The Color and the Structure of Tetramine-platinum(II) Tetrahalogenoplatinate(II)

By Shoichiro Yamada

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Magnus's green salts having an empirical formula of $[Pt(NH_3)_4][PtCl_4]$ and a related compound, $[Pt(NH_3)_4][PtBr_4]$ are peculiar in that the salts in the crystalline state are green, whereas the component complex ions are colorless and red in solution. In order to elucidate this peculiarity of the color, the present author formerly determined the dichroism of the compounds in the visible and near-ultraviolet region, and concluded that the unusually deep color of the compounds was due most probably to a weak bond between platinum ions along the needle axis1). It was also found that compounds represented by a general formula of $[Pt(amine)_4][PtCl_4]$ are colored either red or green, depending upon the amine2). The compounds of the pink series show a dichroism similar to that of $K_2[PtCl_4]$, in which no specific bond is involved between platinum ions, while the green compounds show a dichroism which differs remarkably from that of the potassium salt. The main difference between the two series lies in the following point. The green series shows an absorption band in the longer wavelength region than the red series, and the band is polarized along the c-axis of the crystal, along which the Pt-Pt bond is assumed to occur. The difference in the dichroism as well as in the color between the two series of compounds is so marked that it is possible to tell, by using the dichroism or the color as a criterion, whether a compound with an empirical formula of $[Pt(amine)_4][PtCl_4]$ involves the Pt-Pt bond or not. The results of the examinations are given in Table I, together with the previous data.

A similar examination has been extended to the corresponding bromo-complexes, $[Pt\cdot(amine)_4][PtBr_4]$, the results being included in Table I. Thus dichroism of $[Pt(NH_2CH_3)_4]\cdot[PtBr_4]$, which has been determined by the present author using the microscopic method3), shows the main features similar to that of Magnus's green salt.

Inspection of Table I shows that a drastic change occurs between methylamine and ethylamine in the case of $[Pt(amine)_4][PtCl_4]$. This may be ascribed to the steric factor2). Comparison of $[Pt(amine)_4][PtCl_4]$ with $[Pt\cdot(amine)_4][PtBr_4]$ also indicates that the bromo-complexes are more favorable for the formation of the Pt-Pt bond than the corresponding chloro-complexes. Since the bromide ion is larger than the chloride ion, this difference is not to be ascribed to the steric factor, but must be due to the difference in the inductive effect of the halide ions on the electronic state of the platinum ion. Similar results were obtained when a binuclear complex, $[Pt_2Br_6]^{2-}$, was used instead of $[PtBr_4]^{2-}$.

The same thing is again observed for the iodo-complexes. Thus $[PtI_4]^{2-}$ is colored dark-red, in the form of the potassium salt, but its combination with $[Pt(amine)_4]^{2+}$ ions yields complexes with color of greenish yellow, where amine represents ammonia, methylamine, *n*- and isopropylamine, *n*-butylamine, *n*-amylamine, ethylenediamine and propylenediamine.

The consideration, in the light of the criterion used in the cases of the chloro- and the bromo-complexes, indicates that these iodo-complexes all involve the Pt-Pt bond. It is most probable

TABLE I. Pt-Pt BOND IN THE CRYSTALS OF $[Pt(amine)_4][PtX_4]$

Amine	X=Cl		X=Br		X=I	
	Color	Pt-Pt bond	Color	Pt-Pt bond	Color	Pt-Pt bond
NH_3	Green	Present	Green	Present	Green-yellow	Present
CH_3NH_2	Green	Present	Green	Present	Green-yellow	Present
$C_2H_5NH_2$	Pink	Absent	Green	Present	Green-yellow	Present
n-$C_3H_7NH_2$	Pink	Absent	Green	Present	Green-yellow	Present
iso-$C_3H_7NH_2$	Pink	Absent	Green	Present	Green-yellow	Present
n-$C_4H_9NH_2$	Pink	Absent	Green	Present	Green-yellow	Present
n-$C_5H_{11}NH_2$	Pink	Absent	Green	Present	Green-yellow	Present
$H_2NCH_2CH_2NH_2$	Pink	Absent	Green	Present	Green-yellow	Present
$CH_3CH(NH_2)CH_2NH_2$	Pink	Absent	Green	Present	Green-yellow	Present

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1) S. Yamada, *J. Am. Chem. Soc.*, 73, 1579 (1951); S. Yamada and R. Tsuchida, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), 70 142 (1949).

2) S. Yamada and R. Tsuchida, This Bulletin, 31, 813 (1958).

3) R. Tsuchida and M. Kobayashi, "The Color and the Structure of Metallic Compounds" (Kinzokukagōbutsu no Iro to Kōzō), Zoshindo, Osaka (1944), p. 180.

that in the iodo-complexes the inductive effect, together with the π-bonding, is more important for the Pt-Pt bond formation than the steric factor, since the iodide ion is much larger than the bromide ion as well as the chloride ion.

It is interesting to note the difference between $[Pd(amine)_4][PtCl_4]$ and $[Pd(amine)_4]\cdot[PtBr_4]$, where amine represents those used in the other series of the complexes. It is found that the former show normal color of pink and the latter abnormal color of green. This fact seems to show that the Pd-Pt bond is absent in the former, while the bond exists in the latter. This result is in agreement with the conclusion derived in the foregoing part of the present communication.

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Department of Chemistry
Faculty of Science
Osaka University
Nakanoshima, Osaka