Palladium(II) Complexes of β-Ketoamines Derived from Acetylacetone and Amines

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In previous papers from this laboratory,[1] transition metal complexes of Schiff bases derived from salicylaldehyde and various amines were discussed. A similar study was then made of nickel(II) and copper(II) complexes of β-ketoamines[2] derived from acetylacetone and amines in order to compare the results with those of the corresponding salicylideneimine complexes previously studied.[3,4] Most of the papers about this and similar topics were, however, concerned mainly with complexes of the first transition elements, such as cobalt, nickel and copper. It seemed, therefore, worthwhile to study the corresponding complexes of the second or the third transition elements and to compare them with those of the first transition elements. The present paper will describe palladium(II) complexes of β-ketoamines derived from acetylacetone and monoamines. No palladium(II) complexes of these ketoamines have yet been described in the literature.

Experimental

Materials. — The palladium(II) complexes, Pd(Aca.R)$_2$, were prepared according to either of the following two methods. (A) To a solution of bis(acetylacetonato)palladium(II)[5] in ethanol, a calculated amount or a slight excess of one of the amines was added. The mixture was then stirred while being heated at about 50—60°C for five hours. (B) To a solution of a β-ketoamine in ethanol there was gradually added an aqueous solution of potassium tetrachloropalladate(II) and potassium hydroxide. The mixture was then stirred while being heated at about 40—50°C for about five hours. The yield was generally higher by the method B than by the method A. The method B was, therefore, applied to the preparation of the complexes with aryl amines, ammonia, methyl amine and benzyl amine. Since, however, it was difficult to prepare the β-ketoamines by condensation in the case of alkyl amines (with the exception of methyl amine), the metal complexes with alkyl amines were prepared according to the method A.

A typical example of preparation by the method A is that for bis(*N*-methyl-acetylacetoneaminato)palladium(II), Pd(Aca.CH$_3$)$_2$. To 1.0 g. (1/300 mol.) of Pd(acac)$_2$ in 10 ml. of ethanol, was added 0.67 g. of a 30% solution of methyl amine (2/300 mol.).[6] The reaction mixture was then stirred while being heated at abbut 60°C for about five hours. The coluor of the solution gradually changed from yellow to reddish brown. Then the solution was filtered and allowed to stand at room temperature. Reddish-brown crude crystals were obtained and recrystallized from chloroform.

A typical example of preparation by the method B is that for bis(*N*-phenyl-acetylacetoneaminato)palladium(II), Pd(Aca.C$_6$H$_5$)$_2$. To a slight excess of a β-ketoamine in 10 ml. of ethanol were added 1.0 g. (1/300 mol.) of potassium tetrachloropalladate(II) in 10 ml. of water and 0.38 g. of potassium hydroxide in 5 ml. of water. An orangish-yellow precipitate was produced at once, but the resulting mixture was incessantly stirred at 45—50°C for five hours. Then it was allowed to stand at room temperature. The product was filtered, washed with ether, and recrystallized from benzene-ethanol.

These palladium(II) complexes are all yellow or yellow-orange, with the exception of the *N*-methyl-substituted complex, for which two isomers were obtained as pure crystals, one being yellow and the other orange-red. The yellow form was prepared by the method B, and the orange-red form, by the method A. All the complexes prepared were stable in the atmosphere and were readily soluble in benzene and chloroform and moderately soluble in acetone, ethanol and methanol. The solvents used for the recrystallization of the complexes are shown in Table I, together with elemental analyses of the compounds.

Measurements.—The visible and ultraviolet absorption spectra of the complexes in solution were determined with a Shimadzu QR-50 spectrophotometer and a Beckman DU spectrophotometer. The infrared spectra of the compounds were determined with a Hitachi EPU-2A infrared spectrophotometer. The X-ray diffraction diagrams were obtained with a Toshiba ADX-103 X-ray diffractometer.

Results and Discussion

Many new palladium(II) complexes have been synthesized in the present work with β-ketoamines

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[1] S. Yamada, H. Nishikawa and K. Yamasaki, This Bulletin, **36**, 483 (1963); S. Yamada and H. Nishikawa, ibid., **36**, 755 (1963); S. Yamada, H. Nishikawa and E. Yoshida, *Proc. Japan* Academy, **40**, (1964); etc.

[2] As a matter of convenience, these ligands will be referred to as β-ketoamines, although their electronic state in the metal complexes may be somewhere between the ketoamine and the enolimine.

