NOTES

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ESR Spectra of Quadridentate Salicylaldehyde Schiff Base Complexes of Cobalt(II) and Copper(II) in Chloroform and in Dichloromethane

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Synopsis. ESR parameters for the titled complexes have been obtained from the spectra of "powders of frozen solutions." The spectra of "not crushed frozen solutions" indicated that the axes of g_3 (3.23—3.68) of the cobalt complexes are in the molecular planes.

Chloroform has been frequently used as a solvent for ESR measurements of many metal chelate complexes. However, chloroform does not form good glass at 77 K, and therefore, the typical ESR patterns of frozen solutions cannot be observed for some metal chelate complexes in chloroform. This phenomenon had been explained by Fierz and von Zelewsky for frozen chloroform solutions of bis(1,3-diphenyl-1,3-propanedionato)copper(II) as follows:[1] When the sample tube of the chloroform solution was cooled directly with liquid nitrogen, some metal complexes are aligned in certain orientations in considerably large grains of chloroform crystals. We have observed the same phenomena for salicylaldehyde Schiff base complexes of cobalt(II) and of copper(II) both in chloroform and in dichloromethane. In order to obtain correct ESR parameters of these complexes in these solvents, we measured the ESR spectra of the "powders of the frozen solutions" by the method as explained below.

The dewar and sample tube system is set as shown in Fig. 1. A stream of dry nitrogen is passed through the upper part of the sample tube during the measurement to prevent the condensation of oxygen or moisture into the sample tube. After both the dewar and sample tube were filled with liquid nitrogen, a chloroform solution is added dropwise into the sample tube from the capillary. When the spectra of cobalt(II) complexes were measured, the capillary filled with dry nitrogen or dry argon was used. The solid sample deposited at the bottom of the tube should be further crushed to fine powders by a bamboo rod.

The ESR spectra of *N*,*N'*-ethylene-bis(5-methoxysalicylideneiminato)copper(II) (Cu(5MeOSalen)) in chloroform measured by the two different methods are shown in Fig. 2, where (a) is measured by simply freezing the solution as usual, while (b) is measured by the above-mentioned method. As figure 2 shows, the spectra obtained by the usual method did not show any structures due to $g_{//}$ and $A_{//}$. These phenomena were also observed for commercially obtained chloroform which contains about 1% ethanol. These spectra clearly indicate that when the chloroform solution is rapidly frozen in the sample tube by liquid nitrogen, the chloroform crystal has a tendency to grow toward a certain direction with respect to the sample tube and to align the coordination plane of the complex perpendicular to the direction of the sample tube. The same phenomena were also observed in the case of the other quadridentate salicylaldehyde Schiff base complexes of copper(II). The ESR spectra of *N*,*N'*-ethylene-bis(salicylideneiminato)cobalt(II) (Co(Salen)) in chloroform are shown in Fig. 3. In this case, the intensities of the spectra in the field range

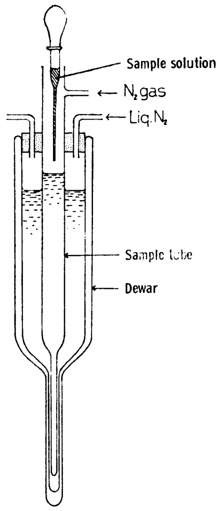

Fig. 1. Dewar and sample tube system.

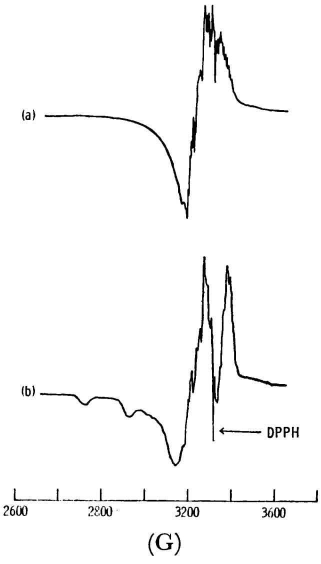

Fig. 2. ESR spectra of Cu(5MeOSalen) in chloroform measured by a), simply freezing the sample solution as usual, and b), improved method.

