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DIOXYGEN COMPLEXES OF NICKEL(I) BOUND TO POLYMERS

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Three polymer-bound Ni(I) complexes were prepared; polymer complex I was prepared from $NiBr(P(C_6H_5)_3)_3$ and resin-substituted triphenylphosphine (polymer I), polymer complex II was from $NiBr(P(C_6H_5)_3)_3$ and resin-substituted pyridine (polymer II), and polymer complex III was from Na[Ni(salen)] and resin-substituted methyltriphenylphosphonium bromide (polymer III). Under atmospheric oxygen these complexes showed esr signals ($g_{/\!/} = 2.035$-2.037, $g_{\perp} = 2.002$-2.003), which were attributed to new dioxygen complexes of Ni(I). Their electronic structures should be formally described as $Ni(II)$-O_2^-.

The dioxygen complexes of nickel are few. Only $Ni(O_2)(PR_3)_2$ (R = C_6H_5, C_6H_{11}, $C_5H_{10}N$)[1)] and $Ni(O_2)(CNR)_2$ (R = t-C_4H_9, C_6H_{11})[2)] have been isolated. $Ni(O_2)$, $Ni(O_2)_2$, $Ni(O_2)(N_2)$, and $Ni(O_2)(N_2)_2$ have been detected with ir spectroscopy using an Ar matrix isolation technique.[3)] The complexes of the other types have been spectroscopically detected neither in solution nor on solid surfaces such as NiO. We could stabilize a dioxygen complex of $TiCl_3$, which is too unstable to be detected in solution, by binding it to polymeric ligands.[4)] Here esr evidences of new dioxygen complexes of Ni(I)(d^9) are presented, which were stabilized by the same way.

Polymer I was prepared by the α, α′-azobis-iso-butyronitrile-initiated copolymerization of diphenylstyrylphosphine,[5)] divinylbenzene, ethylvinylbenzene, and styrene in benzene at reflux temperature, followed by washing and vacuum drying. Polymer II was prepared by the same procedure employing 4-vinylpyridine instead of diphenylstyrylphosphine. Polymer III was prepared quantitatively from polymer I by treatment with excess methyl bromide in toluene. The degrees of cross-linking of polymer complex I, II, and III were about 10, 20, and 10 mole %, respectively.

The contents of coordinating groups were all about 10 mole %.

N, N'-Ethylenebis(salicylideneiminato)nickel(II), Ni(salen), reacted with equivalent sodium naphthalene in tetrahydrofuran under nitrogen at room temperature, yielding green solution which exhibited an esr signal of Ni(I)[6] (g_{11} = 2.256, g_{22} = 2.089, g_{33} = 2.042) at 77 K. A new complex, Na[Ni(salen)], appeared to be formed.

Yellow polymer complex I was obtained by stirring polymer I (0.60 mequiv. P) and $NiBr(P(C_6H_5)_3)_3$ (0.37 mmole) in toluene (40 ml) under nitrogen at room temperature for several hours, and subsequent washing and vacuum drying. The same procedure with polymer II (0.41 mequiv. N) and $NiBr(P(C_6H_5)_3)_3$ (0.33 mmole) yielded yellow-brown polymer complex II. The ratios of incorporated Ni to coordinating atoms of polymer I and II were 0.27 and 0.41, respectively. The ratios of $P(C_6H_5)_3$ (not exchanged for polymer I or II) to incorporated Ni were 0 and 1.65 in polymer complex I and II, respectively. Stirring green tetrahydrofuran solution of Na[Ni(salen)] (0.24 mmole) with polymer III (0.47 mequiv. P), followed by washing and vacuum drying yielded yellow-brown polymer complex III.

