex.

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