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Stereochemistry of 5-Coordinated Compounds

II.* On the Configuration of the Nickel Compound $[NiBr_3(Et_3P)_2]$

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By adding trialkylphosphines to nickel halogenides Jensen[1] in 1936, prepared red compounds of the type $[NiX_2(R_3P_2)]$. These compounds add halogens and NO_2 to form dark-green compounds; the latter are rather unstable, but by the isolation of the compound $NiBr_3,2Et_3P$ they could be shown to contain formally tervalent nickel. The compound $NiBr_3,2Et_3P$ is easily soluble in organic solvents, could be recrystallized from petroleum ether and forms dark violet-black crystals with melting point 83—84°. By determination of the molecular weight in benzene solution the compound was shown to be monomolecular. The formulation of the compound as a binuclear complex with bi- and quadrivalent nickel may therefore be excluded. It is unlikely that the compound is a polybromide or that part of the bromine is bound to triethylphosphine since Et_3PBr_2 does not combine with nickel halogenides; it was, therefore, concluded that the compound in fact contains tervalent nickel.

This conclusion has now been substantiated by magnetic measurements. Values ranging from 1.72 to 1.90 Bohr magnetons were found for the magnetic moment, the lowest values being found just after preparation. This is in good agreement with the value computed for tervalent nickel with covalent bonds (one unpaired electron), *viz.* 1.73 Bohr magnetons, assuming that the magnetism is determined by spin alone, the orbital moment being negligible.

By the magnetic measurements on the solid substance the possibility that the complex might be binuclear (the molecular weight of the dissolved substance being caused by dissociation) is definitely ruled out, as such a compound would be diamagnetic.

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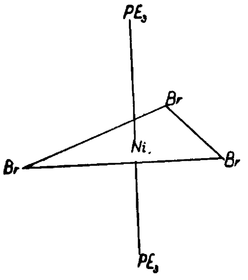
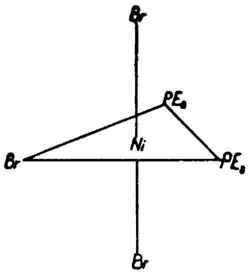
* As no. 1 of this series we wish to consider the paper *Z. anorg. u. allgem. Chem.* **250** (1943) 257.

The compound $NiBr_3,2Et_3P$ accordingly contains tervalent nickel and moreover is one of the rare compounds in which the central atom has coordination number five. For some of the compounds of this type (*e. g.* PF_5) the configuration has been shown to be that of a trigonal bipyramid (*cf.* Jensen [2]). As the compound here discussed is formed by the addition of bromine to the compound $NiBr_2(Et_3P)_2$ which has a trans-planar configuration, it seems possible on the other hand, that it might have the configuration of a tetragonal pyramid (IV).



I.



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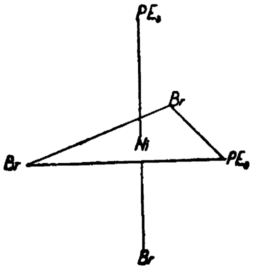
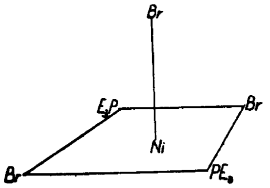
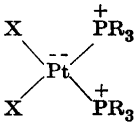


II.



IV.

A choice between these possibilities may be made by means of dipole moment measurements. Because of the instability of the compound $[NiBr_3(Et_3P)_2]$ it is not possible to determine a very exact value for its dipole moment, but we have found a value of about 2.5 D, which at any rate indicates the order of magnitude. If the compound has the configuration of a trigonal bipyramid there are three possibilities for its structure I, II and III. In the first the bond moments compensate each other, and a compound with this structure should therefore have zero dipole moment (like the compounds SbR_3X_2). In the two other cases the two triethylphosphine molecules are in cis positions, and to judge from platinum complexes of the type $[PtX_2(R_3P)_2]$ with two trialkylphosphine molecules in cis position[3] the moment should be in the order of 7—10 D. These large moments are not due to a large moment of the Pt-halogen bonds, but to large moments of the Pt—P bonds, the phosphorus atoms having a large positive charge, when they are coordinated to a metal atom, so that the structure approaches the formula:



The possibility that the configuration of $[NiBr_3(Et_3P)_2]$ might be that of a trigonal bipyramid can therefore be excluded. The configuration of a tetragonal pyramid, on the other hand, is in good agreement with the dipole moment found. With this configuration the ligands in the base are in trans position and the bond moments accordingly compensate each other, so that the dipole moment of this compound should only be that of the Ni-Br bond. One should not expect this to be very large; on the contrary the value 2.5 D seems very plausible. This comparatively low value excludes the possibility that the nickel atom might be situated in the centre of a tetragonal pyramid; because of the large values of the Ni-P bond moment this configuration would give a much higher value for the dipole moment. It is of course not possible to exclude the possibility that the nickel atom is raised somewhat above the base, but the deviation can only be of the order of magnitude of 0.1—0.2 Å (*cf.* Jensen[4]).

