

men was produced by two additional recrystallizations from ethanol, m.p. 198–198.5°. (Found: C 45.93; H 4.72; N 10.81; S 18.13; 1.96 % H<sub>2</sub>O. Calc. for C<sub>20</sub>H<sub>24</sub>O<sub>6</sub>N<sub>4</sub>S<sub>3</sub>·0.5 H<sub>2</sub>O: C 46.06; H 4.83; N 10.74; S 18.44; 1.73 % H<sub>2</sub>O). An additional recrystallization from 80 % ethanol and subsequent drying over calcium chloride *in vacuo* for 27 h did not change the melting point or the analytical composition.

*5,6-Dihydro-2-sulphanilamido-4H-1,3-thiazine* (IV b). The acetylated compound (IV a) (2.3 g) was hydrolyzed on heating for 2 h in 0.25 N HCl (160 ml). The mixture was adjusted to pH 8 with conc. NaOH, and after cooling the precipitate was filtered off. Three recrystallizations from 50 % ethanol, with the use of a little charcoal, afforded a pure specimen of (IV b) (718 mg), m.p. 209–209.5°. (Found: C 44.45; H 4.96; N 15.57; S 23.53. Calc. for C<sub>16</sub>H<sub>13</sub>N<sub>3</sub>O<sub>2</sub>S<sub>2</sub>: C 44.27; H 4.83; N 15.49; S 23.63). The IR-spectrum displayed strong bands at: 3400 (vs); 3300 (s); 3250 (s); 3200 (s); 2900 (w) with shoulders at 2960 and 2860; 1640 (s); 1600 (vs); 1570 (vs); 1500 (s); 1470 (m); 1435 (m); 1370 (vs); 1335 (sh); 1325 (s); 1305 (vs); 1300 (sh); 1280 (s); 1270 (vs); 1180 (m); 1140 (vs); 1100 (s); 1080 (vs); 1045 (w); 1015 (s); 955 (m); 880 (m); 850 (s); 835 (m); 827 (s); 820 (s); 745 (s); 725 (m); 680 cm<sup>-1</sup> (s).

*2-(N<sup>4</sup>-Acetylsulphanilamido)-5,6-dihydro-4H-1,3-thiazine* (IV c). A solution of (IV b) (55 mg) and acetic anhydride (0.1 ml) in 25 % ethanol (13 ml) was left for 24 h at room temperature and then briefly heated to a boil. The residue (41 mg), m.p. 211–211.7°, was recrystallized from 50 % ethanol to give colourless crystals, m.p. 211–212°. (Found: C 45.58; H 4.99; N 13.55; S 20.17. Calc. for C<sub>12</sub>H<sub>11</sub>N<sub>3</sub>O<sub>3</sub>S<sub>2</sub>: C 45.98; H 4.82; N 13.41; S 20.46).

The author wishes to express his gratitude to Professor A. Kjær for valuable advice during this work.

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Received March 24, 1965.

## Reductions with Potassium Graphitate

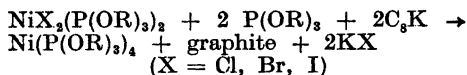
### I. Preparation of Nickel(0) Complexes of Trialkyl Phosphites

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It was already noted during our investigations of nickel complexes of trialkyl phosphines<sup>1-4</sup> that trialkyl phosphites form similar red to violet nickel(II) complexes. In contrast to the phosphine complexes, which crystallise readily; the phosphite complexes are low melting substances which are extremely soluble in inert organic solvents so it has not been possible to isolate them in the pure state. Analyses indicate, however, that they are analogous to the phosphine complexes, *i.e.* of the type [NiX<sub>2</sub>(P(OR)<sub>3</sub>)<sub>2</sub>].

During some attempts to use potassium graphitate as reducing agent it was noted that the red or violet solutions of these compounds in benzene were slowly decolorized at room temperature. When the solutions contained excess trialkyl phosphite, completely colourless solutions could be obtained from which colourless nickel(0) complexes with the general formula [Ni(P(OR)<sub>3</sub>)<sub>4</sub>] were isolated. They are formed according to the equation:



Some reduction also took place by heating with finely dispersed potassium in toluene or xylene. However, it has not been possible to prepare pure compounds in this way.

As expected for compounds based on the configuration d<sup>10</sup> of the metal these compounds were found to be diamagnetic. Their infrared spectra in the NaCl range are almost identical with the spectra of the phosphite ligands (*cf.* the infrared spectra of the corresponding phosphine complexes<sup>5</sup>), especially the establishment of a bond between phosphorus and nickel

does not change the P—O—C vibrations near 960 and 1000  $\text{cm}^{-1}$  significantly.

