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Palladium(II) Complexes of *N*-Substituted Salicylideneimines

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Many new palladium(II) complexes (abbreviated as M(X-SAL·R)$_2$) of Schiff bases obtained from substituted salicylaldehydes and alkyl and aryl amines were prepared as yellow-orange or red crystals, where X denotes H, 3-CH_3O and 5,6-benzo. For R=*n*-alkyl and aryl groups, the complexes Pd(X-SAL·R)$_2$ in non-donor solvents consist of square-planar molecules. The complexes of the type Pd(X-SAL·*t*-C_4H_9)$_2$ show electronic spectra which are different from those of the complexes of the type Pd(X-SAL·*n*-alkyl)$_2$, but all these complexes are diamagnetic. This difference between the two kinds of complexes is discussed in connection with the bonding in, and the structure of, the complexes on the basis of the spectral and magnetic properties. The results for the palladium(II) complexes are compared with those for the corresponding nickel(II) complexes.

Many detailed studies have been reported on nickel(II) complexes (Fig. 1) with Schiff bases obtained from substituted salicylaldehydes.[1–3] Having a d^8 configuration, the palladium(II) ion forms complexes which are similar to the nickel(II) complexes, but there are also many examples of palladium(II) complexes which are remarkably different from the corresponding nickel(II) complexes. On the palladium(II) complexes with the Schiff bases, however, only a few papers have so far been published,[4,5] and systematic studies in particular seem to be lacking.

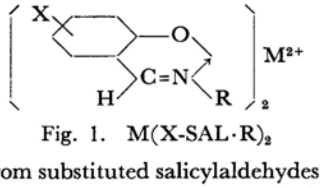

Fig. 1. M(X-SAL·R)$_2$

The present paper deals with preparation of the palladium(II) complexes with the Schiff bases and examination of their stereochemistry for comparison with the results about the corresponding nickel(II) complexes. It is also one of the purposes of the present work to examine the effect of steric hindrance of various degrees on the stereochemistry of these palladium(II) complexes.

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1) 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.

2) S. Yamada, *Coordin. Chem. Revs.*, **1**, 415 (1966).

3) L. Sacconi, "Essays in Coordination Chemistry," ed. by W. Schneider, G. Anderegg and R. Gut, Birkhäuser Verlag, Basel (1964), p. 148.

4) L. Sacconi, M. Ciampolini, F. Maggio and G. Del Re, *J. Am. Chem. Soc.*, **82**, 815 (1960).

5) S. Yamada, H. Nishikawa and K. Yamasaki, This Bulletin, **36**, 483 (1963).

Experimental

Materials. The palladium(II) complexes of the type Pd(X-SAL·R)$_2$, which are shown in Tables 1 and 2, were prepared according to methods similar to those previously reported.[5] A typical example of preparation is as follows. To a solution of potassium tetrachloropalladate(II) (0.01 mol) and potassium hydroxide (0.02 mol) in a small amount of water were added a solution of salicylaldehyde or substituted salicylaldehyde (0.02 mol) in ethanol and an appropriate amine. The resulting solution was stirred at about 50°C for about one hour. The precipitate was collected by filtration and recrystallized from ethanol, chloroform or benzene.

TABLE 1. ANALYTICAL DATA OF THE COMPLEXES OF THE TYPE Pd(X-SAL·alkyl)$_2$

X	Alkyl	Calcd, %			Found, %		
		C	H	N	C	H	N
H	i-C_3H_7	55.72	5.57	6.50	55.84	5.65	6.52
	t-C_4H_9	57.55	6.10	6.10	57.36	6.10	6.28
	i-C_4H_9				57.26	6.09	6.44
5,6-Benzo	n-C_3H_7	63.31	5.31	5.27	63.46	5.17	5.15
	i-C_3H_7				63.50	5.19	5.43
	n-C_4H_9	64.42	5.77	5.01	63.98	5.77	5.13
	t-C_4H_9				63.59	5.81	4.80
3-CH_3O	n-C_3H_7	53.80	5.75	5.70	54.09	5.78	5.61
	i-C_3H_7				53.26	5.62	5.59
	n-C_4H_9	55.52	6.21	5.40	55.04	6.19	5.39
	t-C_4H_9				55.55	6.35	5.19

The complexes Pd(H-SAL·R)$_2$ with R=CH_3, C_2H_5, n-C_3H_7 and n-C_4H_9, which were first reported by Sacconi and others,[4] were prepared in the present work as previously reported.[5]

