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The $(xy)^2(x^2-y^2)$ Vacancy Configuration in Co(II)-Formazan

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ESR spectra of two formazanyl cobalt(II) complexes were observed at room temperature, 77, and 4 K. The parallel components ($g_{//}$) and the perpendicular components ($g_{\perp}$) of their g values satisfied a relation $g_{//} > g_{\perp} > 2$. These results could be interpreted by a rare three-vacancy configuration of $(xy)^2(x^2-y^2)$ in d-orbitals.

Formazans have been known to form complexes with some transition metal ions having the stoichiometries of 2:1 and 1:1.[1] Previously we reported that the magnetic properties of some copper complexes of formazans change drastically with different kinds of substituent to the 1-phenyl ring of 1,3,5-triphenyl-5-formazan (Fig. 1),[2] and that these complexes are classified into three groups corresponding to three types of copper-containing proteins, based on their ESR parameters obtained.[3] These results have motivated us to carry out a preliminary examination of the cobalt complexes and we have found out their unusual ESR absorptions. The ESR spectra of formazanyl-cobalt(II) complexes, bis[1,3,5-triphenyl-5-formazanyl]cobalt-(II)(**1**) and bis[1-parachlorophenyl-3,5-diphenyl-5-formazanyl]cobalt(II) (**2**), in polycrystalline state and in solution could be observed even at room temp. The parallel component of their g values, $g_{//}$, and the perpendicular component, $g_{\perp}$, have a relation, $g_{//} > g_{\perp} > 2$. Such g anisotropy suggests a rare case that the unpaired electron occupies $d(x^2-y^2)$ orbital. We wish to propose here that the $(xy)^2(x^2-y^2)$ three-vacancy configuration in the five d orbitals makes possible a consistent interpretation of the ESR results obtained in these cobalt complexes.

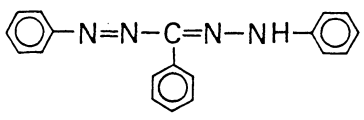
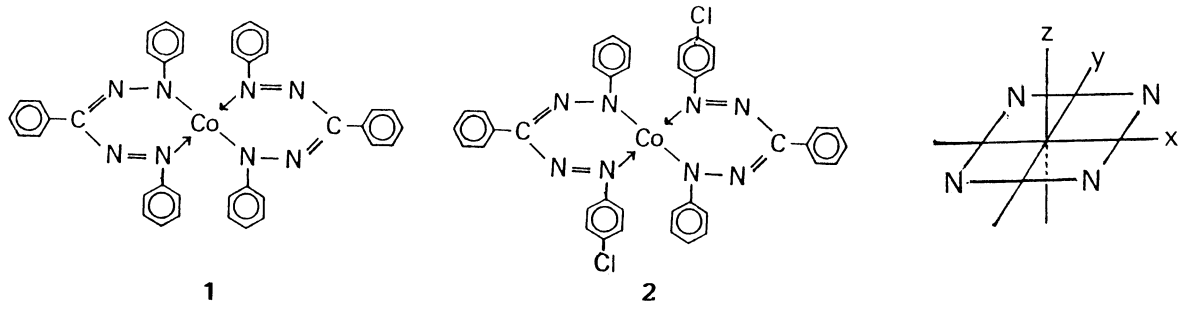


Fig. 1. 1,3,5-Triphenyl-5-formazan.

