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ESR and Optical Spectra of Low-spin Square Planar Cobalt(II) Complexes with Some Quadridentate Schiff Bases of the N_2S_2 Type[1)]

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Synopsis. ESR and electronic spectra of low-spin cobalt(II) complexes with some quadridentate Schiff bases of the N_2S_2 type were measured. Analysis of ESR parameters led to the conclusion that an unpaired electron is in the d_{yz} orbital of the cobalt atom. On this basis the absorption at 10×10^3 cm^{-1} was attributed to the $d_{x^2-y^2}\rightarrow d_{yz}$ transition.

The relative energies of d-orbitals in low-spin square-planar cobalt(II) complexes have been subjects of many investigations and still in controversies. Recently, we have reinvestigated the electronic structures of square planar cobalt(II) complexes with the quadridentate Schiff bases, **1-a**, **1-b**, and **1-c**, as shown in Fig. 1.[2)] As the results, it was concluded that an unpaired electron lies in the d_{yz} orbital and the separations among d_{yz}, $d_{x^2-y^2}$, d_{xz}, and d_{z^2} orbitals are small in these complexes.[2)] In this study the ESR and electronic spectra of cobalt(II) complexes with some quadridentate Schiff bases, **1-d**, were investigated in order to compare the ligand field effect of **1-d** with those of other quadridentate Schiff bases such as **1-a**, **1-b**, and **1-c**.

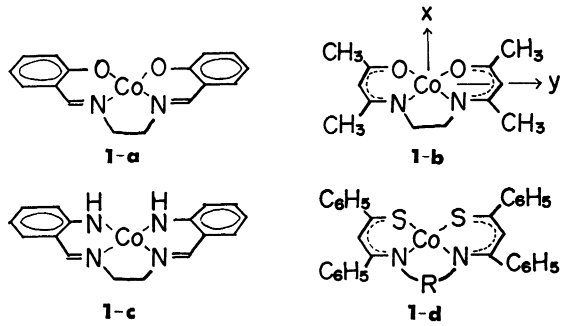

Fig. 1. Some quadridentate ligands cited in this paper. In **1-d**, R represents $-CH_2CH_2-$, $-CH_2CH_2CH_2-$, and $-CH(CH_3)CH_2-$ for H_2(nsen), H_2(nstn) and H_2(nspn), respectively. x and y axes are shown in **1-b**, z axis being perpendicular to the plane.

Experimental

The ligands, *N,N'*-bis(1-phenyl-2-thiobenzoylvinyl)ethylenediamine, *N,N'*-bis(1-phenyl-2-thiobenzoylvinyl)trimethylenediamine and *N,N'*-bis(1-phenyl-2-thiobenzoylvinyl)propylene diamine, abbreviated as H_2(nsen), H_2(nstn) and H_2(nspn), respectively, were prepared according to the modified methods of Uhlemann[3)] and Tang *et al.*[4)] The cobalt(II) complexes were obtained by mixing a methanol solution of cobalt(II) acetate tetrahydrate and a chloroform solution of the ligand under a nitrogen atmosphere. The nickel(II) complexes were also obtained according to the same method as described for cobalt(II) complexes.

ESR spectra were obtained with a JEOL ESR-apparatus model JES-ME-3X using an X-band. DPPH was used as a standad marker. Magnetic susceptibilities were measured by the Faraday method at room temperature, Pascal's constants being used for diamagnetic correction. $HgCo(NCS)_4$ was employed as a standard for magnetic susceptibility. Reflectance spectra were measured with a Shimadzu Multipurpose Spectrophotometer, MPS-5000 at room temperature.

