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A New Optically Active Co(II) (salen) Type Complex Containing a Pentadentate Schiff-Base Ligand

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Synopsis. A new optically active square-pyramidal cobalt(II) complex, *N,N'*-bis(salicylaldehyde)-2-(*S*)4-*S*-methyl-4-thio-1,2-butanediiminatocobalt(II), was synthesized. The structure of this complex was examined.

The square-planar tetradentate Schiff-base complexes of cobalt such as cobaloxime, Co(salen), *etc.* have been widely studied as model compounds for coenzyme B_{12} and as oxygen carriers. Terent'ev[1] and Hipp[2] reported the conformation of *N,N'*-bis(salicylaldehyde)-(−)-propylenediiminatocobalt(II) based on analysis of the CD spectra in solution, stating that the δ conformation about the central chelate ring was preferred. It is well-known in the case of cobalamin that the spin state of Co(II) is low-spin and that the corrin ring is in-plane. Some data are available on Co(II) complexes containing a pentadentate Schiff-base ligand,[3] but in almost all cases the spin state of Co(II) was found to be high-spin. The two chelate rings composed of phenolic oxygen and the Schiff-base were not in-plane because of steric hindrance. It is therefore of interest to prepare a low-spin Co(II) complex containing a pentadentate Schiff-base ligand maintaining planarity and to examine the behavior of the atom coordinated in the apical position.

In this report we will describe the synthesis and structure of *N,N'*-bis(salicylaldehyde)-2(*S*)-4-*S*-methyl-4-thio-1,2-butanediiminatocobalt(II), Co(II)[sal_2-2(*S*)-SMT-BDA], [A], and its properties will be compared with those of *N,N'*-bis(salicylaldehyde)-1(*R*),2(*R*)-1,2-*trans*-cyclohexanediiminatocobalt(II), Co(II)[sal_2-(*R*)-CHXDA], [B], which has been discussed in the preceeding paper.[4]

Experimental

Preparation of Ligands: 2(*S*)-4-S-methyl-4-thio-1,2-butanediamine, [D], was prepared from (*S*)-methionine by the usual method. Bp/2 mmHg=81 °C; $[\alpha]_{589}^{30}=-12.3°$ (in 3% methanolic solution). NMR: (in d_4-MeOH) 1.63 (m, 2H, $-CH_2-$), 2.09 (s, 3H, $-CH_3$), 2.57 (t, 2H, $-CH_2-S$), 2.59 (d, 2H, $-CH_2-N$), 2.60 (m, 1H, $=CH-N$). *N,N'*-bis(salicylaldehyde)-2(*S*)-4-S-methyl-4-thio-1,2-butanediimine, [E], was prepared from salicylaldehyde and diamine [D] in a molar ratio of 2: 1 in ethanol.

Co(II)[sal_2-2(S)-*SMT-BDA*], [A]: 1.56 g of anhydrous cobalt acetate and 3.01 g of ligand [E] were reacted in 40 ml of 1-propanol at 60 °C under a nitrogen atmosphere for 20 min with stirring. After concentrating the solvent to about 10 ml, 20 ml of THF was added with stirring at 60 °C. Brown needle-like crystals precipitated when cyclohexane was added. These were filtered off and washed with cyclohexane. Found: C, 57.16; H, 5.29; N, 6.71%. Calcd. for $C_{19}H_{20}N_2O_2SCo$: C, 57.14; H, 5.05; N, 7.01%. IR: (KBr) 1600 (C=N), 1525 cm^{-1} (C=C).

Co(II)[sal_2-2(S)-*SMT-BDA*]·$2H_2O$, [C]: Similar method to that of complex [A] was used but aqueous ether was added instead of cyclohexane. Found: C, 51.54; H, 5.05; N, 6.43%. Calcd for $C_{19}H_{24}N_2O_4SCo$: C, 52.41; H, 5.56; N, 6.43%. IR: (KBr) 3400 (OH), 1634 and 1603 (C=N), 1537 cm^{-1} (C=C).

