

99. *The Planar Configuration for Quadricovalent Nickel, Palladium, and Platinum.*

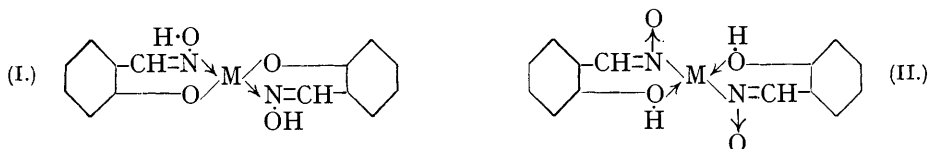
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IN 1931, Pauling (*J. Amer. Chem. Soc.*, **53**, 1367) applied wave-mechanical methods to the problem of covalent linkages and showed that for quadricovalent atoms in which electrons from the first two sub-groups (*s* and *p*) of the outer level were used in chemical bonds, the stable configuration is tetrahedral. In the case of the transition elements, however, one or more electrons used in binding may belong to the *d* sub-group of the incomplete inner level, and in these cases the four covalencies may be distributed in a plane. Moreover, since the *d* electrons are chiefly responsible for the magnetic moment of the atom, sharing of them should reduce this property so that four-covalent nickel compounds should be diamagnetic. Pauling's conclusions have been criticised by Heisenberg (see *Ann. Reports*, 1931, **28**, 367) and others, but appear to be essentially correct. The point to be recognised in connection with his work is that the results are probably permissive, *i.e.*, they show that the metals in question may have, but not necessarily must have, a planar distribution of valencies. These conclusions are particularly interesting in the case of nickel, for Werner did not include this metal in the list of elements which he considered could have planar structures for their quadricovalent compounds. Chemical and physical evidence has definitely established planar structures for quadricovalent platinum and palladium. With nickel, apart from crystallographic evidence, Pauling's prediction seems to be supported by Sugden's proof (J., 1932, 246) that the nickel derivative of benzylmethylglyoxime can occur in two forms which are interconvertible and diamagnetic. Already, in 1911, Tschugaeff (*Chem. Zentr.*, **82**, i, 871) had discovered

that the nickel derivative of monoethylglyoxime could occur in two isomeric forms, also interconvertible, but he did not consider it necessary to make any assumptions as to the distribution of the nickel valencies to explain this isomerism. Nevertheless, these experimental observations of Tschugaeff and Sugden certainly suggest that for quadricovalent nickel a planar structure is probable.

Recently, Brasseur, de Rassenfosse, and Piérard (*Z. Krist.*, 1934, **88**, 210) have shown barium nickelocyanide tetrahydrate,  $\text{BaNi}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ , to be isomorphous with the corresponding platinocyanide and palladocyanide. By means of intensity measurements they were able to find the positions of the barium and nickel atoms, but they were unable to prove that the four Ni-CN bonds are coplanar, or to find the position of the water molecules; *i.e.*, the possibility of the existence in the crystal of the octahedral complex  $\text{Ni}(\text{CN})_4(\text{H}_2\text{O})_2$  was not rigorously eliminated.

With the object of proving conclusively that quadricovalent nickel may be planar and diamagnetic, we have investigated the salicylaldoxime derivatives of platinum, palladium, and nickel. These quadricovalent compounds may have structures (I) or (II), but (I) is considered the more probable by Brady (J., 1931, 105). The conclusions which follow hold good, however, irrespective of the precise structure of the chelate groups.



The nickel compound is well known, and the palladium derivative has recently been suggested for the microchemical estimation of this metal, but the platinum compound had not been investigated. We find that the product of the reaction between a solution of potassium chloroplatinite and salicylaldoxime is a mixture of the *platinum* derivative,  $\text{Pt}(\text{C}_7\text{H}_6\text{O}_2\text{N})_2$ , and *disalicylaldoximinoplatinous chloride*  $\text{Pt}(\text{C}_7\text{H}_7\text{O}_2\text{N})_2\text{Cl}_2$ . All the compounds  $\text{M}(\text{C}_7\text{H}_6\text{O}_2\text{N})_2$ , where  $\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$ , crystallise well without solvent of crystallisation; they are almost insoluble in water, but soluble in carbon tetrachloride, chloroform, and benzene. Molecular-weight determinations prove them to be monomeric, and undoubtedly their properties indicate that they have covalent structures.

The nickel and the palladium compound form good crystals which are isomorphous. X-Ray examination of them has shown that the molecule in each case possesses a centre of symmetry, and therefore has a planar *trans*-configuration. This result follows from space-group considerations, and is thus quite certainly established without the necessity of employing intensity measurements, which, unless very exhaustive, are liable to misinterpretation in the case of complex compounds of this nature. In all cases, *cis*- and *trans*-isomerides could exist. The nickel compound does, in fact, occur in a second crystalline form, but it appears to be merely a dimorphous form of the *trans*-isomeride. The platinum derivative occurs in two modifications, neither of which is isomorphous with the nickel or the palladium compound. One form has definitely a planar *trans*-configuration; the other is not dimorphous but has a complicated tetragonal structure, with 32 molecules of disalicylaldoximeplatinum to the unit cell. The molecules are asymmetric, as would be expected for the *cis*-isomeride on the *trans*-pairing hypothesis or a tetrahedral configuration. The copper derivative has also been examined. This has a structure quite different from that of any of the others mentioned, but owing to the poorness of the crystals it has not been worked out completely.