Results and Discussion

The magnetic moments of cobalt(II) complexes with H_2(nsen), H_2(nstn) and H_2(nspn) were found to be in the range 2.2—2.3 BM at room temperature, indicating that all the complexes are of the low-spin type. Figure 2 shows the ESR spectrum of [Co(nstn)], diluted in [Ni(nstn)]. From the spectrum, it was found that $g_1=3.29$, $|A_1|=164\times10^{-4}$ cm^{-1}, and g_2, $g_3\approx2.0$. The other complexes, [Co(nsen)] and [Co(nspn)], showed ESR patterns similar to that of [Co(nstn)]. It should be noted that the ESR patterns of *cis*-$[CoN_2S_2]$ type complexes obtained here are very similar to those of *cis*-$[CoN_2O_2]$ type complexes with Schiff bases such as **1-a** and **1-b**,[5,6)] for which the $(yz)^1$ ground state* was assumed in our recent investigation.**[,2)] Therefore, it is reasonable to assume that an unpaired electron is localized in the d_{yz} orbital of the cobalt atom in the complexes with quadridentate Schiff bases of the *cis*-$[CoN_2S_2]$ type.

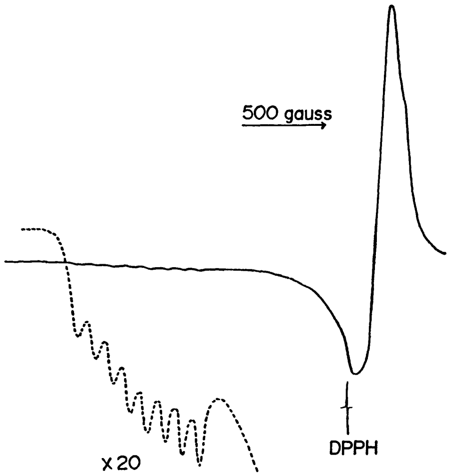

Fig. 2. ESR spectrum of [Co(nstn)] diluted in [Ni(nstn)] obtained at 123 K by an X-band.

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* $(yz)^1$ represents electronic configuration $(d_{x^2-y^2})^2(d_{xz})^2(d_{z^2})^2(d_{yz})^1$.

** Throughout this paper, x, y, and z axes were adopted as shown in Fig. 1.

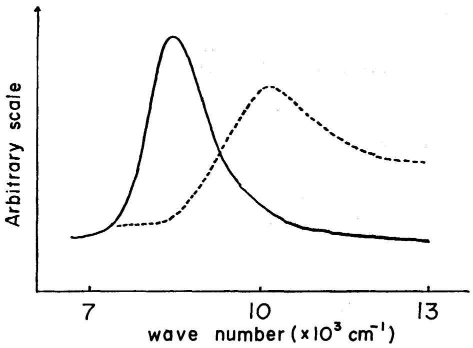

Fig. 3. Reflectance spectra of [Co(nspn)] (------) and [Co(sals)] (——).

The reflectance spectrum of [Co(nspn)] is shown in Fig. 3, together with that of [Co(sals)], which is one of the *cis*-[CoN_2O_2] type complexes, and where H_2(sals) represents *N,N'*-disalicylidene-1,2-diphenylethylenediamine. A broad band was observed at 10×10^3 cm^{-1} for [Co(nspn)], whereas a similar band was observed at 8.4×10^3 cm^{-1} for the *cis*-[CoN_2O_2] type complexes with quadridentate Schiff bases.[7] It is reasonable to assume that both bands are attributed to the same origin, to which the $d_{x^2-y^2} \rightarrow d_{yz}$ transition was assigned for the *cis*-[CoN_2O_2] type complexes with Schiff bases.[2] The blue shift of the band upon substitution of the N_2S_2 ligand for the N_2O_2 ligand suggests that the energy separation between $d_{x^2-y^2}$ and d_{yz} orbitals is larger in the [CoN_2S_2] complexes than those in the [CoN_2O_2] complexes. From the above discussion, it can be concluded that the order of the d-orbitals in the cobalt(II) complexes with Schiff bases, **1-d** is the same as those in the complexes with **1-b** and **1-c**.

References

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