1 and **2** were prepared by the method similar to the copper analogue, which is described in a previous paper.[4] Their elemental analyses fitted well to the values calculated based on the 1:2 stoichiometry of the cobalt(II) ion and formazan: Complex **1**; Found: C,69.2; H,4.5; N,17.1%; Calcd for $C_{38}H_{30}N_8Co$: C,69.4; H,4.6; N,16.7%; and Complex **2**; Found: C,60.2; H,4.3; N,14.7; Cl,9.3%; Calcd for $C_{38}H_{28}N_8Cl_2Co$: C,60.0; H,4.2; N,14.3; Cl,9.3%. Their hypothetical molecular structures based on the analyses are shown in Fig. 2. From the magnetic susceptibility measure-



1 **2**

Fig. 2. Hypothetical molecular structure of **1** and **2** and their coordinate system.

ments in the temperature range of 4.2 K to room temp, the effective magnetic moments of **1** and **2** were estimated to be 1.89 and 2.3 BM, respectively. This result indicates that these complexes take a low-spin (S=1/2) ground state. The samples for ESR measurements were prepared by degassing in vacuo. Their ESR absorptions were observed at room temp, 77, and 4.2 K for both samples of microcrystalline powder and toluene solution. The room-temp ESR spectrum of the microcrystalline sample of **1** is shown in Fig. 3. The spectra at 77 and 4.2 K were quite similar to that at room temp. In these spectra only g anisotropy was observed. This is attributed to the result that the hyperfine structure is smeared out by an exchange-narrowing effect. $g_{//}$ and $g_{\perp}$ were estimated to be 2.23 and 2.03 respectively, as listed in Table 1. The room-temp ESR spectrum of **1** in the solution showed the isotropic hyperfine splittings due to the cobalt nuclear spin of I=7/2, as shown in Fig. 4(a). The fact that the spectrum was observed at room temp means much longer relaxation time of the electron spin in the present complexes than those in many cobalt complexes in which the ESR spectra are observable only at low tempera-

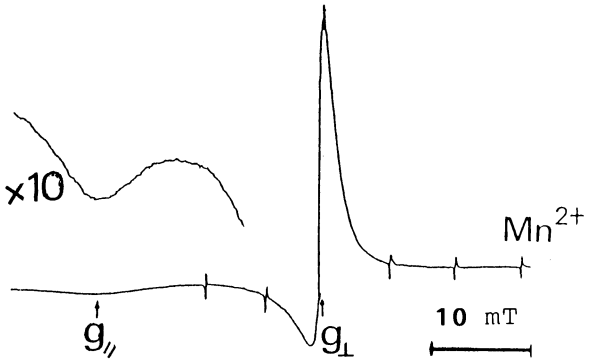


Fig. 3. ESR spectrum of **1** in polycrystalline state.

tures. The hyperfine splitting constant (hfsc) of the cobalt(II) ion, A(iso), was 4.5 mT. The spectrum of the solid solution at 77 K shown in Fig. 4(b) gave the parallel ($A_{//}$) and perpendicular components ($A_{\perp}$) of the hfsc of 8.3 and 3.5 mT, respectively. The results in **2** were quite similar to those in **1**.

Table 1. ESR parameters of **1** and **2**

	$g_{//}$	$g_{\perp}$	$A_{//}$/mT	$A_{\perp}$/mT
1	2.24	2.03	8.3	3.5
2	2.23	2.04	7.6	2.9
$Co(dpe)_2Cl_2$[a)]	2.257	2.056 2.041[b)]		

a) Dichlorodi[1,2-bis(diphenylphosphino)ethane]cobalt(II).
b) Ref. 6.

The elemental analyses showing the 1:2 stoichiometry suggest a CoN_4 ligand configuration in these complexes. Further, the axial g anisotropy described above reflects the tetragonal symmetry of the ligand field. X-Ray crystallographic data of the palladium analogue reported by Siedle and Pignolet showed the planar structure ligated by the nitrogen atoms around the palladium(II) ion.[5)] It can be mentioned from these facts that the most reasonable geometry of the present complexes is planar four-coordinate structure containing four

