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Cobalt(II) Complexes of β-Ketoamines Derived from β-Diketones and Aromatic Amines[*1,*2]

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Many compounds of the $Co(Aca.R)_2$ and the $Co(Bza.R)_2$ type have been synthesized, in order to examine the stereochemistry of bis(β-ketoaminato)cobalt(II) complexes (bis(acetylacetone- and bis(benzoylacetone-aminato)cobalt(II) complexes are abbreviated as $Co(Aca.R)_2$ and $Co(Bza.R)_2$, respectively, R being an aryl group attached to the nitrogen atom.) and compare it with that of bis(salicylideneiminato)cobalt(II)complexes. The configuration of these cobalt(II) complexes in non-donor solvents is tetrahedral, but the complexes in pyridine take a tetrahedral, a penta-coordinate or an octahedral configuration, depending upon the ligand. The complexes of the $Co(Bza.R)_2$ type in pyridine take an octahedral configuration, except for $Co(Bza.2,6\text{-}X_2C_6H_3)_2$, where X denotes CH_3 and C_2H_5. On the contrary, $Co(Aca.CH_3C_6H_4)_2$, $Co(Aca.2,6\text{-}(CH_3)_2C_6H_3)_2$ and $Co(Aca.\alpha\text{-naphthyl})_2$ in pyridine retain a tetrahedral configuration, while the complexes, such as $Co(Aca.C_6H_5)_2$ and $Co(Aca.ClC_6H_4)_2$, take an octahedral configuration with two pyridine molecules bound to the cobalt(II) ion.

Cobalt(II) complexes of salicylideneimines have recently been studied, and a number of interesting conclusions have been obtained.[1-3] It is then thought to be of significance to compare the cobalt(II) complexes of salicylideneimines with those of β-ketoamines. In the present work, cobalt(II) complexes of β-ketoamines derived from aromatic amines and β-diketones, such as acetylacetone and benzoylacetone, are synthesized (Fig. 1), and

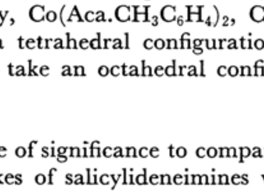

Fig. 1

[*1] Presented, in part, at the Ninth International Conference on Coordination Chemistry (9. I. C. C. C.), St. Moritz, 1966.

[*2] Bis(acetylacetone- and bis(benzoylacetone-aminato)cobalt(II) complexes are abbreviated in this paper as $Co(Aca.R)_2$ and $Co(Bza.R)_2$, respectively, R being an aryl group attached to the nitrogen atom.

1) H. Nishikawa and S. Yamada, This Bulletin, **37**, 8, 1154 (1964); *ibid.*, **38**, 1506 (1965).

2) L. Sacconi, P. L. Orioli, P. Paoletti and M. Ciampolini, *J. Am. Chem. Soc.*, **85**, 411 (1963), *etc.*

3) B. O. West, *J. Chem. Soc.*, **1962**, 1374.

their structure and bonding are discussed. Recently a communication[4] has been published concerning β-ketoamines derived from alkyl amines, but no report has so far been presented about the corresponding cobalt(II) complexes derived from aromatic amines.

Experimental

Materials. The cobalt(II) complexes of *N*-substituted acetylacetoneamines and benzoylacetoneamines were prepared by the following general method. A solution of cobalt acetate tetrahydrate (0.01 mol) and a ligand (0.033 mol) in ethanol was warmed at about 50 to 70°C under the reduced pressure. The mixture was boiled for some minutes and potassium ethanolate (0.03 mol) in ethanol (25 m*l*) was added to the mixture drop by drop with stirring. The stirring was continued for about one hour. After the solution was cooled, orange-colored crystals, which separated out, were collected on a filter, washed with a suitable solvent, and dried *in vacuo*. Purification was made by recrystallization from ethanol, chloroform or acetone. The compounds are stable in the atmosphere at room temperature. However, after standing for many months, some of them were observed to undergo partial decomposition. The elemental analyses of the new cobalt(II) compounds prepared in this work are shown in Tables 1 and 2.

