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Stereochemistry of Bis[*N*-(2,6-diisopropylphenyl)salicylideneaminato]cobalt(II) Complexes

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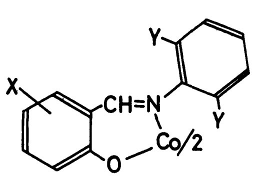
The compounds bis[*N*-(2,6-diisopropylphenyl)salicylideneaminato]cobalt(II) and analogous species with substituents at the 5-position of the salicyl moiety have been synthesized. They prefer the tetra-coordinate tetrahedral geometry in non-donor solvents, while some of them are forced into planar structures in the solid state. In pyridine, exclusively predominant species are five-coordinate complexes with the base bound with the cobalt(II) ion. Monopyridine adducts, which consist of five-coordinate complexes, have been isolated as crystals.

The stereochemistry of the cobalt(II) complexes with bidentate *N*-aryl- and *N*-alkylsalicylideneaminates, abbreviated as Co(X-sal-R)$_2$, has been widely studied.[1,2] In order to investigate the steric and electronic effects of the Schiff bases on the stereochemistry of these cobalt(II) complexes, a series of bis[*N*-(2,6-dialkylphenyl)salicylideneaminato]cobalt(II) complexes were studied previously, the alkyl being methyl and ethyl.[3]



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In the present work, cobalt(II) complexes of the type Co(X-sal-R)$_2$, for which R is 2,6-diisopropylphenyl, have been examined. It is anticipated that the steric effects arising from the substituents at the 2- and 6-positions may become more explicit in the complexes of this series, since the isopropyl group is more bulky than the methyl and ethyl groups. During this study, we have isolated for the first time the spin-paired planar cobalt(II) complexes with the *N*-arylsalicylideneaminates.

Experimental

Materials. 2,6-Diisopropylaniline was obtained commercially.

Bis[*N*-(2,6-dissopropylphenyl)salicylideneaminato]cobalt(II) and analogous species, which are abbreviated as Co(X-sal-dpp)$_2$, were synthesized in red-orange crystals in the same manner as reported previously.[2,3] They are readily soluble in chloroform, benzene, and acetone, but slightly soluble in ethanol.

TABLE 1. ANALYTICAL DATA OF BIS[*N*-(2,6-DIISOPROPYLPHENYL)SALICYLIDENEAMINATO]COBALT(II), Co(X-sal-dpp)$_2$

Compound	Calcd (%)			Found (%)			μ[a)]
	H	C	N	H	C	N	BM
Co(H-sal-dpp)$_2$	7.15	73.65	4.52	7.18	73.93	4.63	4.5
Co(5-Br-sal-dpp)$_2$	5.45	58.70	3.60	5.32	58.72	3.61	2.4
Co(5-Cl-sal-dpp)$_2$	6.15	66.28	4.07	6.22	66.23	4.13	2.6
Co(5-NO$_2$-sal-dpp)$_2$	5.97	64.31	7.89	6.06	63.99	7.75	5.1
Co(H-sal-dpp)$_2$·py[b)]	7.07	73.90	6.01	6.97	73.82	6.07	5.0
Co(5-Br-sal-dpp)$_2$·py	5.53	60.29	4.91	5.33	60.26	4.95	4.8
Co(5-Cl-sal-dpp)$_2$·py	6.17	67.27	5.47	6.15	67.27	5.46	4.9
Co(5-NO$_2$-sal-dpp)$_2$·py	6.01	65.47	8.88	6.13	65.44	9.15	4.8

a) At room temperature. b) py: Pyridine.

Monopyridine adducts were also obtained in orange crystals as described previously.[2,3]

Analytical data of these complexes are given in Table 1.

Measurements. Electronic absorption spectra of the complexes in solution and in Nujol were recorded on a Shimadzu MPS-500 spectrophotometer. Magnetic measurements at room temperature were carried out by the Gouy method using CoHg(SCN)$_4$ as a calibrant.

Results and Discussion

Previous extensive studies of cobalt(II) complexes with bidentate *N*-alkyl- and *N*-arylsalicylideneaminates have disclosed that all these cobalt(II) complexes are tetrahedral,[1,2] with the exception of bis(*N*-methylsalicylideneaminato)cobalt(II), which consists of binuclear molecules with the cobalt(II) ion in five-coordinate environment.[4]

In the complexes (I), the steric constraint due to the bulky substituent (R-2,6-Y$_2$-C$_6$H$_3$) seems to be appreciable. In view of the conformations observed in all known crystal structure analyses, the phenyl group in the complexes is expected to be essentially perpendicular to the salicylideneaminate plane.[1] The cobalt(II) complexes with R=2,6-Me$_2$-C$_6$H$_3$ and 2,6-Et$_2$-C$_6$H$_3$ prefer the tetra-coordinate tetrahedral geometry in the solid state and in non-donor solvents, although the steric constraint is not slight.[3] In the cobalt(II) complexes with R=2,6-(*i*-Pr)$_2$-C$_6$H$_3$, which is more bulky than 2,6-Et$_2$C$_6$H$_3$, there is remarkable steric constraint not only on the tetrahedral configuration but also on the planar one. However, either of the two configurations is not precluded from the steric condition alone.