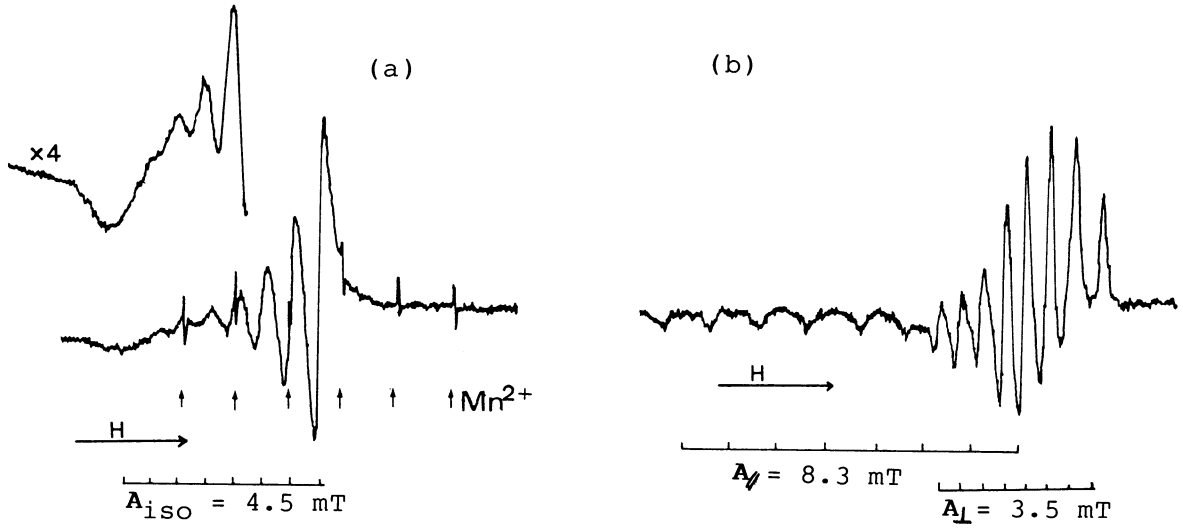


Fig. 4. ESR spectra of **1** in toluene solutions; (a) room temp and (b) 77 K.

nitrogen atoms in the plane. Horrocks et al. reported that the cobalt(II) complexes of 1,2-bis(diphenylphosphino)ethane, $Co(dpe)_2X_2$($X=Cl^-$, Br^-),[6)] have a $g_z > g_x \cong g_y > 2.0$. They concluded by the optical measurements and the calculations of the complexes that the $(xy)^2(x^2-y^2)$ configuration interprets well the ESR parameters obtained.[7)] For comparison with the present results, their g values are also listed in Table 1. Here, $g_{//}$ corresponds to g_z and $g_{\perp}$ to g_x and g_y. The g values of both **1** and **2** nicely coincide

with their g values. So the vacancy configuration of **1** and **2** is expected to be attributed to the $(xy)^2(x^2-y^2)$. Such configuration was reported for only a few complexes with strong ligands as phosphorus and sulfur atoms.[8] Since the $(xy)^2(z^2)$ is usual configuration for planar cobalt(II) complexes, the $(xy)^2(x^2-y^2)$ vacancy configuration is very rare for the cobalt complexes with the nitrogen atoms as ligands.[9]

The cobalt(II) complexes with the $(xy)^2(z^2)$ vacancy configuration are sensitive to the axial ligand and have the oxygen-carrying property in many cases. On the contrary, the complexes with the $(xy)^2(x^2-y^2)$ configuration are less sensitive to the axial ligand and do not make any oxygen complex. This oxygen-binding property was not recognized in **1** and **2**. This fact also suggests that our complexes have the latter configuration. Further, we suppose that the $(xy)^2(x^2-y^2)$ vacancy configuration results in a lifting of their excited states to higher energy level than those in the $(xy)^2(z^2)$ configuration. Consequently the mixing between the ground and the excited states would be small and the ESR relaxation time would become longer. Thus this configuration enables us to observe the room-temp ESR signals.

Conclusively, the $(xy)^2(x^2-y^2)$ vacancy configuration consistently interprets those results obtained. More detailed analysis is now in course of study.

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