Table 1. Elemental analyses of bis(acetylacetoneaminato)cobalt(II), Co(Aca.R)$_2$

R		C, %	H, %	N, %
2-$CH_3C_6H_4$	Calcd	66.24	6.43	6.43
	Found	65.88	6.51	6.35
4-$CH_3C_6H_4$	Found	66.49	6.47	6.44
2,6-$(CH_3)_2C_6H_3$	Calcd	67.38	6.96	6.04
	Found	66.57	7.10	5.97
2-ClC_6H_4	Calcd	55.50	4.62	5.88
	Found	54.11	4.55	5.50
3-ClC_6H_4	Found	55.59	4.68	5.80
4-ClC_6H_4	Found	54.95	4.71	5.55
α-Naphthyl	Calcd	70.99	5.56	5.52
	Found	68.13	5.47	6.21

Table 2. Elemental analyses of bis(benzoylacetoneaminato)cobalt(II), Co(Bza.R)$_2$

R		C, %	H, %	N, %
2-$CH_3C_6H_4$	Calcd	73.01	5.72	5.01
	Found	73.06	5.91	5.00
3-$CH_3C_6H_4$	Found	72.86	5.82	4.95
4-$CH_3C_6H_4$	Found	72.61	5.82	4.75
2,6-$(C_2H_5)_2C_6H_3$	Calcd	74.67	6.84	4.35
	Found	73.27	6.85	4.12
2,6-$(CH_3)_2C_6H_3$	Calcd	73.58	6.18	4.77
	Found	72.60	6.34	4.53
2-ClC_6H_4	Calcd	64.04	4.33	4.67
	Found	64.45	4.45	4.54
3-ClC_6H_4	Found	63.26	4.47	4.49
4-ClC_6H_4	Found	63.51	4.32	4.61
α-Naphthyl	Calcd	76.09	5.07	4.44
	Found	76.27	5.22	4.33

Measurements. The electronic absorption spectra of the compounds in solution were determined with a Shimadzu QR-50 spectrophotometer in the near-infrared, visible and ultraviolet regions at room temperature. Pyridine for a solvent was purified by distillation after having been dried with potassium carbonate. The reflection spectra of the compounds in the solid state were determined with a Hitachi EPU-2A spectrophotometer.

The magnetic measurements were carried out by the Gouy's method at room temperature.

Results and Discussion

Many cobalt(II) complexes of benzoylacetoneamines and acetylacetoneamines, Co(Bza)$_2$ and Co(Aca)$_2$, have newly been synthesized in the present work (Tables 1 and 2). As has been shown already,[1,2] the electronic absorption spectrum of the cobalt(II) complex depends upon the configuration of the complex and may be used diagnostically in the discussion of the configuration of the cobalt(II) complex.[5] The electronic spectra of the complexes prepared in the present work (Figs. 2 and 3) exhibit the main features characteristic of the corresponding salicylideneiminato-complexes of cobalt (II), which were concluded previously to have a tetrahedral configuration of a high-spin type. It is concluded, therefore, that all these complexes are tetrahedral and of a high-spin type. Magnetic moment of Co(Bza.*m*-ClC_6H_4)$_2$, for example, was determined to be 4.55 B. M. at room temperature.

It is interesting to examine the configuration of these complexes in pyridine. The electronic spectra

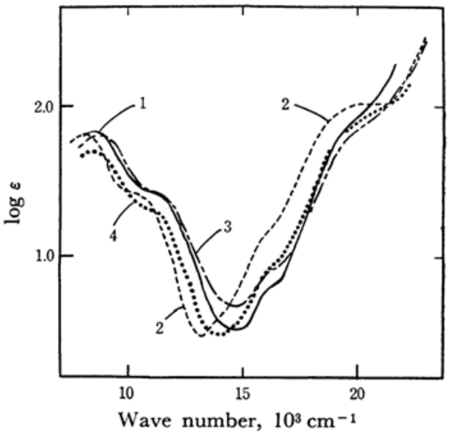

Fig. 2. Electronic absorption spectra of Co(Aca.R)$_2$ in chloroform: 1, R=4-ClC_6H_4; 2, R=2-$CH_3C_6H_4$; 3, R=4-$CH_3C_6H_4$; 4, R=α-naphthyl.

