The Electronic Configuration and Oxygenation of *NN'*-Ethylenebis-salicylaldehydeiminato)cobalt(II) Studied by Electron Spin Resonance Spectroscopy

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Summary An e.s.r. study of [Co(salen)] in different solvents revealed that the electronic configuration $(d_{yz})^2(d_{zx})^2(d_{xy})^2(d_{z^2})^1(d_{x^2-y^2})^0$ is required for the compound to be able to oxygenate, while another configuration $(d_{yz})^2(d_{zx})^2(d_{z^2})^2(d_{xy})^1(d_{x^2-y^2})^0$ which is realized in certain solvents does not permit oxygenation of the compound at room temperature.

THE mechanism of the reversible oxygenation of cobalt(II) complexes and the factors which control their ability to oxygenate are still unknown.

One of the compounds which undergoes reversible oxygenation is [Co(salen)][1,2] [salen = bis(salicylaldehyde)ethylendi-imine]. The factors which control the ease of oxygenation of this compound are the crystal structure[1] and the solvent used.[2] It has been reported[2] and confirmed that the oxygenation of this compound to form peroxo-bridged species readily takes place in pyridine, dimethyl sulphoxide, and dimethylformamide while virtually no oxygenation occurs in toluene, chloroform, acetone, and dimethylacetamide. The addition of NCS^-, N_3^-, or $MeCO_2^-$ to a dimethylacetamide solution, however, allows[2] the compound to oxygenate.

The e.s.r. spectral data[a,b] *and oxygenation of* [Co(salen)] *in different solvents*

Type	Solvent	g_x	g_y	g_z	A_x[f]	A_y[f]	A_z[f]	P[f]	κ	Oxygenation[c]
A	Dimethylacetamide	2·18	2·13	1·855	123	120	(≤40)			—
			(calc.)		+126	+120	−40	153	−0·39	
	CH_2Cl_2–toluene(1:1)	(2·17)	(2·07)	1·833						
B	+NCS^-,	2·54	2·31	2·011	(≤70)	(≤40)	98			+
	dimethylacetamide		(calc.)		+60	+22	+98	170	−0·07	
	Me_2SO	2·353	2·353	2·011	(≤66)	(≤66)	109			+
			(calc.)		+40	+40	+109	170	−0·12	
	Pyridine–toluene(1:1)	2·354	2·27	2·028	(≤20)	(≤20)	77			+
			(calc.)		+20	+10	+77	170	−0·02	
	[Co(acacen)py][d]	2·534	2·225	2·012	49·4	(12)	98·3			[e]
			(calc.)		+57	+26	+113	156	−0·20	

[a] The spectra were recorded at 77 K. The complications[6,9] due to the crystallization of solvent and the segregation of solute molecules have carefully been avoided. [b] The values in parentheses are estimates. [c] + : The reversible oxygenation ($2Co + O_2 \rightleftharpoons CoO_2Co$) occurs at room temperature. — : No oxygen at room temperature. [d] Refs. 4, 7, and 10; (acacen) = bis(acetylacetone)-ethylendi-imine. [e] Reversible oxygenation $Co + O_2 \rightleftharpoons Co^{III}O_2^-$ at −6 °C. [f] 10^{-4} cm^{-1}.

We investigated this solvent effect by studying the electronic structure of the compound by e.s.r. Our results are summarized in the Table. There are two groups of solvent in which the compound gives distinctly different e.s.r. spectra (A and B type); this classification by e.s.r. corresponds to that based on ease of oxygenation. The type A spectrum can most readily be fitted to the configuration $(d_{yz})^2(d_{zx})^2(d_{z^2})^2(d_{xy})^1(d_{x^2-y^2})^0$ (x, y axes lie along the Co–O and Co–N bonds); *i.e.*, the odd electron is in the orbital d_{xy}. The type B spectrum requires that the odd electron is in the orbital d_{z^2}. The estimated values of P and κ (according to the method of Maki *et al.*[3]) for both A and B types which are also included in the Table are reasonable.[3,4] This difference in the electronic configuration can be explained by the co-ordinating strength of the solvent molecule. A strong axial fifth (and sixth) ligand raises the d_{z^2} level above the d_{xy}, thus bringing about the configuration B. It has been recognized[2,5] that at least one axial ligand of strongly co-ordinating ability such as an amine is required for a square planar Co^{II} complex to oxygenate. However, a square planar Co^{II} complex could have the configuration B and oxygenate without any axial ligand, as found for Co^{II}(*p*-OMe)(tpp) in pure toluene,[6] where (*p*-OMe)(tpp) is tetra-(*p*-methoxyphenyl)porphin. Thus, all of the Co^{II} compounds which can oxygenate and of which the electronic structures have been elucidated have the B type configuration.[6-8] However, it has not been checked whether or not the configuration B is essential. The present result strongly indicates that the B configuration is required in order for, at least, [Co(salen)] to oxygenate reversibly forming the peroxo-bridged species at room temperature under a pressure of about 1 atmosphere of oxygen.

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