Polyhedron Vol. 2, No. 7, pp. 672–673, 1983
Printed in Great Britain.

0277-5387/83 $3.00 + .00

Synthesis and studies on dichloro iodo triphenylphosphine oxide nickel(III)

K. P. SARMA and RAJ K. PODDAR*
Department of Chemistry, North-Eastern Hill University, Bijni House, Shillong 793 003, India

(*Received* 29 *September* 1982, *accepted* 10 *January* 1983)

Abstract—A new compound of nickel(III), [Ni(OPPh$_3$)Cl$_2$I] has been prepared by the action of nitrosyl chloride or chlorine gas on [Ni(PPh$_3$)$_2$I$_2$]. Various physical studies of the compound are reported.

During the investigation on the reactions of [Ni(PPh$_3$)$_2$X$_2$] (X = Cl, Br, I, NCS and NO$_3$) with nitrosyl chloride, it was found that the nickel(II) complexes gave dimeric species, viz. [Ni(PPh$_3$)XCl]$_2$ (X = Cl, Br, NCS, NO$_3$) and the oxidation of the liberated triphenylphosphine molecule to triphenylphosphine oxide.[1] However, reaction of [Ni(PPh$_3$)$_2$I$_2$] with nitrosyl chloride resulted in the oxidation of nickel(II) to nickel(III) with formation of [Ni(OPPh$_3$)Cl$_2$I]. In this work, the synthesis and studies of the complex [Ni(OPPh$_3$)Cl$_2$I] are reported.

EXPERIMENTAL

Diiodo bistriphenylphosphine nickel(II) was prepared according to the method of Venanzi.[2]

Preparation of dichloro iodo triphenylphosphine oxide nickel(III)

A suspension of powdered [Ni(PPh$_3$)$_2$I$_2$] (1 g) was taken in dry cyclohexane (50 cm^3) and nitrosyl chloride was bubbled slowly through the suspension for about 20 min while stirring the mixture. Slowly the suspended material went into solution. After discontinuing the bubbling of the gas, the mixture was stirred at room temperature for about 8 hr, when yellow compound (m.p. 100–105°d) separated out. During the reaction, colour of the solution changed from dark reddish brown to light red through green. The compound was filtered out and washed several times with dry diethyl ether and dried under vacuum. It was analysed for [Ni(OPPh$_3$)ICl$_2$]: Found: Ni, 10.95; Cl, 13.57; I, 24.12; P, 5.80; C, 40.68; H, 3.12; [N: (OPPh$_3$)ICl$_2$] requires: Ni, 10.97; Cl, 13.27; I, 23.74; P, 5.79; C, 40.37; H, 2.80%. The same compound was also obtained by using chlorine gas instead of nitrosyl chloride.

The mother liquor, after the separation of the compound, on concentration yielded triphenylphosphine oxide, characterised by m.p. (157°C) and IR spectrum ($\nu_{P=O}$ at 1185 cm^{-1}).

The total halide content in the compound was obtained by decomposing the compound with KNO$_3$, KOH mixture, acidifying with dil. nitric acid to make the solution just acidic and then precipitating as silver halide using silver nitrate. Chloride estimation was done by decomposing the compound with dilute nitric acid and heating for about 30 min to oxidise iodide to iodine and get liberated and then precipitating silver chloride by silver nitrate. Iodide content was obtained by subtracting chloride content from the total halide content. For phosphorus estimation, the compound was decomposed with a mixture of sugar, KNO$_3$ and Na$_2$O$_2$ in a Parr–Bomb, extracted with water, acidified with slight excess of dilute sulphuric acid, heated to dryness, extracted again with water, filtered and estimated it as phosphate using ammonium molybdate.