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[4] G. W. Everett, Jr., and R. H. Holm, *J. Am. Chem. Soc.*, **87**, 5266 (1965).

[5] H. Nishikawa and S. Yamada, This Bulletin, **37**, 8 (1964).

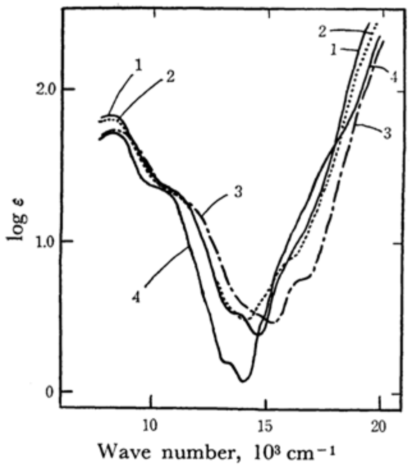

Fig. 3. Electronic absorption spectra of $Co(Bza.R)_2$ in non-donor solvents: 1, $R=4\text{-}ClC_6H_4$, in benzene; 2, $R=3\text{-}ClC_6H_4$, in chloroform; 3, $R=4\text{-}CH_3C_6H_4$, in chloroform; 4, $R=2,6\text{-}(CH_3)_2C_6H_3$, in benzene.

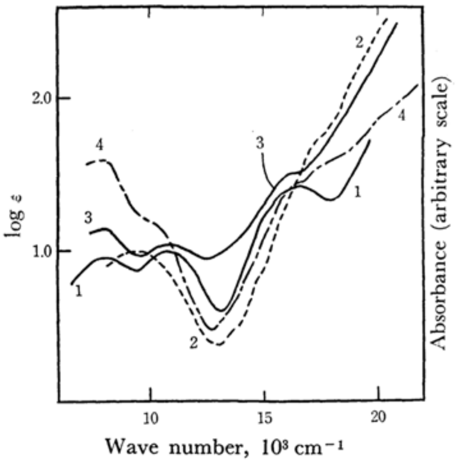

Fig. 4. Electronic absorption spectra of $Co(Sal.2,6\text{-}(CH_3)_2C_6H_3)_2\cdot Py$ (compound A) and $Co(Bza.R)_2$: 1, compound A (by reflectance); 2, $R=4\text{-}ClC_6H_4$, in pyridine; 3, $R=2,6\text{-}(C_2H_5)_2\text{-}C_6H_3$, in pyridine; 4, $R=2,6\text{-}(C_2H_5)_2C_6H_3$, in chloroform. The curve 1 is taken from S. Yamada and H. Nishikawa, This Bulletin, **38**, 683 (1965).

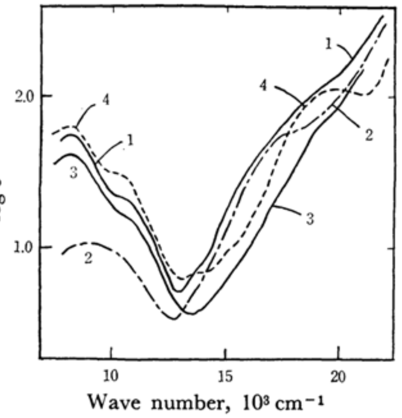

Fig. 5. Electronic absorption spectra of $Co(Aca.R)_2$ in pyridine: 1, $R=4\text{-}CH_3C_6H_4$; 2, $R=4\text{-}ClC_6H_4$; 3, $R=\alpha$-naphthyl; 4, $R=2,6\text{-}(CH_3)_2C_6H_3$.