The planar distribution for the valencies in this quadricovalent nickel compound having been established, it was obviously an excellent case to test the validity of Pauling's deduction that it should be diamagnetic. Dr. L. C. Jackson, of the University of Bristol, very kindly examined this compound and finds the deduction to be correct.

#### EXPERIMENTAL.

*Disalicylaldoximenickel*.—An aqueous solution of nickel chloride (2 g. in 250 ml.) was mixed with a slight excess of aqueous salicylaldoxime (2.5 g. in 200 ml.), and then solid sodium acetate

(4 g.) stirred in. The bright green precipitate was washed with water and dried over phosphoric anhydride. The dried product was dissolved in hot chloroform, and emerald-green crystals slowly separated on standing (Found: Ni, 17.79; N, 8.6. Calc.: Ni, 17.74; N, 8.5%).

The molecular weight was determined ebullioscopically in chloroform. The following results were obtained ( $M$ , calc.: 330.7):

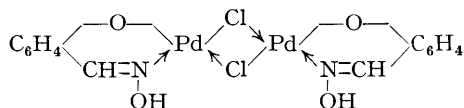
$c$ (g./1000 ml.).....	5.420	6.670
$\Delta t$ .....	0.045°	0.050°
$M$ .....	313.2	346.8

*Disalicylaldoximepalladium*.—To an aqueous solution of potassium chloropalladite (1 g. in 70 ml.) was added a slight excess of aqueous salicylaldoxime (1 g. in 70 ml.). The bright yellow precipitate which immediately formed was purified and recrystallised as above. The orange-yellow crystals are isomorphous with the nickel compound (Found: Pd, 28.19; N, 7.6. Calc.: Pd, 28.17; N, 7.4%).

The molecular weight was determined as above ( $M$ , calc. = 378.8):

$c$ (g./1000 ml.).....	4.418	3.698
$\Delta t$ .....	0.032°	0.025°
$M$ .....	358.8	384.7

*Monosalicylaldoximepalladous Chloride*.—Aqueous solutions of potassium chloropalladite (2 g. in 250 ml.) and salicylaldoxime (1 g. in 100 ml.) were cooled in ice, and the latter added to the former with constant stirring. The chocolate-coloured precipitate was washed, dried, and extracted with 15 ml. of cold acetone, giving an orange-red solution. Light petroleum was added to this solution until no further precipitation occurred, and the brown amorphous powder which had been thrown out was filtered off as rapidly as possible [Found: Pd, 38.8. Pd(C<sub>7</sub>H<sub>6</sub>O<sub>2</sub>N)Cl requires Pd, 38.4%]. This compound is decomposed by further addition of salicylaldoxime solution to give the normal disalicylaldoximepalladium. The filtrate on standing deposits crystals of the latter, together with some palladous chloride. The probable structure of this derivative is



*Disalicylaldoximeplatinum*.—Aqueous solutions of potassium chloroplatinite (2 g. in 200 ml.) and salicylaldoxime (1.5 g. in 150 ml.) were mixed and kept for 48 hours; the yellow precipitate which had formed was then filtered off, and the filtrate set aside for a further crop. The precipitate had a platinum content of about 37% and was a mixture of disalicylaldoximeplatinum and disalicylaldoximinoplatinous chloride. This was dissolved in cold acetone and the solution allowed to evaporate in a dark cupboard, since light causes decomposition. The *disalicylaldoximeplatinum* separates out in yellow anhydrous crystals, leaving the very soluble disalicylaldoximinoplatinous chloride in solution. After a further recrystallisation from acetone or carbon tetrachloride, the crystals were pure [Found: Pt, 41.83; N, 6.1. Pt(C<sub>7</sub>H<sub>6</sub>O<sub>2</sub>N)<sub>2</sub> requires Pt, 41.78; N, 6.0%]. This compound crystallises in two forms; the crystals usually obtained are monoclinic prisms, but occasionally a darker yellow type separates in the form of tetragonal needles. The two forms are readily interconvertible merely by dissolving them in acetone or carbon tetrachloride and allowing the solution to crystallise, whereupon either form may separate out. The type of crystal obtained does not depend on temperature, and there seems to be no criterion by which one can forecast which form will separate from solution.

The molecular weight was found ebullioscopically in acetone, the monoclinic crystals being used as starting point ( $M$ , calc. = 467.2):

$c$ (g./1000 ml.).....	6.513	8.023
$\Delta t$ .....	0.029°	0.041°
$M$ .....	498.6	434.4

A solution of the tetragonal form in acetone was prepared, and the molecular weight determined by Barger's method, with naphthalene as the standard substance. It was found that the vapour pressure of a 0.4016% disalicylaldoximeplatinum solution was greater than that of a 0.00938*N*- and less than that of a 0.00816*N*-solution of naphthalene. Hence the molecular weight lies between 428 and 496 (calc., 467.2).

