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Low-spin Cobalt(II) Complexes with 6,13-Diaryl-1,8-dihydrodibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecene[1)]

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Synopsis. The ESR spectra of the title compounds were measured at 77 K. From the results, it was concluded that an unpaired electron is localized in the d_{yz} orbital of the cobalt atom of the complexes.

In the last several years we have investigated the electronic structures of low-spin square planar cobalt(II) complexes in terms of their ESR spectra. Very recently we found that 6,13-diaryl-1,8-dihydrodibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecene, **1**(a) and **1**(b), shown in Fig. 1, can be readily obtained from the reaction mixture of 4-aryl-1,2-dithiolium salt and *o*-phenylenediamine.[2)] In this study we have synthesized the cobalt(II) complexes with **1**(a) and **1**(b) and measured their ESR spectra. This is the first report on the ESR spectra of low-spin square planar cobalt(II) complexes with a 14-membered tetraazacyclotetradecene.

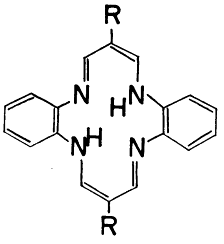

Fig. 1. Tetraaza-macrocyclic ligands. **1**(a) : R=phenyl **1**(b) : R=*p*-tolyl

Experimental

Preparation of the Ligands. The ligand, **1**(a)(or **1**(b)), was obtained from the reaction mixture of 4-phenyl(or 4-*p*-tolyl)-1,2-dithiolium hydrogensulfate and *o*-phenylenediamine.[2)]

Preparation of the Cobalt(II) Complexes. A DMF solution(15 ml) containing cobalt(II) acetate tetrahydrate (0.001 mol) and the ligand(0.001 mol) was refluxed at 150 °C for 3 h. On cooling the solution, the complex was separated as dark violet needles.

Measurements. ESR spectra were obtained with a JEOL ESR spectrometer model JES-ME-3X at 77 K. For the ESR measurements, cobalt(II) complexes were diluted in the corresponding nickel(II) complexes. DPPH was employed as a standard marker. Magnetic susceptibilities were measured at room temperature by the Faraday method, Pascal's constants being used for diamagnetic correction.

Results and Discussion

The magnetic moments of the cobalt(II) complexes with **1**(a) and **1**(b) were 2.28 BM and 2.30 BM at room temperature, respectively, indicating that these complexes are of low-spin type. These cobalt(II) complexes are stable against air in the solid state.

The ligands, **1**(a) and **1**(b), are 14-membered tetraazamacrocyclic ligands with 16 π-electrons, while porphyrins are 16-membered tetraaza-macrocyclic ligands with 18 π-electrons. Therefore it is interesting to compare the electronic states of the complexes of **1**(a) and **1**(b) with those of cobalt(II) porphyrins.

In Fig. 2, the ESR spectrum of cobalt(II) complex with **1**(a) is shown, which is very similar to that of **1**(b). One absorption (g_1=4.256) with eight hyperfine structures due to ^{57}Co was observed in the range 1000—2200 G(G=10^{-4} T). In the range of 3700—4500 G, two absorptions(g_2=1.71, g_3=1.53) were observed, their

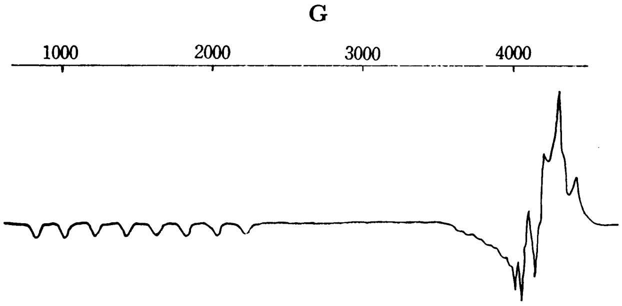

Fig. 2. ESR spectrum of cobalt(II) with **1**(a).

Table 1. ESR parameters of cobalts(II) complexes

Type	Complexes	g_x	g_z	g_y	$\lvert A_x\rvert$	$\lvert A_z\rvert$ (10^{-4} cm^{-1})	$\lvert A_y\rvert$	Ref.
I	[Co(tpp))]	3.322	1.798	3.322	315	197	315	3
	[Co(pc)]	2.92	1.91	2.89	270	160	260	5
II	[Co(acen)]	3.26	2.00	1.88	116	34	38	6
	[Co(sacsac)$_2$]	3.280	1.899	1.904	105	35	35	7
	Co-**1**(a)	4.256	(1.71, 1.53)[a)]		397	(30, 55)[b)]		
	Co-**1**(b)	4.057	(1.70, 1.55)[a)]		352	(——)[c)]		

a) The definite assignment of the experimental values to g_z and g_y is difficult. b) Roughly estimated.
c) Unresolved.

hyperfine splittings being smaller than that observed for g_1. It should be noted that this ESR pattern is quite different from that of Co-tpp,[3] where H_2tpp represents $\alpha,\beta,\gamma,\delta$-tetraphenylporphyrin. The latter complex shows an axial pattern with $g_{//}=1.798$ and $g_{\perp}=3.322$, and the hyperfine splitting observed for $g_{//}$ is very large. (*cf.* Table 1).

Recently we have investigated the ESR spectra of low-spin cobalt(II) complexes in detail[4] and found that square planar cobalt(II) complexes can be classified into two types, Type-I and Type-II, in terms of their ESR parameters, as shown in Table I. These two types are different from each other in two points, (1) the anisotropy of $\boldsymbol{g}$-tensors and (2) the value of $|A_z|$. The origin of such differences was attributed to the different ground state configurations, $(d_{x^2-y^2})^2(d_{xz})^2(d_{yz})^2$-$(d_{z^2})^1$ for Type-I and $(d_{x^2-y^2})^2(d_{z^2})^2(d_{xz})^2(d_{yz})^1$ for Type-II.[4,*]

As clearly seen in Table I, the cobalt(II) complexes with **1**(a) and **1**(b) belong to Type-II, and their ESR parameters can be elucidated in terms of our calculated results[4] based on the $(d_{x^2-y^2})^2(d_{z^2})^2(d_{xz})^2(d_{yz})^1$ ground state configuration.

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*) In this paper, x and y axes were adopted to be in the molecular plane and to bisect the nitrogen-cobalt bond angles, z axis being perpendicular to the plane.