It is of great interest that this configuration, which has not hitherto been found for any complex, was predicted by Daudel and Bucher[5]. These authors conclude from quantum mechanical calculations that compounds of the type XY_5 should have the trigonal bipyramidal structure if the bonds involved are formed by means of s-, p- and d-electrons having the same principal quantum number, but the tetragonal pyramidal structure if the dsp-bonds are formed by means of d-electrons having a lower and s- and p-electrons having a higher principal quantum number, as in the case of tervalent nickel, where the bonds are formed from 3d, 4s and 4p orbitals. The bonds may be dsp^3 bonds; the odd electron may, however, also occupy a 4p orbital, so that the bonds are d^2sp^2 bonds.

The problem of the bond arrangement for the coordination number 5 has also been treated by Kimball[6] from a group theory point of view. Kimball comes to the conclusion that the trigonal bipyramid is the stable configuration for dsp^3 bonds, whether the d orbital has the same principal quantum number as the s- and p-orbitals or a lower one. For the configuration d^2sp^2 the bonds, according to Kimball, are directed from the centre to the corners of a tetragonal pyramid. According to the theory of Daudel and Bucher, on the contrary, the central atom is situated in the centre of the base in the case of the tetragonal pyramidal configuration. Our measurements, therefore, are in better accordance with the predictions of Daudel and Bucher than with those of Kimball.

The theory of Daudel and Bucher generally predicts the tetragonal pyramidal structure for compounds with dsp^3 bonds; this structure should therefore also be possible for compounds of bivalent nickel and copper, although in this case the fifth bond should only be weak. Bjerrum[7] has shown that the diethylendiamine cupric ion in strongly ammoniacal solution takes up an ammonia molecule with the formation of a pentammine complex $[Cuen_2NH_3]^{++}$, and in the triethylendiamine cupric ion $[Cuen_3]^{++}$ one of the ethylendiamine molecules is only bound by one amino group to the cupric ion. The configuration of these complexes is not known, but as the 4-coordinated cupric complexes has a planar configuration[8], it seems very plausible that the fifth bond is perpendicular to the plane formed by the first four ligands.

It may further be predicted from the theory of Daudel and Bucher that iron pentacarbonyl should have the tetragonal pyramidal structure, the bonds being dsp^3-bonds, while Kimball expects the bipyramidal structure. The dipole moment of $Fe(CO)_5$ was found by Graffunder and Heymann[9] and by Bergmann and Engel[10] to be greater than zero, but may be zero, if the atomic polarisation is properly allowed for. Duncan and Murray[11] attempted to obtain Raman spectra of iron pentacarbonyl, but without success. Ewens and Lister[12], however, conclude from electron diffraction measurements that the molecule has the trigonal bipyramidal structure. This evidence can hardly be considered as conclusive, and it would be of great importance to get an exact determination of the structure of iron pentacarbonyl.

EXPERIMENTAL

$[NiBr_2(Et_3P)_2]$. To an ice-cold solution of 4 g of anhydrous nickel bromide in 50 ml of ethanol were added 2.30 g of triethylphosphine. Ruby-red crystals separated at once. The crystals were filtered off and washed with a little ethanol and dried over P_2O_5 (at room temperature and atmospheric pressure). Yield 5.3 g = 85 %. M. p. 103—105°. For purification 2.5 g were dissolved in 35 ml of dry petroleum ether, the solution was filtered and concentrated in vacuo without heating. Large, dark violet-red crystals separated. Yield 1.14 g. M. p. 106—107°.

$[NiBr_3(Et_3P)_2]$. To a solution of 2.5 g of $[NiBr_2(Et_3P)_2]$ in 4.5 ml of benzene (dried over sodium) was added 0.45 g of bromine dissolved in 1.5 ml of benzene. The dark-red solution turned dark-green. The benzene was removed as fast as possible in vacuo without heating (the receiver was cooled with solid carbon dioxide + ethanol). The residue was dissolved in 25 ml of petroleum ether (dry), the solution was filtered and evaporated in vacuo at 0°. Glittering violet-black crystals separated. The crystals were transferred to a desiccator with P_2O_5 and paraffin, but measurements thereon must be carried out as quickly as possible. In the course of two hours it generally decomposed with evolution of hydrogen bromide and triethylphosphine and formation of nickel bromide. Yield 1.10 g = 63 %. M. p. 83–84°.