TABLE 2. ANALYTICAL DATA OF THE COMPLEXES OF THE TYPE Pd(H-SAL·aryl)$_2$

Aryl	Calcd, %			Found, %		
	C	H	N	C	H	N
Ph*	62.81	3.62	5.64	62.08	3.96	5.48
o-CH_3Ph	63.79	4.56	5.32	63.37	4.61	5.04
m-CH_3Ph				63.57	4.52	5.32
p-CH_3Ph				63.73	4.65	5.32
o,o'-$(CH_3)_2$Ph	64.90	5.05	5.05	64.56	5.06	5.05
o-ClPh	55.00	3.20	4.93	54.89	3.42	4.63
m-ClPh				54.61	3.32	5.07
p-ClPh				55.08	3.26	4.79

* The notation Ph denotes a phenyl group.

All these palladium(II) complexes are yellow or yellowish orange, with the exception of the N-t-butyl-substituted complexes, which are brownish red. They are insoluble in water but soluble in methanol, ethanol, chloroform, benzene and acetone.

Analytical data of the new compounds are given in Tables 1 and 2.

Measurements. The electronic absorption spectra of the compounds in solution were determined with a Shimadzu MPL-50 and a Shimadzu QR-50 spectrophotometer.

Diamagnetism of the complexes was detected by the Gouy method.

Results and Discussion

Many new compounds, which are listed in Tables 1 and 2, have been prepared in the present work. Sacconi and others[4] formerly prepared the complexes of the type Pd(H-SAL·R)$_2$ with R=CH_3, C_2H_5, n-C_3H_7 and n-C_4H_9, and concluded them to be *trans*-planar. Moreover, it is well known that the palladium(II), in general, takes a planar, four-coordinated configuration. It seems, therefore, to be most likely that the complexes of the type Pd(X-SAL·n-alkyl)$_2$ prepared in the present work may also be planar. Electronic spectra of these complexes, as shown in Figs. 2 and 3, are quite similar to each other, showing that their configuration is all alike. The absorption peak at about 25.5 kK may be due to an electronic transition within the ligand bound with the palladium(II) ion. The ligand field bands mainly due to the palladium(II) ion are considered to be hidden by the strong absorption bands of other origins. In a similar way, it is considered that the planar configuration is most likely for the complexes of the type Pd(H-SAL·R)$_2$ with R=phenyl and substituted phenyl groups.

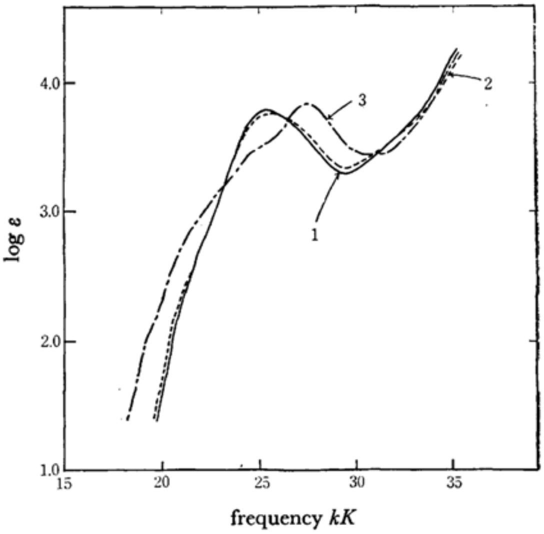

Fig. 2. Electronic absorption spectra of Pd(H-SAL·R)$_2$ in chloroform; 1, R=n-C_4H_9 (——); 2, R=i-C_3H_7 (-----); 3, R=t-C_4H_9 (—-—-—).

It is to be noted that Beer's law holds for all these palladium(II) complexes, so that no association of the square-planar complexes occurs in solution, in contrast to the behavior of the correspond-