Results and Discussion

The main purpose of this study was to synthesize a low-spin square-pyramidal Co(II) complex containing a pentadentate Schiff-base ligand. It is generally accepted that the values of μ_{eff} of low-spin square-planar Co(II) complexes and the low-spin octahedral Co(II) complexes fall in the range 2.1—2.9 and 1.8—1.9 B.M., respectively, while the values of μ_{eff} of high-spin five-coordinated Co(II) complexes fall in the range 4.5—4.8 B.M.[5,6]

The planarity of the ligand can be discussed in terms of the shape of the CD spectrum at the π-π^* transition

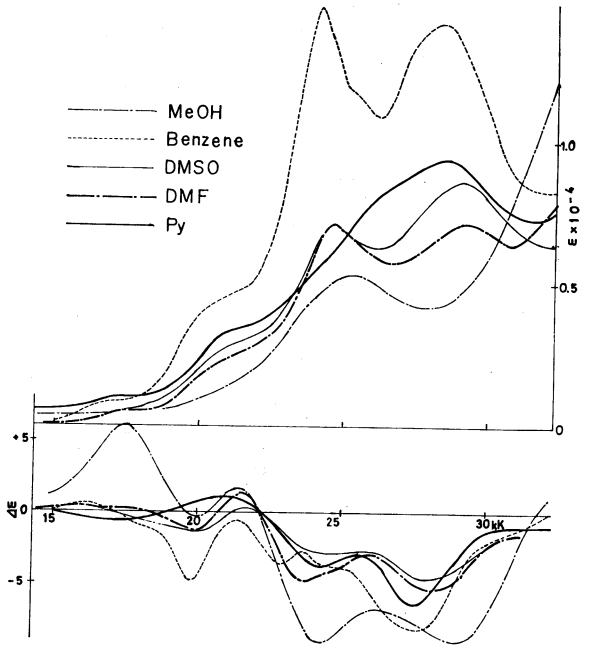

Fig. 1. The CD and absorption spectra of Co(II) [sal_2-2(*S*)-SMT-BDA] in various solvents.

region.[2,7,8] The π-π^* transition appears at about 28 kK and shows only one component in the cases of Co(II) and Ni(II) complexes with tetradentate Schiff-base ligands while in the corresponding Zn(II) complex the π-π^* transition contains two components with nearly equal magnitudes of positive and negative CD due to the T_d symmetry.

The magnetic moment, μ_{eff}, of complex [A] measured

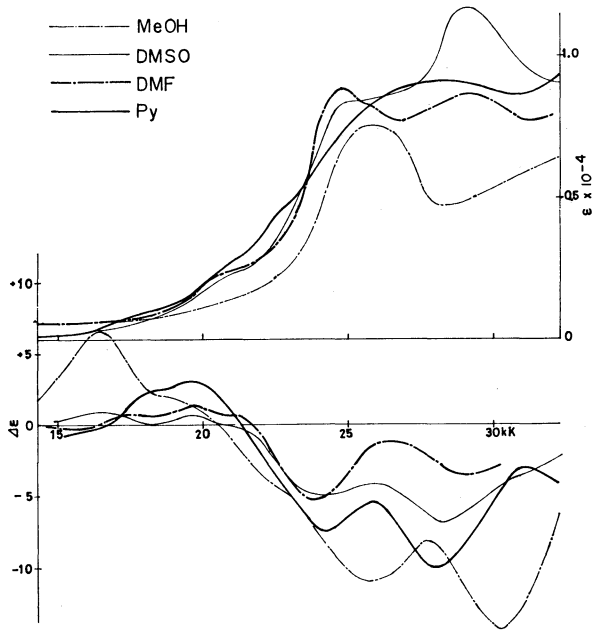

Fig. 2. The CD and absorption spectra of Co(II) [Sal_2-(*R*)-CHXDA] in various solvents.