Calc.	Br 44.83,	Ni 10.98
Found	» 44.66 (Volhard)	» 10.83 (as dimethylglyoxim nickel)

Magnetic measurements

The magnetic measurements were performed by the Gouy method. After some orienting measurements (which gave values from 1.78 to 1.90 Bohr magnetons) the preparation, of which the analysis is given above, was measured as quickly as possible after isolation (T = 293.3° K):

Field strength in Ørsted	3750	3750	6970	6970	6970
$\chi_g \times 10^6$	2.33	2.35	2.62	2.62	2.63
$\chi_M \times 10^6$	1246	1256	1400	1400	1406
$\mu_{eff} = 2.84\sqrt{T \times \chi_M}$	1.72	1.72	1.82	1.82	1.82

The higher values at the higher field strenght are probably due to the onset of decomposition during the first measurements. The paramagnetism increases considerably with the time.

The first values are in close agreement with the value 1.73 Bohr magnetons, calculated for one unpaired electron. The accordance is of course much better than could be expected, because the values of χ_M are not corrected for the diamagnetic susceptibility (χ_M = about − 300), nor for the Curie temperature. The first correction would change the value of μ_{eff} from 1.72 to 1.91, but a positive Curie temperature might compensate for this. No attempt was made to determine the Curie temperature by measurements at lower temperature; these measurements would namely have to be carried out on different samples, on account of the instability of the compound and the time involved in the measurements, and the difference between the susceptibilities of different samples might completely compromise this determination. The value 1.91 of μ_{eff} may be real and be caused by the start of decomposition or be due to an orbital contribution to the moment. It was not deemed of importance to investigate this question further, because the tervalency of the nickel atom has been proved, whether the value 1.72 or 1.91 be accepted.

Dipole moment

The measurement of the dielectric constants of solutions of $[NiBr_3(Et_3P)_2]$ in benzene was carried out in an apparatus from Kipp and Zonen (*cf.* Jensen and Friediger[13]). The measurements were carried out as fast as possible (ca. 15 min.) after the isolation of the compound; it slowly decomposed in solution as indicated by an increase in the dielectric constant of the solution in the course of some minutes. This decomposition goes more quickly in dilute solutions and in these a deposite of nickel bromide separates in the course of 1—2 hours. Extrapolation of the dielectric constants found to the concentration 0 is therefore probably without meaning, and the best values are those found in the strongest solutions, which contain about 10 % of the complex. It has previously been found by cryoscopic measurements that the compound is monomolecular in benzene.

Because of the very intensive colour of the solutions, the refractive index could not be determined, and would also be valueless because of anomalous dispersion. The molecular polarizations were therefore calculated from the dielectric constants only, using the formula [14]:

$$P_M = \frac{1000}{c}\left[\frac{\varepsilon_{12}-1}{\varepsilon_{12}+2} - \frac{\varepsilon_1-1}{\varepsilon_1+2}\right]$$

where c is the *molar* concentration of the solute, ε_{12} the dielectric constant of the solution and ε_1 the dielectric constant of the solvent, benzene (2.2725 at 25°). For large dipole moments this formula gives values almost identical with those calculated from the formula $P_M = P_O - P_E - P_A$, and even for moments about 2 D the deviation is only a few percent.

After some orienting measurements, in which values of about 2.5 D were obtained, the following measurement was performed:

c	$\Delta\varepsilon$	ε_{12}^{25}	P_M
0.0297	0.0244	0.2969	134.3
0.0624	0.0443	0.3168	115.4
0.1333	0.0914	0.3639	110.4

From the lowest value of P_M, which is probably the best, the value $\mu = 2.30$ D is calculated. The value of P_M extrapolated to the concentration 0, *viz.* 150, gives $\mu = 2.68$ D. We may therefore safely conclude that the dipole moment of $[NiBr_3(Et_3P)_2]$ is not greater than $\mu = 2.7$ D and not much lower than 2.3 D.

SUMMARY

The magnetic moment and dipole moment of the compound $[NiBr_3(Et_3P)_2]$ have been measured. According to these measurements the compound contains tervalent nickel and has the configuration of a tetragonal pyramid.

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