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Cobalt(III) Complexes with Schiff Bases Obtained from Salicylaldehyde Derivatives and Alkanol Amines[*1]

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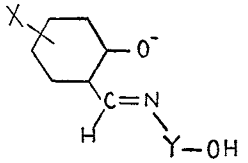
Cobalt(III) complexes with Schiff bases (X-SAL.Y-OH) obtained from salicylaldehyde derivatives and alkanol amines ($H_2N.Y\text{-}OH$) were synthesized as crystals. Two types of diamagnetic cobalt(III) complexes were obtained, one being green (type A) and the other red (type B). In the complexes of type A with the general formula $[Co(H\text{-}SAL.R)_3]$, where $R=CH_2CH_2CH_2OH$ and $CH_2CH_2CH_2OCH_3$, the ligands are considered to function as bidentate ligands, the terminal hydroxyl or methoxy groups not being bound with the cobalt(III) ion. In the complexes of type B with the general formula Co(X-SAL.Y-OH)(X-SAL.Y-O), where X=H and $3\text{-}CH_3O$, and $Y=CH_2CH_2$, $CH_2CH(CH_3)$ and $C(CH_3)_2CH_2$, the ligands function as terdentate ligands.

In previous papers[1-3] we reported nickel(II) and copper(II) complexes with Schiff bases obtained from salicylaldehyde derivatives and alkanol amines (formula I), and disclosed that the behaviour of the alcoholic hydroxyl group varies depending upon the kind of the central metal ions on the one hand and upon the nature of the ligands on the other. In this connection, it seems worthwhile to examine the corresponding complexes with other metal ions and to compare the results with the previous ones. The present paper deals with cobalt(III) complexes with the ligands denoted by formula I.



Formula I

Experimental

Materials. The cobalt(III) complexes, which are shown in Table 1, were prepared according to the following three methods, (1) from cobalt(II) acetate, (2) from bis(salicylaldehydato)- or bis(substituted salicylaldehydato)-cobalt(II) and an alkanol amine, and (3) from cobalt(II) acetate and a Schiff base. These methods are similar to those previously described.[4,5] In methods (1) and (3), sodium carbonate or sodium ethanolate was added to the reaction mixture. Purification was carried out by recrystallizing the crude products from suitable organic solvents like methanol, ethanol or chloroform.

The complexes of the $[Co(H\text{-}SAL.R)_3]$ type (type A), obtained as dark-green crystals, are insoluble in water but soluble in methanol, ethanol, chloroform, benzene and pyridine.

The complexes of the Co(X-SAL.Y-OH)(X-SAL.-Y-O) type (type B), obtained as red or brownish red crystals, are insoluble in water, slightly soluble in chloroform and benzene, and souble in methanol and ethanol. The solubility in any of these solvents is not high enough to allow any determination of the molecular weights of these complexes.

Analytical data of these complexes are shown in Table 1.

Measurements. Electronic absorption spectra were determined with a Shimadzu MPS-50L spectrophotometer and a Shimadzu QR-50 spectrophotometer. Infrared spectra were determined with a Hitachi-EPI-2 IR-spectrophotometer.

The diamagnetism of the complexes was detected by the Gouy method.

Results and Discussion

Two types of complexes were obtained with the ligands of formula I, one being green (type A) and the other red (type B). Since both these complexes

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2) S. Yamada, Y. Kuge and K. Yamanouchi, *Inorg. Chim. Acta*, **1**, 139 (1967); S. Yamada, H. Nishikawa, Y. Kuge and K. Yamanouchi, *Sci. Rep. Coll. Gen. Educ. Osaka Univ.*, **16**, 11 (1967).

3) S. Yamada, E. Ohno, Y. Kuge, A. Takeuchi, K. Yamanouchi and K. Iwasaki, *Coordin. Chem. Rev.*, **3**, 247 (1968).

4) S. Yamada, *ibid.*, **1**, 415 (1966).