clearly show that the complexes of the $Co(Bza.R)_2$ type in pyridine exist mostly as hexa-co-orinated complexes of the $Co(Bza.R)_2(Py)_2$ type*3 for $R=ClC_6H_4$, $CH_3C_6H_4$ and α-naphthyl; the curve for $R=ClC_6H_4$ is shown in Fig. 4. This seems to be quite reasonable, since in this case there is no steric hindrance against the six-co-ordination. On the contrary, this is found not to be the case with the compounds for $R=2,6\text{-}(CH_3)_2C_6H_3$ and $2,6\text{-}(C_2H_5)_2C_6H_3$. The electronic spectra of the two cobalt(II) complexes in pyridine differ considerably from the spectrum expected for the hexa-co-ordinated complex, and bear a close resemblance to that of $Co(Sal.2,6\text{-}(CH_3)_2C_6H_3)_2$ in pyridine, which consists mainly of the penta-co-ordinated complex, $Co(Sal.2,6\text{-}(CH_3)_2C_6H_3)_2\cdot Py$ (Fig. 4).⁶⁾ It is, therefore, concluded that the complex in pyridine takes up only one molecule of pyridine to form a penta-co-ordinated complex, $Co(Bza.2,6\text{-}X_2C_6H_3)_2\cdot Py$, X being$CH_3$ and C_2H_5. It is to be noted that Beer's law is found to be obeyed for $Co(Bza.2,6\text{-}X_2C_6H_3)_2$ in pyridine, so that there is no equilibrium consisting of the two species, that is, the complexes and the pyridine solvate, in the concentration range from 5×10^{-3} to 5×10^{-5} molar.

The electronic spectra, as shown in Fig. 5, indicate that the complexes of the $Co(Aca.ClC_6H_4)_2$ type in pyridine take up two pyridine molecules to form hexa-coordinated complexes. On the contrary, the complexes of the $Co(Aca.CH_3C_6H_4)_2$ type do not combine a pyridine molecule, but retain the tetrahedral configuration, when dissolved in pyridine. It is also found from electronic spectra (Fig. 5) that $Co(Aca.\ \alpha\text{-naphtyl})_2$ and $Co(Aca.2,6\text{-}X_2C_6H_3)_2$ keep the tetrahedral configuration in pyridine, X being CH_3 and C_2H_5. This result is quite different from the result obtained for the corresponding complexes of benzoylacetoneamines. The difference in this behavior between $Co(Aca.R)_2$ and $Co(Bza.R)_2$ may be due not to the steric factor, but to the difference in the ligand field strength and in the nature of the metal-ligand bond. Similarly, since the steric condition in $Co(Aca.CH_3C_6H_4)_2$ and $Co(Aca.ClC_6H_4)_2$ does not forbid the formation of the addition compound with co-ordination number

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*3 The notation Py denotes a molecule of pyridine.

6) S. Yamada and H. Nishikawa, This Bulletin, **38**, 683 (1965).

exceeding four, the observed difference between $Co(Aca.CH_3C_6H_4)_2$ and $Co(Aca.ClC_6H_4)_2$ may be ascribed to the difference in the inductive effect between Cl and CH_3. If comparison on the basis of all these findings is made among the cobalt(II) complexes having a tetrahedral configuration, it seems that the stronger the ligand field is, the higher the tendency of the cobalt(II) complex to favor the tetrahedral configuration *vis-à-vis* the penta-coordinate or the hexa-co-ordinate one.

It is interesting to compare Bza.R, Aca.R and Sal. R¹⁾ as ligands with each other concerning the coordination number of the cobalt(II) complexes which they form; the strength of the ligand field produced increases in the order: Sal.R$<$Bza.R$<$Aca.R. Th ecompairson reveals definitely that in pyridine the complexes of the $Co(Aca.R)_2$ type show higher tendency to retain the tetrahedral configuration than $Co(Bza.R)_2$ and $Co(Sal.R)_2$. Inspection of the results for these ligands indicates that the penta-coordination may occur, where the hexa-coordination might not be forbidden because of the orbital energy alone, but is greatly hindered for steric reasons.⁷⁾

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7) S. Yamada, *Coordin. Chem. Rev.*, **1** 415 (1966); S. Yamada, E. Yoshida and Y. Kuge, Proceedings 9. International Conf. Coordin. Chem. (9. I. C. C. C.), St. Moritz (1966), p. 68.