The cobalt(II) complexes Co(X-sal-dpp)$_2$ (X=H, 5-Cl, 5-Br, and 5-NO$_2$) in chloroform show electronic spectra typical of the tetrahedral cobalt(II) complex.[2] Some of the representative spectra are shown in Fig. 1, the main absorption maxima being set out in Table 2.

In the solid state, the configuration of these cobalt(II) complexes depends upon the substituent X at the 5-position of the salicyl moiety. The cobalt(II) complex (X=H) in the solid state is concluded to have a tetrahedral configuration on the basis of the magnetic moment (4.4 BM) and an electronic spectrum with a broad d-d band consisting of double humps at about 8.2

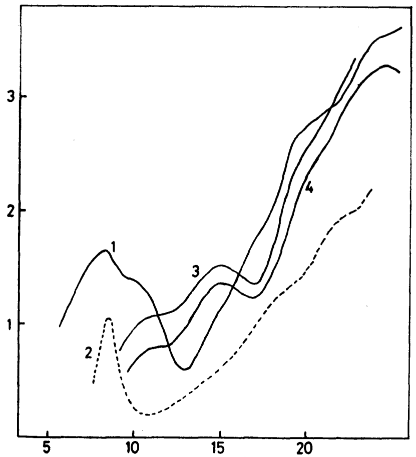

Fig. 1. Electronic absorption spectra of Co(5-Br-sal-dpp)$_2$ (curves 1—3) and Co(5-Br-sal-dpp)$_2$·py (curve 4).
1: In $CHCl_3$, 2: in Nujol (arbitrary absorbance scale), 3: in pyridine; 4: in Nujol (arbitrary absorbance scale).

and 10.7×10^3 cm^{-1}. On the contrary, the two complexes (X=5-Cl and 5-Br) in the solid state are paramagnetic with magnetic moments at room temperature of 2.6 and 2.4 BM, respectively, which lie in the range expected for the spin-paired planar cobalt(II) complex.$^{5)}$ Their electronic spectra have a comparatively sharp d-d band at about 8.5 and 8.4×10^3 cm^{-1}, respectively, in agreement with the spin-paired planar structure.$^{6)}$ Thus they provide new examples of spin-paired planar cobalt(II) complexes with bidentate *N*-arylsalicylideneaminates. Since the two complexes are tetrahedral in chloroform, the energy gap between the tetrahedral and the planar configurations seems to be small.

In pyridine, these cobalt(II) complexes Co(X-sal-dpp)$_2$ (X=H, 5-Cl, 5-Br, and 5-NO_2) exist exclusively as five-coordinate species with a pyridine molecule coordinated. Beer's law is found to hold good, so that no assumption of equilibria among various species with different structures is needed. The five-coordinate pyridine adducts have been isolated in crystals from the pyridine solutions, their spectra (Fig. 1 and Table 2) being in agreement with the proposed five-coordinate structure. Six-coordinate bis(pyridine)adducts have neither been detected in the solutions, nor isolated in crystals.

The complex (X=5-NO_2) in the solid state has magnetic moment of 5.1 BM, which is in the range expected for the 6-coordinate cobalt(II) complex. Its electronic spectrum (Table 2) is also typical of the 6-coordinate cobalt(II) complex. A multinuclear structure is most likely, although a definitive conclusion about the precise structure must await further studies.

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TABLE 2. MAIN ABSORPTION MAXIMA OF BIS[*N*-(2,6-DIISOPROPYLPHENYL)-SALICYLIDENEAMINATO]COBALT(II), Co(X-sal-dpp)$_2$

Compound	Medium	$\tilde{\nu}/10^3$ cm^{-1} (log ε)		
Co(H-sal-dpp)$_2$	$CHCl_3$	8.2 (1.77)	10.3 (1.46) sh	
	Nujol	8.2	10.7 sh	
	py	7.3 (0.85)	11.0 (1.06)	15.1 (1.46)
Co(H-sal-dpp)$_2$·py	Nujol	7.2	11.1	15.2
Co(5-Cl-sal-dpp)$_2$	$CHCl_3$	8.3 (1.59)	10.1 (1.36) sh	
	Nujol	8.4 (sharp)		
	py	7.3 (0.85)	11.3 (1.07)	15.3 (1.52)
Co(5-Cl-sal-dpp)$_2$·py	Nujol	7.2	11.3	15.3
Co(5-Br-sal-dpp)$_2$	$CHCl_3$	8.3 (1.65)	10.2 (1.35) sh	
	Nujol	8.4 (sharp)		
	py	7.3 (0.82)	11.0 (1.05)	15.2 (1.51)
Co(5-Br-sal-dpp)$_2$·py	Nujol	7.1	11.2	15.2
Co(5-NO_2-sal-dpp)$_2$	$CHCl_3$	8.1 (1.84)	10.2 (1.60) sh	
	Nujol	9.6	16.3 sh	26.0 (CT) str
	py	7.2 (0.81)	11.4 (1.25) sh	15.2 (1.78)
Co(5-NO_2-sal-dpp)$_2$·py	Nujol	7.0	11.3	15.3

sh: Shoulder. str: Strong. CT: Charge transfer band.