[3] These metal complexes are abbreviated in this paper as M(Sal. R)$_2$ and M(Aca. R)$_2$, R being an alkyl or an aryl group attached to the nitrogen atom.

[4] S. Yamada, H. Nishikawa and E. Yoshida, Proceedings 8. I. C. C. C. (International Conference on Co-ordination Chemistry), Vienna (1964), p. 373.

[5] Bis(acetylacetonato)palladium(II) was prepared according to the method of A. A. Grinberg and L. K. Simonova (*Zhur. Priklad. Khim.*, **26**, 880 (1953)).

[6] The symbol *acac* denotes an acetylacetonate anion.

TABLE I. ELEMENTAL ANALYSES OF PALLADIUM(II) COMPLEXES OF β-KETOAMINES, Pd(Aca.R)$_2$

R	Analyses Calcd., % C	H	N	Found, % C	H	N	Solvents for recrystalliz.
H	39.42	5.91	9.20	40.0	5.38	9.10	Chloroform
CH_3*	43.60	6.05	8.47	43.70	6.22	8.32	Methanol
CH_3**	43.60	6.05	8.47	43.10	6.00	8.51	Chloroform
C_2H_5	46.90	6.70	7.81	46.34	6.59	8.00	Chloroform
n-C_3H_7	49.71	7.24	7.24	49.16	7.28	7.41	Chloroform
n-C_4H_9	52.14	7.72	6.75	51.54	7.67	6.65	Chloroform
$CH_2C_6H_5$	59.70	5.80	5.80	59.18	5.82	5.66	Ethanol
C_6H_5	58.10	5.28	6.16	58.21	5.31	5.95	Benzene-ethanol
o-tolyl	59.70	5.80	5.80	58.52	5.70	5.71	Benzene-ethanol
m-tolyl	59.70	5.80	5.80	59.87	5.77	5.77	Benzene-ethanol
p-tolyl	59.70	5.80	5.80	59.84	5.75	5.69	Benzene
o, *o'*-xylidyl	61.13	6.27	5.48	60.50	6.11	5.39	Benzene-ethanol

* Yellow form ** Orange-red form

derived from acetylacetone and alkyl amines. The elemental analysis of the complexes, which agrees with the general formula of Pd(Aca.R)$_2$, definitely excludes the formation of the sexa-co-ordinate complexes of Pd(acac)$_2$(RNH$_2$)$_2$, as may also be inferred from the property of palladium(II) of being generally reluctant to take a co-ordination number exceeding four. This is borne out by the infrared spectra of the complexes, which show no absorption due to the CO-group of the acetylacetonate ion co-ordinated with the metal ion, but instead absorption peaks at about 1510—1520 and 1590—1600 cm^{-1}. These two peaks are most probably due to the β-ketoamines in the metal complexes[7]. Of the three possible forms for the β-ketoamines (Fig. 1), the structure B was considered to be most likely.[8] For the metal complexes of the β-ketoamines, however, the structures corresponding to the complexes of A and B may be surmized.[7] The extent of the contribution of these forms in the metal complexes has not been determined in the present work.

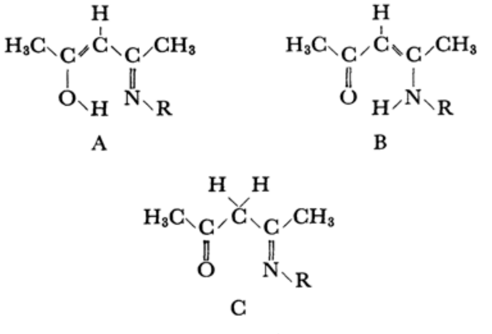

Fig. 1. Possible structures for the condensation products from acetylacetone and an amine, RNH$_2$: A, enolimine; B, ketoamine; c, ketoimine.

It should be noted that the palladium(II) complexes, Pd(Aca. R)$_2$ (R being *n*-propyl and *n*-butyl), have been prepared as crystals, although the free ligands have never been isolated as pure substances. This is regarded as an example of the stabilization of the otherwise unstable ligands through co-ordination with a metal ion. No reaction of a similar type with nickel(II), which also has a d^8 configuration, was found to take place at all; that is, the color of the mixed solution did not show any sign of the reaction taking place. The difference in this respect between palladium(II) and nickel(II) seems to be in agreement with the current view that the palladium(II)-ligand bond is generally stronger than the nickel(II)-ligand bond.