5) R. H. Holm, G. W. Everett, Jr., and A. Chakravorty, "Progress in Inorganic Chemistry," Vol. VII, ed. by F. A. Cotton, Interscience Publishers, New York, N. Y. (1966), p. 83.

TABLE 1. ANALYTICAL DATA OF [Co(H-SAL.R)$_3$] (type A) AND Co(X-SAL.Y-OH)(X-SAL.Y-O) (type B)

X	Y or R	Found, % C	Found, % H	Found, % N	Calcd, % C	Calcd, % H	Calcd, % N	type
H	CH_2CH_2	55.48	5.13	6.93	55.96	4.96	7.25	B
	$CH_2CH(CH_3)$	52.87	6.05	5.94	53.34	6.04	6.22	B*
	$CH_2CH_2CH_2OH$	59.78	6.12	6.91	60.70	6.11	7.08	A
	$CH_2CH_2CH_2OCH_3$	62.53	6.70	6.51	62.37	6.62	6.62	A
	$C(CH_3)_2CH_2$	58.75	6.23	5.92	58.54	6.25	6.20	B
3-CH_3O	CH_2CH_2	53.36	5.29	6.22	53.34	6.04	6.22	B*
	$CH_2CH(CH_3)$	50.08	6.51	5.46	50.01	6.29	5.30	B**
	$C(CH_3)_2CH_2$	55.69	6.36	5.44	55.40	6.35	5.38	B***

* With two water molecules of crystallization
** With three water molecules of crystallization
*** With one water molecule of crystallization

are diamagnetic, they are concluded to be cobalt(III) complexes of a low-spin type. It is well known that cobalt(III) (d^6) complexes of a low-spin type usually have an octahedral configuration.

The electronic spectra of these complexes are shown in Fig. 1. The spectra of the complexes of type A are very similar to those of Co(H-SAL.-alkyl)$_3$.[4,6,7] The close similarity in the spectra indicates that these green complexes (type A) may take a configuration similar to that of the Co(H-SAL.-alkyl)$_3$ type, namely a *mer*-configuration.[8] Their spectra in pyridine are nearly the same as those in non-donor solvents, showing that the configuration of the complexes in non-donor solvents is retained, when dissolved in pyridine. It is thus found that the ligands H-SAL.R function as bidentate ligands in the complexes of type A, the terminal hydroxyl and the methoxy group not being bound with cobalt(III) ion. Inspection of the steric condition shows that the hydroxyl group at the γ-position may not be as favorable as that at the β-position, as in the complexes of the B-type, for coordination with the central metal ion.[1,4,5] It is known that the coordinating ability of the methoxy group is much lower than that of the hydroxyl group.

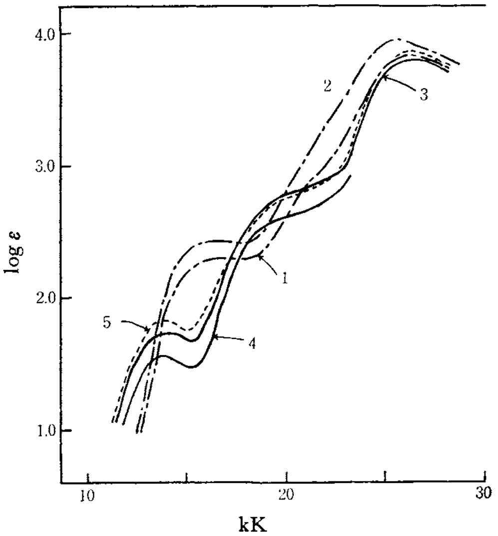

Fig. 1. Electronic absorption spectra of Co(H-SAL.R)$_3$ (type A) and Co(H-SAL.Y-O) (H-SAL.Y-OH) (type B): 1, R=$CH_2CH_2CH_2OH$ (type A), in ethanol; 2, R=n-C_3H_7 (type A), in ethanol; 3, Y=$C(CH_3)_2CH_2$ (type B), in methanol; 4, Y=$C(CH_3)_2CH_2$ (type B), in the solid state (by reflectance); 5, Y=$CH_2CH(CH_3)$ (type B), in chloroform.