The compounds are easily soluble in organic solvents and are slowly decomposed by water. In air they rapidly turn green because of oxidation. Preliminary experiments have shown that phosphite complexes of cobalt(II) halides, iron(II) halides and copper(I) halides may similarly be reduced by potassium graphitite to halogen-free metal compounds.

*Experimental.* *Trialkylphosphites* were prepared according to the procedure given for triethyl phosphite.<sup>5</sup> The phosphites were carefully fractionated to separate them from the isomeric phosphonic esters. Boiling points found: trimethyl phosphite 112–113°C (760 mm), triethyl phosphite 51–51.5°C (13 mm), tripropyl phosphite 67–68°C (3 mm), triisopropyl phosphite 66.5–67°C (13 mm), tributyl phosphite 107–08°C (5 mm).

*Potassium graphitite.* The bronze-coloured  $\text{C}_6\text{K}$ <sup>6</sup> was prepared portionwise from 3 g of finely powdered graphite and 1.4 g of pure potassium which were heated in a highly evacuated vessel at 350°C for 4–5 h.

*Trialkyl phosphite complexes of divalent nickel.* For the preparations anhydrous nickel halides were at first applied, but later experiments showed that this is not essential, and the application of the hydrates seems even to be advantageous, possibly because their reaction with the alkyl phosphites is less violent. The nickel halide (0.01 mole), e.g.  $\text{NiBr}_2 \cdot 3\text{H}_2\text{O}$ , was rubbed with cooled, freshly distilled trialkyl phosphite (0.02 mole). The reactions are exothermic and a strongly coloured oil (red-violet with nickel chloride, brown-violet with nickel bromide, and violet with nickel iodide) was formed together with some drops of a green aqueous phase. The oil was dissolved in light petroleum, the solution dried with sodium sulfate and the solvent removed *in vacuo*. On standing in a vacuum desiccator over paraffin some of the compounds became crystalline:  $[\text{NiBr}_2(\text{P}(\text{OEt})_3)_2]$ , black;  $[\text{NiI}_2(\text{P}(\text{OEt})_3)_2]$ , black-violet;  $[\text{NiBr}_2(\text{P}(\text{O}i\text{Pr})_3)_2]$ , black-violet. The compounds melt unsharply a little above room temperature; they deliquesce in vapours of organic solvents and could not be recrystallised. Analyses for C, H, and halogen have, however, given values which do not differ seriously from the theoretical ones. In the other cases the complexes were only obtained as viscous oils.

On contact with bromine vapour,  $\text{NO}_2$ , or  $\text{NOCl}$ , the red to violet solutions of these complexes in benzene become intensely green or blue, without doubt because of oxidation to

complexes of trivalent nickel similar to the corresponding phosphine complexes.<sup>4</sup>

A characteristic difference from the red phosphine nickel complexes is that the red or violet solutions of the phosphite complexes in benzene, ether, or acetone become yellow or brown on addition of a small amount of an alcohol, especially methanol. The deep violet solution of  $[\text{NiI}_2(\text{P}(\text{OEt})_3)_2]$  in benzene shows absorption maxima at 338 and 557  $\text{m}\mu$ , which disappear on addition of ethanol and are replaced by an absorption maximum at 449  $\text{m}\mu$ . This colour change is reversible: on addition of more benzene the solution regains its violet colour. The reversibility of the colour change makes it improbable that it should be due to a solvolysis process and rather indicates a distortion of the planar complex into a tetrahedral complex or perhaps the formation of a hexacoordinated, octahedral complex.

*Reduction of the nickel(II) complexes to nickel(0) compounds.* The nickel(II) trialkylphosphite complex, prepared from 0.01 mole of the nickel halide (usually the bromide: but chlorides and iodides behaved similarly), and 0.02 mole of the corresponding phosphite were dissolved in 30–40 ml of pure, dry benzene and the solution added to a cooled evacuated flask containing potassium graphitite prepared from 3 g of graphite. The red or violet colour of the solution rapidly changed to yellow, but to get pure compounds it is essential that a completely colourless solution is obtained (this may take some days at room temperature). When the reaction was completed the benzene solution was decanted from the graphite, filtered, and the benzene removed *in vacuo*. Addition of methanol to the oily residue usually caused the nickel compound to precipitate in crystalline form. However, in the case of the trimethyl phosphite compound, which is very soluble in all organic solvents, water had to be added to the methanolic solution. The compounds of triethyl, tripropyl, and tributyl phosphite were dissolved in methanol by heating at 40°C and separated again by cooling to about  $-10^\circ\text{C}$ . The triisopropyl phosphite derivative is less soluble in methanol and was not reprecipitated.