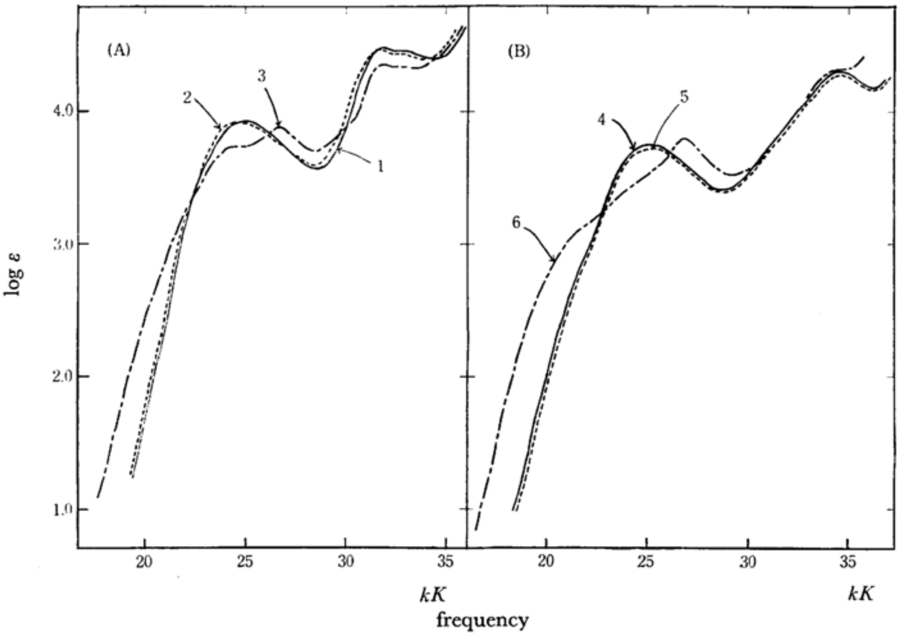

Fig. 3. Electronic absorption spectra in chloroform of (A) Pd(5,6-benzo-SAL·R)$_2$; 1, R=n-C_4H_9; 2, R=i-C_3H_7; 3, R=t-C_4H_9 and (B) Pd(3-CH_3O-SAL·R)$_2$; 4, R=n-C_4H_9; 5, R=i-C_3H_7; 6, R=t-C_4H_9.

ing nickel(II) complexes. This finding is in agreement with the current view that the tendency of palladium(II) to take coordination number larger than four is extremely low and, in fact, much lower than that of nickel(II).

With Pd(H-SAL·2,6-$(CH_3)_2$Ph)$_2$, the steric condition is not quite favorable for the square-planar configuration. However, since the corresponding nickel(II) and copper(II) complex have been found to be square-planar,[6] the square-planar configuration may also be most likely for Pd(H-SAL·2,6-$(CH_3)_2$Ph)$_2$ in spite of the possible steric hindrance. This is borne out by the electronic spectrum of this palladium(II) complex, which is quite similar to those of Pd(H-SAL·CH_3Ph)$_2$ and related complexes, as shown in Fig. 4.

For Pd(X-SAL·i-C_3H_7)$_2$, the steric condition is not quite favorable for the square-planar configuration. However, these complexes are diamagnetic, and their electronic spectra are similar to those of Pd(X-SAL·n-alkyl)$_2$, as may be seen in Figs. 2 and 3. It is, therefore, presumed that all these complexes are square-planar. It is to be noted that this is not the case with the corresponding nickel(II) complexes. The nickel(II) complexes of the type Ni(X-SAL·i-C_3H_7)$_2$ are square-planar or distorted-tetrahedral, depending upon the nature of X.[3,7]

