〔N,N'-o-フェニレンビス(サリシルアルジミナト)〕コバルト(II)の溶液中の分子種

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Molecular Species in Solutions of [N,N'-o-Phenylenebis(salicylaldiminato)]Cobalt(II)

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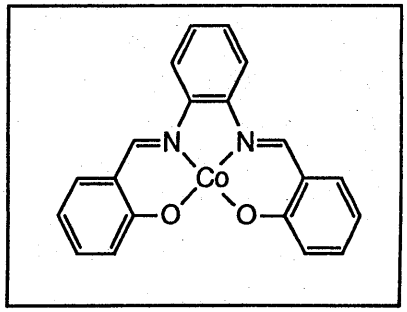
Introduction

The Schiff–base complexes of cobalt(II) ion have been investigated with interest of the reversible reactions with an oxygen molecule[1]. We have investigated the properties of the complexes in solution on the basis of the experimental results of the UV–VIS absorption spectra, the transient UV–VIS absorption spectra, the proton NMR spectra[2] and the cyclic voltammetry. We proposed that several molecular species are formed depending on solvents, temperature and the concentrations of the complexes[2]. In order to discuss the stability of these species, we aimed to examine the electronic structures by a calculational method. In this paper, we will report the results for the cobalt(II) Schiff–base complexes by the extended Hückel method and discuss the assignment of the observed absorption spectra.

Results and Discussions

In this work we carried out calculations of the molecular orbitals for all the valence electrons for [N,N'-o-phenylenebis(salicyldiminato)]cobalt(II), [Co(saloph)]. This cobalt (II) complex is a big system composed of 39 atoms, 119 atomic base orbitals and 125 valence electrons, so that we used the extended Hückel method[3]. The calculations were carried out by Hitac 3020 computer.



[Co(II)(saloph)]

The Results of Saloph^{2-}. In order to examine an availability of the extended Hückel method to this complex, we calculated first the molecular orbitals of the free ligand anion (saloph^{2-}) and compared the results with the observed spectra. The molecular structures of a free ligand (salophH$_2$) and [Co(saloph)] were

reported[4]. SalophH_2 has a non-planar structure due to a steric hindrance between the two O–H groups but [Co(saloph)] has a planar structure. Then, for the calculation of saloph^{2-} we used the structure of the saloph^{2-} part in [Co(saloph)]. Saloph^{2-} has 110 atomic orbitals and 118 electrons. Fig. 1 shows the electron distribution of the occupied orbitals (a) and the vacant orbitals (d). The transition energy is approximated by a difference of the orbital energies and the oscillator strength (f) was estimated without configuration interactions.

$f = 8.68 \times 10^{14} \cdot cQ^2$ (c in eV and Q in cm).

Because of the planar structure of the molecule, the molecular orbitals are divided into the π orbitals and the σ orbitals. The strong transitions between the σ orbitals do not appear in low energy region, so hereafter we will discuss only about the π orbitals. Fig. 2 (a) shows the transition energies and the oscillator strengths for saloph^{2-}. The transitions of 2–3 eV are the excitations to the lowest vacant orbital, in which the electron density is high on N = C bonds. The absorption spectrum of salophNa_2 in N,N'-dimethylformamide (DMF) was measured in a range from 600 nm to 300 nm (2.08–4.2 eV). One band was observed at 3.2 eV (f=0.4) with a weak shoulder of 2.9 eV. Considering from the approximations used here, the extent of coincidence between the observed and calculated values are enough, so we tried to use the extended Hückel method to the cobalt(II) complex.

The Results of [Co(saloph)]. For 3d orbitals of a cobalt ion linear combination of two Slater atomic orbitals[5] was used. The valence state ionization potentials of the cobalt ion depend on the charge of the cobalt ion[6]. The cobalt ion of [Co(saloph)] is in a divalent state (7d electrons) and considered to be neutralized due to a coordination of a saloph^{2-} ligand. First we postulated a charge on the cobalt ion, which determines the ionization potentials of the cobalt orbitals. We repeated the calculation of the molecular orbitals until the calculated net charge on the cobalt ion coincides with the starting charge. The self–consistent charge on the cobalt ion was determined as +0.17. Fig. 1 (b) shows the calculated occupied orbitals of [Co(saloph)]. By comparing them with the orbitals of saloph^{2-}, it is evident that

Table 1. The observed absorptions of [Co(saloph)] (10^{-3} mol dm^{-3}). The oscillator strengths are shown in the parentheses.

solvent	temperature	transition energy	molecular species
CH_2Cl_2	0–40 ℃	3.2, 2.9 eV (0.6)	
		2.1–2.5 eV (0.05)	[Co(saloph)]
DMF	70–90 ℃	3.24 (0.3), 3.0 eV (0.15)	
		2.5 eV (0.05)	[Co(saloph)](DMF)
DMF	−55–0 ℃	3.3 eV (0.4)	
		2.6 eV (0.2)	[Co(saloph)](DMF)$_2$

the cobalt ion interacts strongly with the phenoxide parts. The vacant orbitals are quite similar to those of saloph^{2-}.