It is most likely that the palladium(II) complexes prepared in the present work are square-planar in non-donor solvents as well as in the solid state, since it is known that the palladium(II) ion strongly demands the quadri-co-ordinate square-planar configuration. A recent X-ray study has revealed that Pd(Aca.H)$_2$ takes a trans-square-planar configuration.[9] However, it has not yet been definitely concluded whether the complexes reported here belong to a trans- or a cis-series.

For Pd(Aca.CH$_3$)$_2$, two kinds of crystals were obtained according to the method of the preparation, one being yellow and the other a brownish orange. The X-ray powder patterns of the two forms are difinitely different. Furthermore, the electronic spectrum of the one is quite different from the spectrum of the other in solution, the red form displaying an absorption band in a far lower frequency region than the yellow form (Fig. 2).

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7) H. F. Holtzclaw, Jr., J. P. Collman and R. M. Alire, *J. Am. Chem. Soc.*, **80**, 1100 (1958).

8) N. H. Cromwell, F. A. Miller, A. R. Johnson, R. L. Frank and D. J. Wallace, ibid., **71**, 3337 (1949); etc.

9) G. E. Gurr, *Inorg. Chem.*, **3**, 614 (1964).

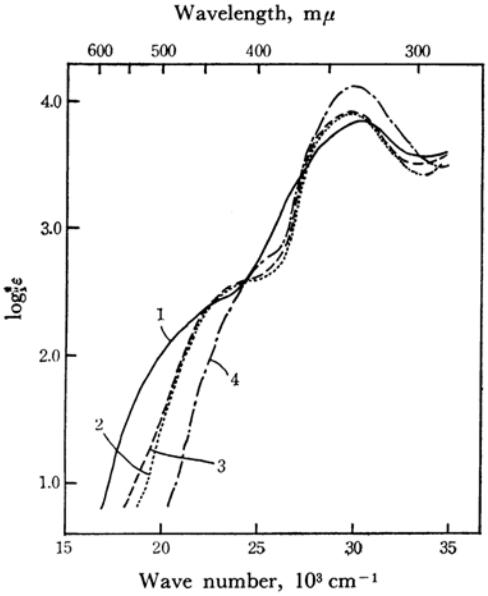

Fig. 2. Electronic spectra of ketoamine complexes of palladium(II) in chloroform: 1, Pd(Aca.-CH_3)$_2$, orange-red form (——); 2, Pd(Aca.-CH_3)$_2$, yellow form (----); 3, Pd(Aca.n-C_4H_9)$_2$ (— — —); 4, Pd(Aca.H)$_2$ (-----).

Consequently, the difference in color between the two is not due to the difference in the mere effect of the packing of the molecules in the crystal, but to the difference in the molecular configuration. The two forms presumably correspond to cis- and trans-isomers. No definite conclusion has been reached in the present work about which is the cis- and which the trans-form.[10]

Judging from the similarity in the electronic spectrum (Fig. 2), the compounds prepared in the present work, which have the general formula of Pd(Aca.R)$_2$, R being ethyl, *n*-propyl and *n*-butyl, probably have the same geometrical configuration as the yellow form of Pd(Aca.CH_3)$_2$. The absorption band at about 24×10^3 cm^{-1} is presumably due to an electronic transition between an orbital in the ligand and a d-orbital in the metal ion. The strong absorption band at about 30×10^3 cm^{-1} may be due to an electronic transition within the ligand combined with the palladium(II) ion.

Many new complexes of palladium(II) β-ketoamines derived from acetylacetone and aryl amines have been prepared in the present work. As in the case of the corresponding alkyl complexes, the elemental analysis indicates that these palladium(II)-complexes are quadri-co-ordinate, with the formula of Pd(Aca.R)$_2$, while the infrared spectra show the formation of the ligands, Aca.R, combined with the metal ion.

The free ligands can be isolated in the pure form with aryl group for R, while the isolation of the corresponding compounds in the pure form is possible only with methyl or ethyl for R throughout the alkyl series. The preparation of the metal complexes, therefore, is generally easier with the aryl than with the alkyl group for R.

As has been discussed in connection with the alkyl-derivatives, these palladium(II) complexes may also be considered square-planar. It is not certain at the present stage whether they should take a cis- or a trans-configuration. It might be argued that Pd(Aca.*o*, *o*′-xylidyl)$_2$ would take a configuration distorted from the square-plane due to the possible steric hindrance of the two methyl groups at the *o*- and *o*′-carbon atoms. However, this complex is also considered to be square-planar, since the formation of the corresponding nickel(II) complex with a square-planar configuration indicates that the probable steric hindrance of the two methyl groups is not so serious as to prohibit the square-planar configuration,[4] and since palladium(II) generally demands the square-planar configuration more strongly than nickel(II). This seems to be borne out by the electronic spectrum of this complex in non-donor solvents, (cf. Fig. 3); the spectrum is nearly superposable upon the spectra of Pd-(Aca.tolyl)$_2$, which are all presumed to be square-planar since no steric hindrance is present in these complexes.