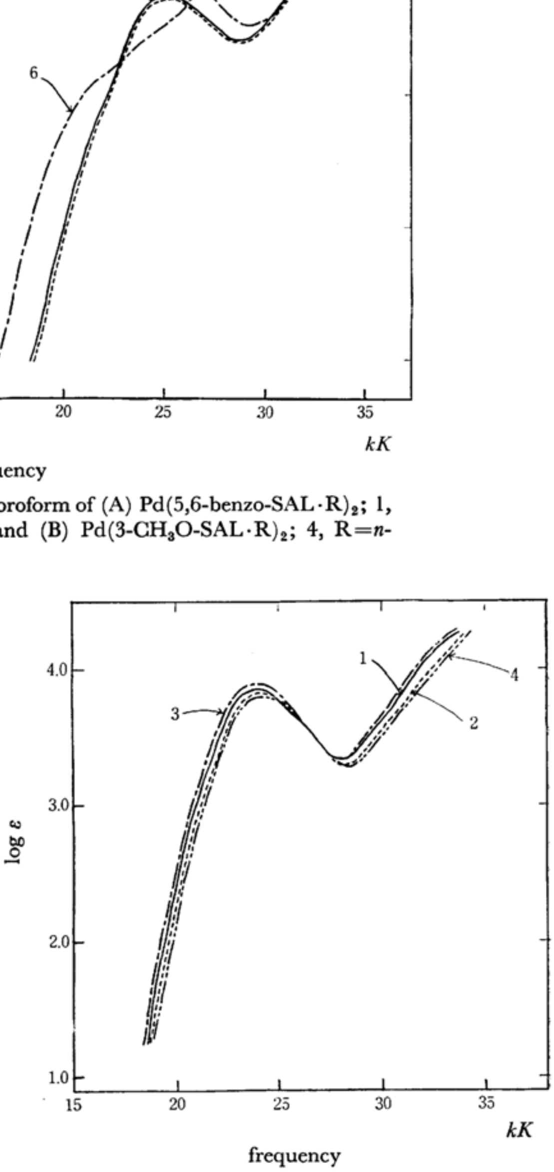

Fig. 4. Electronic absorption spectra of Pd(H-SAL·R)$_2$ in chloroform; 1, R=Ph (——); 2,R=o-CH_3Ph (-----); 3, R=p-CH_3Ph (—— —— ——); 4, R=o,o'-$(CH_3)_2$Ph (—·—·—·—).

For Pd(X-SAL·t-C_4H_9)$_2$, the steric condition is considered to be highly unfavorable for the planar configuration. Their electronic spectra are apparently different from those of the complexes of the type Pd(X-SAL·n-alkyl)$_2$, as clearly seen in Figs. 2 and 3. This difference in the spectrum between the complexes of the above two types may

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[6] S. Yamada, H. Nishikawa and E. Yoshida, This Bulletin, **39**, 994 (1966).

[7] S. Yamada and H. Nishikawa, *ibid.*, **36**, 755 (1963).

be ascribed to either of the following two possibilities.

(1) The configuration of Pd(X-SAL·*t*-$C_4H_9)_2$ is distorted from the planar one.

(2) In Pd(X-SAL·*t*-$C_4H_9)_2$, the coordination configuration of the palladium(II) ion, namely $[Pd(N)_2(O)_2]$, is planar, but the remarkable steric hindrance in this case is exerted to the ligands, giving rise to considerable perturbation in the electronic state of the ligand.

Since the present work reveals that all these palladium(II) complexes are diamagnetic, the latter possibility seems to be higher than the former. The diamagnetism fo Pd(X-SAL·*t*-$C_4H_9)_2$, however, might also be explained, if we assume that the deviation from the planar coordination of $[Pd(N)_2(O)_2]$ is so small that the energy separation between the highest $d_{x^2-y^2}$ and the next highest d orbital of the palladium(II) ion is still large enough to allow the spin-paired state to remain the lowest. Definite conclusion on the precise configuration of the complexes Pd(X-SAL·*t*-$C_4H_9)_2$ must await X-ray examination.

The conclusion on the configurations of Pd(X-SAL·*t*-$C_4H_9)_2$ and Pd(X-SAL·*i*-$C_3H_7)_2$ is found to be different in many respects from that obtained previously about the corresponding nickel(II) complexes. This difference may be considered to arise from the following two points.

(1) The ionic radius of the palladium(II) ion is known to be considerably larger than that of the nickel(II) ion.

(2) The stability of the planar configuration *vis-a-vis* the tetrahedral one is higher for the palladium(II) than for the nickel(II) ion.

The spectra of all these Schiff base palladium(II) complexes in a donor-solvent like pyridine are nearly the same as those of the same complexes in non-donor solvents. It is, therefore, most likely that their configuration in non-donor solvents may be retained in pyridine, namely that the coordination of the pyridine molecule with the palladium(II) ion does not take place. It was previously shown that this was not the case with the nickel(II) complexes.[8] This difference between the nickel(II) and the palladium(II) complexes seems to show that the palladium(II) ion has less tendency to form sexa-coordination than the nickel(II) ion, as was also observed with related ligands as well as many others.[9]

In these respects, the platinum(II) ion is similar to the palladium(II) ion, and the difference between the platinum(II) and the nickel(II) ion is known to be even more marked than that between the palladium(II) and the nickel(II) ion. Therefore, with the platinum(II) complexes Pt(H-SAL·R$)_2$, a similar result to that with the corresponding palladium(II) complexes may be expected. This is borne out by the electronic spectra of these platinum(II) complexes. Thus the spectrum of Pt(H-SAL·*n*-alkyl$)_2$ is similar to that of Pt(H-SAL·*i*-$C_3H_7)_2$ but different from that of Pt(H-SAL·*t*-$C_4H_9)_2$.[5] The details of this phase of the study will be published later.

We wish to thank Mrs. Kayo Fujita for her experimental assistance at the earlier stage of the present work. Financial assistance of the Education Ministry of Japan is also gratefully acknowledged.

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

[9] E. Yoshida and S. Yamada, This Bulletin, **38**, 2179 (1965).