The transition energies and the oscillator strengths are shown in Fig. 2 (b). The transitions in a region of 2–3 eV are excitations from the orbitals with large population on the cobalt atom to the vacant orbitals localized in saloph^{2-}, that is, charge-transfer transitions from metal to ligand. The transitions near 3.5 eV are ligand-localized transitions. The UV-VIS absorption spectra of [Co(saloph)] were measured and changed with variation of solvent and temperature. Table 1 lists the observed data. The observed bands near 3 eV and 2.5 eV are assigned to ligand–localized excitations and charge–transfer excitations, respectively.

It was reported that a cobalt ion deviates from a plane of Schiff-base ligand[7]. Then we calculated the molecular orbitals, assuming that a cobalt ion deviates from the ligand plane by 0.45 Å. The orbitals and the transition energies are shown in Fig. 1 (c) and Fig. 2 (c), respectively. For this structure, interactions occur between the σ and π orbitals and give different type of orbitals such as the orbital 61. Other orbitals are similar to those of planar [Co(saloph)] (Fig. 1 (b)). The transition energies and the oscillator strengths are considerably different from those of planar [Co(saloph)]. As is seen in Fig. 2, the lowest transition is sensitive to this molecular deformation. The observed solvent dependence of the absorption spectra is remarkable for the low-energy charge-transfer bands. Therefore, it is possible that planarity of the complex changes accompanied by axial ligation of solvent molecules.

The extended Hückel method is a simple calculational method and useful for a rough understanding of the electronic structures of metal complexes with large planar ligands.

References

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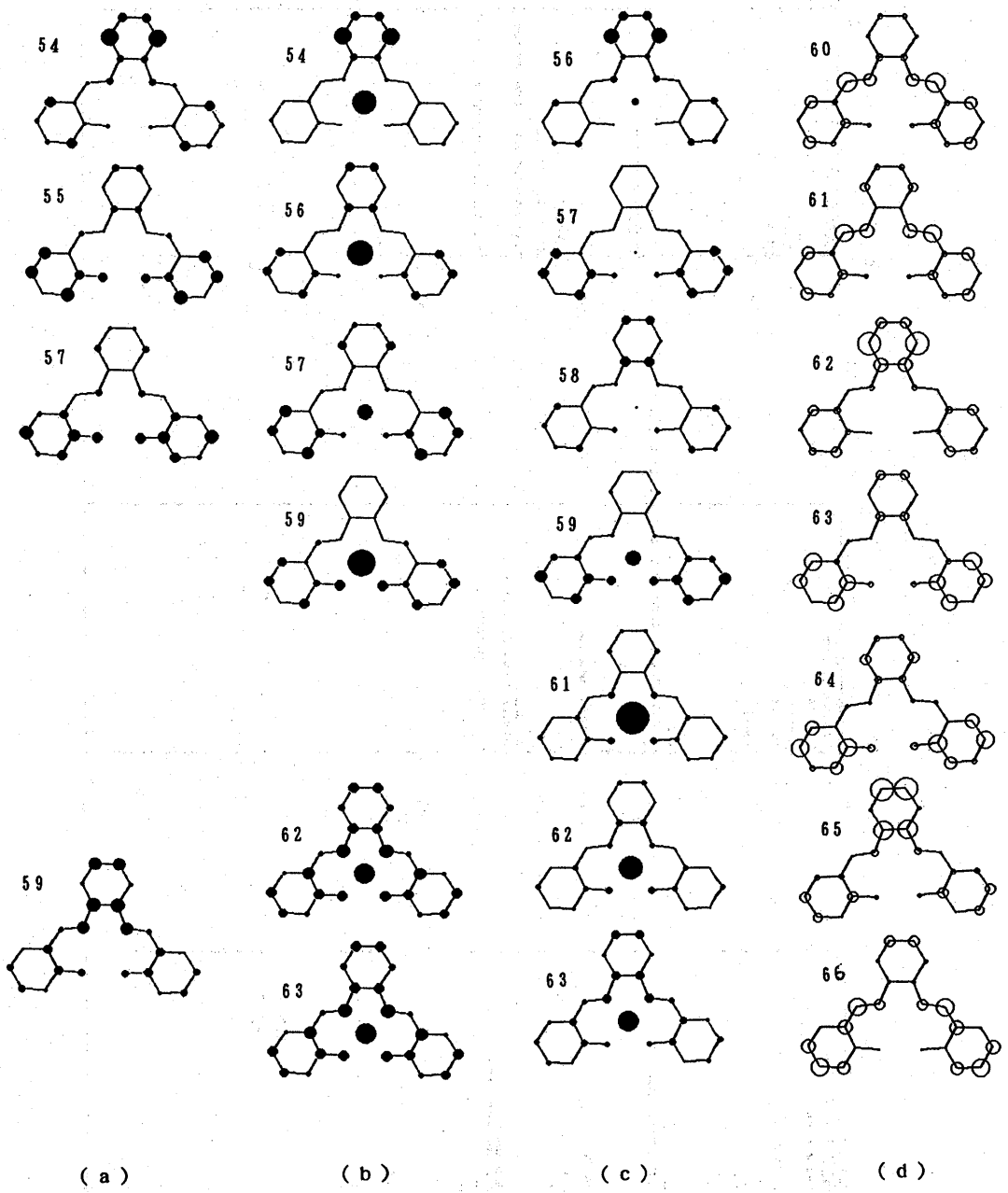