by the method of Guoy was 1.99 B.M.; it was 2.41 B.M. in complex [B].[4] This shows that the spin state of complex [A] is low-spin, suggesting that complex [A] is square-pyramidal. The CD and associated absorption spectra of complex [A] were measured in various solvents and are given in Fig. 1. Those of complex [B] are given in Fig. 2. All the CD spectra in Fig. 1 show only one component at about 28 kK. These results suggest that the two chelate rings, composed of phenolic oxygen and Schiff-base, are coplanar in complex [A]. In complex [B] the central chelate ring is locked in the λ conformation.[4] Comparing the CD spectra of complex [A] and [B], shown in Figs. 1 and 2, the shapes of spectra are similar. Nevertheless, the CD spectra of the ligands [E] and [F][9] are almost opposite in sign, reflecting the difference of chirality of the asymmetric carbon. This would be attributed to the similarity of the central chelate ring conformation in complexes [A] and [B]. These results in the measurements of the CD spectra support the view that complex [A] is a low-spin square-pyramidal Co(II) complex. A possible structure of complex [A] is shown

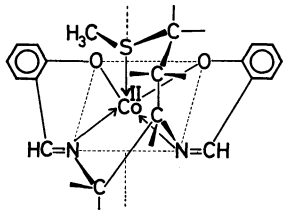

Fig. 3. The structure of Co(II) [sal_2-2(*S*)-SMT-BDA]

in Fig. 3.

A drastic change was observed in the CD spectrum of complex [A] in Py solution after dissolving complex [A] in aqueous methanol and evaporating off the solvent. This change would depend on whether or not H_2O coordinates in the *trans* position of the sulfur atom. When the *trans* position of the sulfur atom is occupied by H_2O, a Py molecule would attack at the coordinated sulfur atom, resulting in substitution of the sulfur atom. On the other hand, the Py molecule would simply interact with the vacant site in the *trans* position of the sulfur atom if no H_2O molecule was present in this position.

The complex [C], Co(II)[sal_2-2(*S*)-SMT-BDA]·$2H_2O$, was synthesized to confirm such a drastic change in the CD spectrum in Py solution. The CD spectra of complex [C] were measured in various solvents (Fig. 4). A drastic change in the CD spectrum was observed in Py solution, while similar CD spectra were seen in DMF, DMSO and methanol solutions. This drastic change also supports the view that complex [A] is a square-pyramidal Co(II) complex.

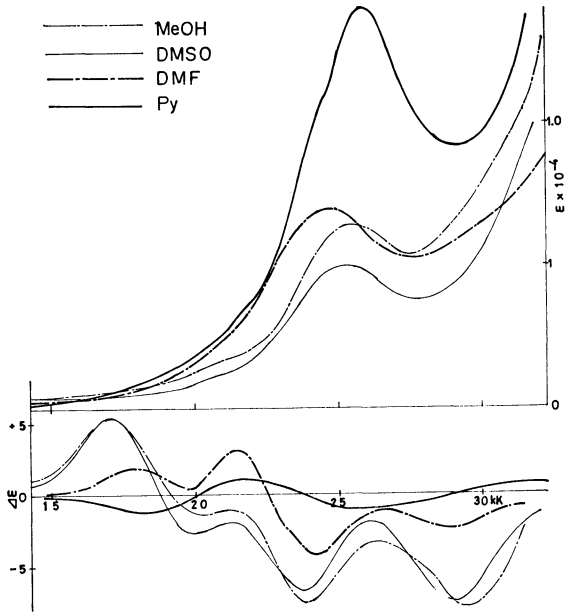

Fig. 4. The CD absorption spectra of Co(II) [sal_2-2(*S*)-SMT-BDA]·$2H_2O$ in various solvents

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9) ligand [F]: *N,N'*-bis(salicylaldehyde)-1(*R*),2(*R*)-1,2-*trans*-cyclohexanediimine.