The red cobalt(III) complexes of type B may be formulated as Co(X-SAL.Y-O)(X-SAL.Y-OH), where Y denotes CH_2CH_2, $CH_2CH(CH_3)$ and $C(CH_3)_2CH_2$ for X=H and 3-CH_3O. The presence of the ligand X-SAL.Y-OH in these complexes is supported by infrared spectra, which have absorption peaks at about 3000 to 3500 cm^{-1} due to the hydroxyl group.*2 The electronic absorption spectra of all the complexes of type B in solution or in the solid state (Fig. 1) are similar to each other, showing that these cobalt(III) complexes have a similar configuration, and that the configuration in the solid state is retained in solution. It should be noted that the main features of these spectra, with absorption maxima at about 14 kK (log ε 1.5—2.0), about 20 kK (log ε 2.5—3.0) and about 26.5 kK (log ε 3.7—4.0), are remarkably similar to those of bis[2-(salicylideneamino)alkanoato]cobaltate(III) complexes, which show absorption maxima at 15.0 kK (log ε 1.95), 19.8 kK (log ε 2.75) and 26.5 kK (log ε 3.7)[9]. It seems, therefore, very likely that the red complexes of type B have a configuration similar to that of the bis[2-(salicylideneamino)alkanoato]-complexes, which were

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6) H. Nishikawa and S. Yamada, This Bulletin, **37**, 1154 (1964).

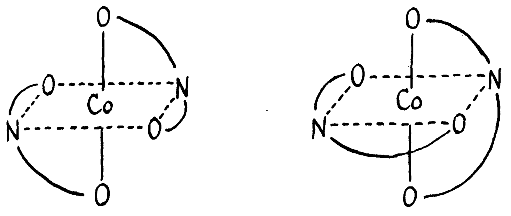
7) S. Yamada, *Coordin. Chem. Rev.*, **2**, 83 (1967).

8) M. Ciampolini, F. Maggio and F. P. Cavasino, *Inorg. Chem.*, **3**, 1188 (1964).

9) R. C. Burrows and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **88**, 4150 (1966).

concluded previously to be uninuclear, octahedral cobalt(III) complexes.[9] Thus, in the complexes of type B, the ligands are found to act as terdentate ligands.

For coordination compounds of type $M(ABC)_2$, many isomers are possible, where the notation ABC denotes a terdentate ligand bearing three different ligating atoms. It is to be noted that the *d-d* band maxima at the lowest frequencies of the complexes of type B lie at remarkably low frequencies (about 14.0 kK), as compared with those of the complexes of the $[Co(X\text{-}SAL.alkyl)_3]$ type (about 16.1 kK). It is expected that the complexes of the *trans*-$[Co(N)_2(O)_4]$ type may show remarkable splitting of the *d-d* band, and the splitted component might appear in the region of considerably low frequencies. The arrangement of the ligand atoms shown in Fig. 2(a) or (b) is highly probable for the structure of the complexes of type B, since such a configuration would yield a *d-d* band maximum at the lowest frequency. However, it is not possible at the present stage to draw a definite conclusion about the precise configuration. Another possibility like a binuclear configuration might not be completely excluded. The low solubility of the complexes of type B did not allow any determination of molecular weight.



(a) (b)

Fig. 2. Proposed configurations for Co(X-SAL.-Y-O)(X-SAL.Y-OH).

It has thus been revealed that all the cobalt(III) complexes obtained are octahedral, six-coordinated. This result, which is different from that for the corresponding nickel(II) and copper(II) complexes,[1,2] is in agreement with the general tendency of cobalt(III) to form much more stable, octahedral complexes as compared with nickel(II) or copper(II).

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[*2] It is probable that the hydroxyl group forms a hydrogen bond with an oxygen atom of the neighbouring ligand. More detailed study was not carried out.