*Disalicylaldoximinoplatinous Chloride*.—The first product from the reaction between salicylaldoxime and potassium chloroplatinite was extracted with boiling carbon tetrachloride until

the extract was almost colourless. The pale greenish-yellow residue was dried over phosphoric anhydride [Found : Pt, 35.89; N, 5.2.  $\text{Pt}(\text{C}_7\text{H}_7\text{O}_2\text{N})_2\text{Cl}_2$  requires Pt, 36.13; N, 5.1%]. The presence of chlorine was also proved.

It is readily soluble in acetone and alcohol, giving pale yellow solutions which decompose on standing and do not crystallise. Sodium acetate solution reacts with this compound to give disalicylaldoximeplatinum and sodium chloride. The former is extracted from the product of reaction by means of hot carbon tetrachloride.

*Crystallographic and X-Ray Results.*—X-Ray investigations were carried out by means of single-crystal rotation and oscillation photographs using  $\text{Cu}_{K\alpha}$  radiation.

*Disalicylaldoximepalladium.* Crystals prepared as above were found to be monoclinic holohedral combinations of  $a\{100\}$ ,  $r\{101\}$ ,  $R\{10\bar{1}\}$ , and  $m\{110\}$ ,  $R$  predominating, and the crystals being elongated along the  $b$ -axis. The absence of a pyro-electric effect (tested for by the liquid-air method) confirmed the holohedral symmetry both of this compound and of the isomorphous nickel derivative. Angles observed :  $a\{100\} : r\{101\} = 40^\circ 21'$ ;  $a\{100\} : R\{10\bar{1}\} = 67^\circ 09'$ ;  $a\{100\} : m\{110\} = 69^\circ 11'$ ; whence  $a : b : c = 2.81 : 1 : 2.10$  and  $\beta = 110^\circ 42'$ .

From X-ray measurements,  $a = 13.63$ ,  $b = 4.89$ ,  $c = 10.20$  Å.U.,  $\beta = 110^\circ 30'$  ( $a : b : c = 2.79 : 1 : 2.09$ ).

With two molecules in the unit cell,  $d = 1.97$  g./c.c. (obs. = 1.96).

Reflections not occurring :  $\{hol\}$  when  $h + l$  is odd,  $\{oko\}$  when  $k$  is odd; whence the space-group is  $P2_1/m(C_{2h}^5)$ . Each molecule in the crystal has therefore a centre of symmetry, so that the co-ordinated groups are arranged in *trans*-positions, the four metal valencies being coplanar.

*Disalicylaldoximenickel.* As normally occurring, this is isomorphous with the palladium compound, corresponding axes in the two cases being almost identical :  $d$  (calc. for two molecules per unit cell) = 1.73 (obs. = 1.74). The space-group is  $P2_1/m(C_{2h}^5)$ , and the molecule has a centre of symmetry. This compound is sometimes obtained in irregular thin plates, which give X-ray photographs closely similar to those of the usual crystals, indicating that the substance is dimorphous.

*Disalicylaldoximeplatinum.* This exists in two crystalline forms, neither of which is isomorphous with the palladium or the nickel compound.

(a) *trans*-Form. The crystals are monoclinic prisms, being combinations of  $c\{001\}$ ,  $b\{010\}$ ,  $p\{011\}$ ,  $a\{100\}$ , and  $r\{101\}$ ; usually elongated along  $[a]$  with  $p$  predominating, but sometimes elongated along  $[c]$ .

X-Ray measurements give  $a = 5.79$ ,  $b = 24.23$ ,  $c = 4.53$  Å.U.,  $\beta = 97^\circ 36'$ ;  $d$  (calc. for two molecules per unit cell) = 2.46 g./c.c. (obs. = 2.45).

Reflections not occurring :  $\{hol\}$  when  $h + l$  is odd,  $\{oko\}$  when  $k$  is odd; therefore the space-group is  $P2_1/m(C_{2h}^5)$ , and the molecule has a centre of symmetry.

(b) The second form crystallises in ditetragonal bipyramidal needles  $a\{100\}$  terminated by  $\{hol\}$ .

From X-ray measurements,  $a = 26.60$  and  $c = 14.40$  Å.U. With 32 molecules in the unit cell,  $d = 2.43$  g./c.c. (obs. = 2.42). The  $[111]$  axis is 20.1 Å.U., showing that the cell is body-centred, and since  $\{110\}$  is halved, the space-group is probably  $I4/am\bar{d}(D_{4h}^{19})$ . The molecules are asymmetric : this result, coupled with the observation that this form can be obtained under suitable conditions from the *trans*-isomeride by recrystallisation from either hot or ice-cold solutions, makes it very improbable that this is a dimorphous form of the *trans*-compound. On the other hand, the observed lack of symmetry is in accordance with expectations for a *cis*-isomeride with non-equivalent *cis*-valencies.