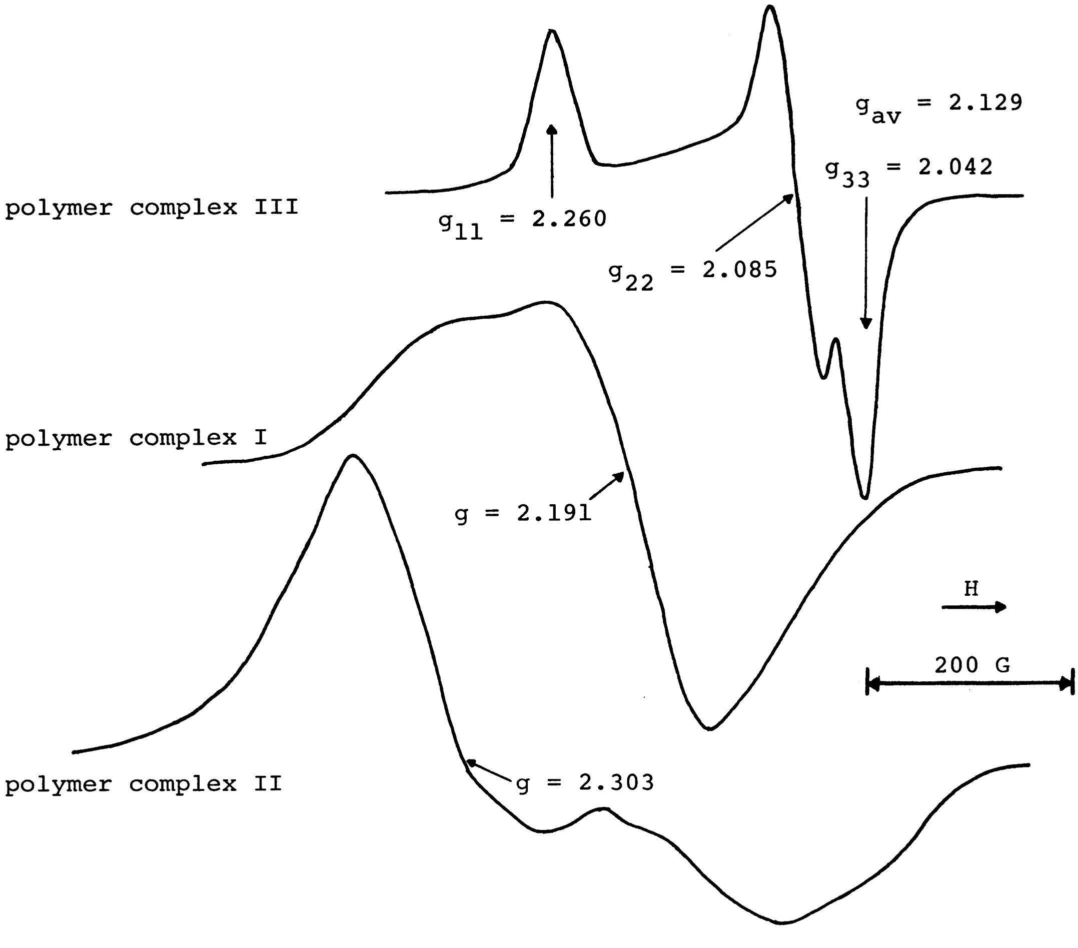

Fig. 1. Esr spectra of Ni(I)-polymer complexes under vacuum at 77 K.

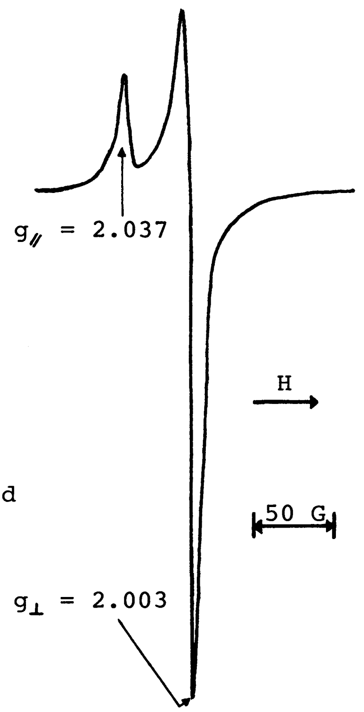

Fig. 2. Esr spectrum of polymer complex II under O_2 at 77°K.

Esr spectra of polymer complex I, II, and III under vacuum at 77 K are shown in Fig. 1. These spectra were ascribed to Ni(I) because of their g values, line widths, and intensities.[6,7]

By introduction of atmospheric oxygen, these spectra diminished or disappeared, and new sharp axial-symmetry signals ($g_{/\!/}$= 2.035-2.037, $g_\perp$= 2.002-2.003) (α-signals) appeared. Fig. 2 shows α-signal of polymer complex II as a representative.

α-Signals should be first examined as signals resulted from oxygen-centered radicals since they were formed only after introduction of oxygen. The average g values of alkoxy radicals (2.003-2.004)[8] are smaller than those of α-signals (2.013-2.014). The order of $g_{/\!/}$ and $g_\perp$ of O^- is contrary to those of α-signals.[9] In addition, alkoxy radicals and O^- are so reactive[10] that they may not be stabilized by such organic polymers as we employed here. Table lists g values of some alkylperoxy radicals (ROO·) and O_2^-. The average g values of α-signals are within the range of those of ROO· and O_2^-. The g_{33} values of ROO· exceed largely g_e (2.0023), while the $g_\perp$ values of α-signals not. The $g_{/\!/}$ and $g_\perp$ values of

Table. Principal and average g values of some ROO· and O_2^-

	$g_{11}(g_{/\!/})$	g_{22}	$g_\perp$	g_{33}	g_{av}
$CF_3\underset{OO\cdot}{\underset{\mid}{C}}FCONH_2$[11]	2.0267	2.0193		2.0102	2.0187
α-Tetralylperoxy[12]	2.0306	2.0085		2.0073	2.0155
Cumylperoxy[10a]	——	——		——	2.0146
O_2^- in CH_3OH[13]	2.077		2.0031		2.028
$Co(TPP)(CH_3CN)(O_2)$[14),a]	2.076	2.004		1.995	2.025
$TiCl_3(O_2)$ in polymer[4]	2.022	2.010		2.004	2.012
O_2^- on Mo-SiO_2[15]	2.017	2.010		2.004	2.010
$Co(CO)_4(O_2)$[16]	2.010		2.004		2.006
This work	2.035 -2.037		2.002 -2.003		2.013 -2.014

a) TPP = tetraphenylporphyrin.

α-signals fall within the range of the corresponding g values of O_2^-. Therefore, α-signals were attributed to dioxygen complexes of Ni(I), whose electronic structures should be formally described as Ni(II)-O_2^-.

The dioxygen complexes diminished slowly at room temperature, but were stable at 77 K. The yields of the dioxygen complexes based on reacted Ni(I), estimated from integrated esr spectra, were 0.1, 2, and 30 % for polymer complex I, II, and III, respectively. The low yields of the dioxygen complexes for polymer complex I and II may be due to the intramolecular reduction of the dioxygen ligands by $P(C_6H_5)_3$ in the most dioxygen complexes formed transiently. Polymer complex III without such an easily oxidizable ligand gave the dioxygen complex in fairly good yield.

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