Fig. 1 The occupied orbitals of saloph^{2-} (a), planar [Co(saloph)] (b) and non-planar [Co(saloph)] (c) and the vacant orbitals of saloph^{2-} (d).

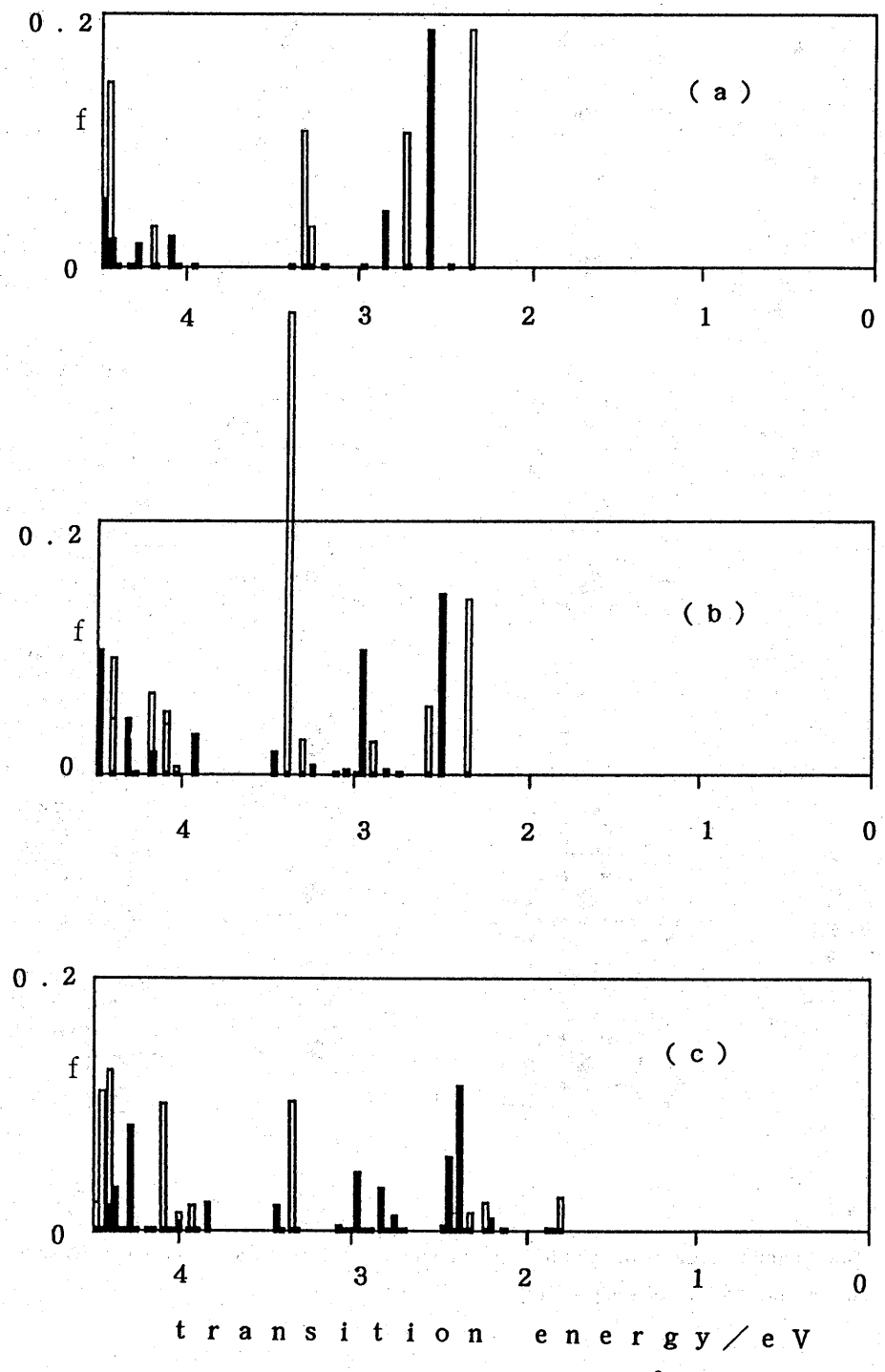

Fig. 2 The transition energies and the oscillator strengths of saloph^{2-} (a), planar [Co(saloph)] (b) and non-planar [Co(saloph)] (c).