Palladium(II)- and Platinum(II)-complexes of Schiff Bases Derived from Salicylaldehyde and Alkylamines

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Previous studies of metallic complexes with Schiff bases of a type shown in Fig 1 have revealed that it depends much upon the nature of the metal ion as well as upon that of the ligand whether the quadri-co-ordinate complex of a transition element takes a squareplanar configuration or a configuration distorted from it. Thus, the stability of the tetrahedral co-ordination around the metal ion, as compared with that of the square-planar one, is higher for cobalt(II)[1], a little lower for nickel(II)[2], and much lower for copper(II)[3].

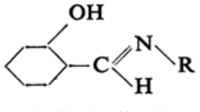

Fig. 1. *N*-Alkylsalicylideneimine.

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[1] H. Nishikawa, S. Yamada and R. Tsuchida, *Z. Naturforsch.*, **17b**, 78 (1962); H. Nishikawa and S. Yamada, This Bulletin, **35**, 1430 (1962); B. O. West, *J. Chem. Soc.*, **1962**, 1374; L. Sacconi, M. Ciampolini, F. Maggio and F. P. Cavasino, *J. Am. Chem. Soc.*, **84**, 3246 (1962).

[2] H. Nishikawa and S. Yamada, unpublished. Cf. R. H. Holm, *J. Am. Chem. Soc.*, **83**, 4683 (1961).

[3] S. Yamada and H. Nishikawa, unpublished.

A similar study has now been extended to palladium(II) and platinum(II) in order to examine the stereochemistry of these compounds and to explore the possibility of obtaining complexes of palladium(II) and platinum(II) with a configuration distorted from the square-plane, a configuration which is quite rare for these metal ions. For example, in the complexes with R=*t*-butyl the square-planar configuration of the complex is impossible because of serious steric hindrance, so that these complexes, if prepared at all, are expected to have a configuration distorted from the square-plane. Platinum(II) complexes with neither *N*-*n*- nor isoalkyl-salicylideneimines have been reported previously, nor has the preparation of the corresponding *N*-isopropyl or *t*-butyl derivative been described, although *N*-*n*-alkylsalicylideneimines of palladium(II) were reported$^{4)}$. The present communication reports on the successful preparation of palladium(II)- and platinum(II)-complexes of these Schiff bases, including those complexes with a configuration distorted from the square-plane.

The platinum(II)-complexes were prepared by the following two methods: (1) To an aqueous solution of potassium tetrachloroplatinate(II) were added solutions of potassium hydroxide in water, salicylaldehyde in ethanol, and one of the alkylamines in ethanol, the molar ratio being 1 : 2 : 2 : 2. After the solution had been left at room temperature for a few days, a black mass containing a small orange-colored part was precipitated. By treating the mass with a suitable solvent, such as chloroform, benzene, ethanol and ether, the platinum(II)-complex with the Schiff base was obtained as orange crystals. (2) To a solution of [Pt(*salal*)$_2$] in ethanol was added a solution of an alkylamine in ethanol in the molar ratio of 1 : 4 ; the solution was then warmed gently$^{5)}$. In a few hours, the platinum(II)-complex with the Schiff base separated out.

The second method was adopted in the preparation of the *t*-butyl and the isopropyl derivative. The platinum(II)-compounds with R=methyl, ethyl, *n*-propyl and *n*-butyl were obtained in either way, while the palladium-complexes with R=methyl, ethyl, *n*- and isopropyl, and *n*- and *t*-butyl were prepaerd by the first method. The elemental analyses for carbon, hydrogen and nitrogen agree with the calculated values for the bis(*N*-alkylsalicylideneimine) complexes.

Since palladium(II) and platinum(II) strongly demand the square-planar co-ordination, the configuration of $Pt(N)_2(O)_2$ or $Pd(N)_2(O)_2$ in the *n*-alkyl complexes is most likely to be planar. The co-ordination around the palladium(II) was reported to be trans-planar with the methyl derivative$^{6)}$. In general, the cis configuration is very difficult sterically with complexes of this series, and it is usually regarded as unlikely for the modification obtained under ordinary conditions.

When *t*-butyl groups are substituted for the *n*-alkyl groups in the complex, the square-planar co-ordination around the metal ion is completely prevented by the serious steric hindrance, so that the configuration around the metal ion is distorted from the plane. The ultraviolet spectra of the *t*-butyl complex of palladium(II) and platinum(II) differ significantly from the spectra of the corresponding *n*-alkyl complexes of the same central ion, whereas the spectra of the Schiff bases of the type examined in the present work are quite similar to one another both in the frequency of maxima and minima and in band intensity. This is in agreement with the conclusion based on the steric condition that the co-ordination around the palladium(II) or the platinum(II) in the *t*-butyl complex is distorted from the square-plane.

In the case of the isopropyl group, the steric hindrance seems to be considerable, but it may not be as serious as in the case of the *t*-butyl group. The present measurements indicate that the ultraviolet spectra of the isopropyl derivatives of palladium(II) and platinum(II) are nearly identical with the spectra of the corresponding compounds of the *n*-alkyl groups. This fact is taken as showing that the co-ordination around the palladium(II) or platinum(II) in the isopropyl derivative is similar to that of the corresponding complexes of the *n*-alkyl groups, which are most probably planar. In this connection, it is worth noting that bis(*N*-isopropylsalicylidene)-nickel(II)$^{2)}$, cobalt(II)$^{1)}$ and copper(II)$^{3)}$ were found to be distorted from the square-planar co-ordination. The comparison clearly indicates that the stability of the square-planar co-ordination, as compared with that of the tetrahedral one, is higher for palladium(II) and platinum(II) than for cobalt(II), nickel(II) and copper(II).

The present measurements also indicate that the spectra of these complexes of palladium(II) and platinum(II) in pyridine show very little difference from the spectra of the same complexes in chloroform, ethanol or benzene.

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

5) The notation, *salal*, represents an anion derived when a molecule of salicylaldehyde loses a proton. The preparation of the complex will be reported shortly by the present authors.

6) B. Meuthen and M. V. Stackelberg, *Z. anorg. u. allgem. Chem.*, **305**, 279 (1960).

This shows that the pyridine molecules are not co-ordinated with the palladium(II) or platinum(II), whereas it is well-known that the nickel(II) ions in all these complexes except the *t*-butyl complex[2)] do take up pyridine molecules to form a sexa-co-ordinate complex. This is also in agreement with the current view that it is much more difficult for the palladium(II) and platinum(II) ions to take sexa-co-ordination than for the nickel(II) ions, for which sexa-co-ordination is quite common.

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