The capacity of nickel(II) in a square-planar

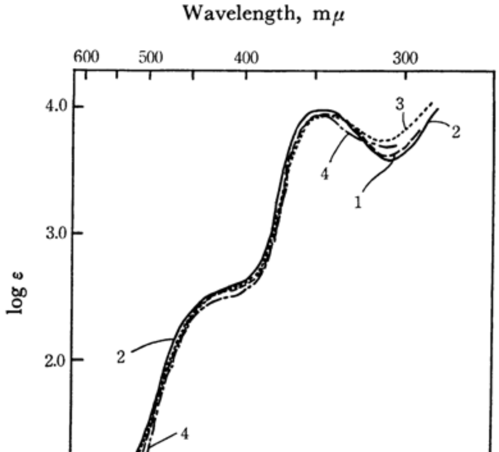

Fig. 3. Electronic spectra of ketoamine complexes of palladium(II): 1, Pd(Aca. *o*-tolyl)$_2$ in chloroform (----); 2, Pd(Aca. *m*-tolyl)$_2$ in chloroform (——); 3, Pd(Aca.*o*, *o*′-xylidyl)$_2$ in chloroform (----); 4, Pd(Aca.*o*, *o*′-xylidyl)$_2$ in pyridine (—-—-).

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[10] A reaction similar to that employed in the preparation of the orange-red isomer does not yield the corresponding orange-red complex in the case of the aryl-substituents.

complex to take the six-co-ordination by combining additional ligands was formerly examined, with pyridine used as the ligand.[4] In order to compare palladium(II) with nickel(II) in this respect, the electronic spectra were examined with the palladium(II) complexes prepared in the present work. The present measurements reveal that the spectra of these palladium(II) complexes in pyridine are almost superposable upon the spectra of the same compounds in non-donor solvents. This fact shows that these complexes keep the square-planar configuration, taking up no additional pyridine molecules at the fifth or the sixth site, even in pyridine. The corresponding nickel(II) complexes, $Ni(Aca.R)_2$ (R being aryl radicals), are found to form sexa-co-ordinated complexes by combining two pyridine molecules in the pyridine solution[4] (with the exception of Ni(Aca. *o*, *o'*-xylidyl)$_2$, which is square-planar in pyridine). It is found again that the palladium(II) has less of a tendency to form sexa-co-ordination than has nickel(II), as was also observed with other ligands.

No difference was observed in this property of the nickel(II) and palladium(II) complexes between the corresponding β-acetylacetoneamines and the salicylideneimines. A similar result was obtained with the corresponding complexes of salicylideneimines. The palladium(II) complexes of the $Pd(Sal.R)_2$ type (R being *o*, *o'*-xylidyl, *o*-, *m*- and *p*-tolyl, and phenyl) are all square-planar in pyridine as well as in non-donor solvents,[11] while the corresponding nickel(II) complexes, $Ni(Sal.R)_2$, are sexa-co-ordinated in pyridine (with the exception of Ni(Sal. *o*, *o'*-xylidyl)$_2$).[4]

Summary

Numerous new palladium(II) complexes, $Pd(Aca.R)_2$, have been synthesized with β-ketoamines derived from acetylacetone and amines, where R represents methyl, ethyl, *n*-propyl, *n*-butyl, benzyl, phenyl, *o*-, *m*- and *p*-tolyl, and *o*, *o'*-xylidyl. It should be noted that when R denotes *n*-propyl or *n*-butyl, the palladium(II) complexes have been prepared successfully, although the free ligands can not be isolated in a pure form. This may be regarded as an example of the stabilization of a molecular configuration through co-ordination with a metal ion. The visible and ultraviolet spectra indicate that the palladium(II) complexes prepared in the present paper, which are considered to be square-planar in non-donor solvents as well as in the solid state, combine no additional pyridine molecules, even in pyridine. This is contrary to the previous observation that $Ni(Aca.R)_2$ complexes combine two molecules of pyridine to form a sexa-co-ordinated complex in pyridine.

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[11] S. Yamada and K. Fujita, unpublished.