The yields were only 1.5–2 g instead of the calculated 6–10 g but this is mainly due to the high solubility of the compounds.

The compounds were obtained as colourless leaflets which were filtered on a glass filter and dried *in vacuo*. The methyl and ethyl derivatives rapidly turned green on exposure to air. The higher homologues are more stable. The tripropyl phosphite compound has in repeated experiments been found to be the one most easily obtainable in the pure state.

On heating these compounds sublime or decompose without melting. They are easily soluble in organic solvents, but less soluble in methanol than in ethanol. They are almost insoluble in water but are slowly decomposed with liberation of the phosphite and formation of a green nickel(II) compound.

The compounds were found to be diamagnetic (measured on a Gouy balance at room temperature).

Molecular weight determinations were done cryoscopically in benzene.

*Tetrakis(trimethyl phosphite)nickel(0)*,  $[\text{Ni}(\text{P}(\text{OMe})_3)_4]$ . (Found: C 25.96; H 6.76. Calc for  $\text{C}_{12}\text{H}_{36}\text{NiO}_{12}\text{P}_4$ : C 25.45; H 6.49).

*Tetrakis(triethyl phosphite)nickel(0)*,  $[\text{Ni}(\text{P}(\text{OEt})_3)_4]$ . (Found: C 39.30; H 8.53; Ni 8.05, 8.20, 8.08; Mol.wt. 714. Calc. for  $\text{C}_{24}\text{H}_{60}\text{NiO}_{12}\text{P}_4$ : C 39.85; H 8.36; Ni 8.11; Mol.wt. 723).

*Tetrakis(triisopropyl phosphite)nickel(0)*,  $[\text{Ni}(\text{P}(\text{OPr})_3)_4]$ . (Found: C 48.50; H 9.34; Ni 6.67, 6.54; Mol.wt. 890. Calc. for  $\text{C}_{36}\text{H}_{84}\text{NiO}_{12}\text{P}_4$ : C 48.52; H 9.43; Ni 6.55; Mol.wt. 891).

*Tetrakis(triisopropyl phosphite)nickel(0)*,  $[\text{Ni}(\text{P}(\text{OiPr})_3)_4]$ . (Found: C 49.05; H 9.57. Calc. for  $\text{C}_{36}\text{H}_{84}\text{NiO}_{12}\text{P}_4$ : C 48.52; H 9.43).

*Tetrakis(tributyl phosphite)nickel(0)*,  $[\text{Ni}(\text{P}(\text{OBu})_3)_4]$ . (Found: C 53.90; H 10.01; Ni 5.84. Calc. for  $\text{C}_{48}\text{H}_{108}\text{NiO}_{12}\text{P}_4$ : C 54.39; H 10.20; Ni 5.55).

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Received March 23, 1965.

## On the Alleged *cis-trans*-Isomeric Forms of Bis(benzylmethylglyoximato)nickel(II)

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Sugden,<sup>1</sup> in 1931, isolated two forms of bis(benzylmethylglyoximato)nickel(II) which differed considerably in solubilities and melting points. The  $\beta$ -form (m.p. 75–77°C) was more soluble than the  $\alpha$ -form (m.p. 168°C) in cold acetone. The two forms were considered to be *cis-trans*-isomeric square-planar nickel complexes and this seemed to be corroborated by measurements of their electric dipole moments. These were found by Cavell and Sugden<sup>2</sup> to be 1.60 and 1.30 D, respectively.

During an investigation of the paper-chromatographic separation of *cis-trans*-isomeric complexes we have come to the conclusion that these two forms are not *cis-trans*-isomers. We have confirmed the existence of the two forms of this nickel compound; however, the following observations indicate that the appearance of two forms has to be interpreted in another way than as a case of *cis-trans*-isomerism.

*Paper chromatography.* On circular paper chromatography, using pentane as the eluant, both forms behaved similarly: Some of the compound dissolved and moved as a red-brown ring in the solvent front leaving an apparently immobile dark-brown spot at the starting point. However, during continued elution this spot disappeared slowly and formed a faintly yellow "tail". With other eluents and on aluminium oxide columns there was a similar indication that some transformation took place during the elution. Melting points of the products isolated from the spots varied between the m.p. of the pure  $\alpha$ - and  $\beta$ -form (see below).

*Interconversion of the two forms.* In a sealed flask containing dry pentane and the  $\beta$ -form as the bottom phase, crystals of the  $\alpha$ -form deposited after some days on the walls of the flask. The same transformation was shown to occur in other