Table 1. Magnetic parameters

Complex	Solvent	g_1	g_2	g_3			A_1[a)]	A_2[a)]	A_3[a)]		
Co(Salen)	$CHCl_3$	—	—	3.34	3.28	3.23	—	—	153	141	125
	CH_2Cl_2	1.91	1.96		3.32		38	34		149	
Co(Salbn)[b)]	$CHCl_3$	—	—	3.61	3.35	3.28	—	—	223	164	142
	CH_2Cl_2	—	—		3.32					147	
Co(Salibn)[c)]	$CHCl_3$	—	—	3.68	3.59		—	—	250	221	
	CH_2Cl_2	1.85	1.89		3.64		48	48		233	
Co(Salstn)[d)]	$CHCl_3$	—	—	3.66	3.42		—	—	234	177	
	CH_2Cl_2	1.91	1.98		3.30		35	36		146	

a) $\times 10^4$ cm^{-1}. b) *N,N'*-Bis(salicylidene)-2,3-butylenediaminocobalt(II) (*racemic*). c) *N,N'*-Bis(salicylidene)-isobutylenediaminocobalt(II). d) *N,N'*-Bis(salicylidene)stilbenediaminocobalt(II) (*meso*).

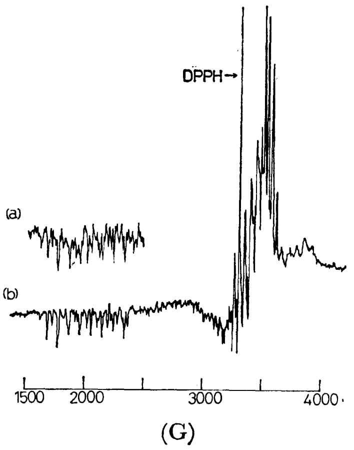

Fig. 3. ESR spectra of Co(Salen) in chloroform measured by a), simply freezing the sample solution as usual, and b), improved method.

between 1600 and 2400 gauss measured by the usual method did not decrease so much as that of the $g_{//}$ component of Cu(5MeOSalen) did, though the patterns of the spectra in this region became very complicated. It is naturally supposed that the orientation of Co(Salen) in rapidly frozen solutions is similar to those of Cu(5MeOSalen) in chloroform crystals. Therefore, if the principal axis of the g tensor corresponding to the progressions between 1600 and 2400 gauss had directed perpendicular to the molecular planes of the cobalt complexes, similar decrease in the intensity of these progressions could have been observed. These experimental results suggest that the peaks observed in this region are not due to the component of the g tensor perpendicular to the molecular plane. The ESR spectrum of Co(Salen) in chloroform indicates that more than 3 kinds of paramagnetic centers exist in the chloroform crystals. The observed ESR parameters were slightly different from those reported by Busset, *et al.* for the ESR spectra measured at 113 K.[2)] Though they have reported the time development of the signals, we could not observe such phenomena but always observed the reproducible spectra. Similar phenomena due to the crystallizations of the solvents were observed for the dichloromethane solutions of cobalt(II) complexes. In the case of dichloromethane solutions, the peaks due only to one paramagnetic centers were more intensely observed than those of any other centers, so that various magnetic parameters could be estimated. This is the first report that the high field part of the ESR spectra of the low spin planar salicylaldehyde Schiff base complexes of cobalt(II) in the non-coordinating solvent like dichloromethane could be clearly analysed.

In Table 1, the magnetic parameters of various quadridentate salicylaldehyde Schiff base complexes of cobalt(II) in chloroform and in dichloromethane are shown. It should be noted that the g_2 values obtained in this experiment are considerably smaller than those reported for Co(Salen) in chloroform by Busset, *et al.*[2)] All the attempts to correlate these parameters to the possible ground electronic configurations of these complexes by the usual second-order perturbation calculations[2–4)] have failed. It seems necessary to calculate the g values by diagonalizing the spin orbit interactions for several possible electronic configurations.

Experimental

The salicylaldehyde Schiff base complexes of cobalt(II) and copper(II) were obtained according to the literature.[5)] Chloroform and dichloromethane were purified by the usual methods.[6)] Deoxygenated solutions of cobalt(II) complexes were prepared with a vaccum line and transfered into the sample tube in an atmosphere of dry argon. ESR spectra at X-band were measured with a Hitachi 771 spectrometer. The resonance fields were calibrated with that of powders of DPPH.

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