IR spectra were recorded on Perkin–Elmer 297 in the range 4000–600 cm^{-1} and on Polytec FIR 30 spectrophotometer in the range 600–100 cm^{-1}. The UV-visible spectral studies were carried out on Beckman 26 spectrophotometer. The ESR spectrum was recorded at liquid nitrogen temperature using Varian E 104 spectrophotometer. The magnetic measurements were made by the Gouy method. Conductivity measurements in nitrobenzene was made on an Elico type CM 82 conductivity bridge. The oxidation state of nickel in the compound was determined iodometrically by the reduction of a known amount of the compound with aqueous potassium iodide solution, followed by titration of the liberated iodine with standard sodium thiosulphate solution.

RESULTS AND DISCUSSION

The compound was characterised by the elemental analyses and the physical studies mentioned above. The compound has the empirical formula [Ni(OPPh$_3$)Cl$_2$I]. The magnetic moment of the complex at room temperature was found to be 1.68 B.M., characteristic of nickel(III) having one unpaired electron. The conductivity measurements in acetonitrile and nitrobenzene solvents did not shown any conductance, confirming that all the anions are coordinated to the metal ion.

The presence of triphenylphosphine oxide was confirmed by the infrared studies. A strong band at 1180 cm^{-1} could be assigned to $\nu_{P=O}$ of the triphenylphosphine oxide molecule[3] coordinated with the metal. After decomposing the complex with water, the liberated ligand was isolated and characterised as triphenylphosphine oxide (m.p. and IR spectrum). The IR spectrum in the region 600–100 cm^{-1} showed the presence of bands at 548, 520, 452, 365, 308 and 225 cm^{-1}. The bands at 548 and 520 cm^{-1} are due to triphenylphosphine oxide. The band at 452 cm^{-1} could be assigned to ν_{Ni-O}, at 365 and 308 cm^{-1} to ν_{Ni-Cl} (terminal) and at 225 cm^{-1} to ν_{Ni-I} (terminal). These assignments are made in accordance with that of isotopically labelled nickel complexes, viz. [Ni(PPh$_3$)$_2$X$_2$](X = Cl, Br, I).[4]

The ESR spectrum of a powdered sample at liquid nitrogen temperature showed two absorption lines from which the g-values calculated are, $g_{\perp} = 2.085$ and $g_{\parallel} = 2.430$. If we choose the z coordinate such that it bisects the ClNiCl angle and x and y coordinates perpendicular to the above, then a possible configuration is $(d_{x^2-y^2})^2\ (d_{z^2})^2\ (d_{xz})^2\ (d_{yz})^{\pm}$. Following the detailed treatment of d^7 system with the above configuration,[5,6] we can predict $g_{zz} > g_{yy}$, which is observed experimentally too. Due to the lack of the availability of all the d–d-transitions, it is not possible to interpret the ESR data quantitatively, at present. On the basis of the observed g-values, we can make a tentative assignment of 25,000 cm^{-1} ($\epsilon = 70$) band to $d_{x^2-y^2} \rightarrow d_{yz}$ and 16,000 cm^{-1} ($\epsilon = 13$) band to $d_{z^2} \rightarrow d_{yz}$ transitions. Thus, the compound has a tetrahedral geometry with tetragonal distortions.

The complex, on treatment with triphenylphosphine in acetic acid resulted a dark brown crystalline compound with probable composition [Ni(PPh$_3$)$_2$ClI], with nickel in +2 oxidation state. The nickel(III) complex acts as a catalyst in the oxidation of triphenylphosphine to triphenylphosphine oxide. The catalytic oxidation reaction using the complex and triphenylphosphine in varying

---

*Author to whom correspondence should be addressed.

proportions (up to 1:25) in cyclohexane or nitrobenzene gave quantitative yield of the oxide. The method of reaction and characterization is similar to the one reported earlier.[7] The complex is found to oxidise cyclohexanol to cyclohenanone in pyridine solvent. More studies concerning the oxidising property of the complex are being carried out.

Acknowledgements—One of the authors (K.P.S.) is grateful to UGC (New Delhi) for the award of a fellowship (SRF). The authors thank Dr. J. Subramanian for getting the ESR spectrum and for discussions on it.

REFERENCES

1. K. P. Sarma and Raj K. Poddar, *Trans. Met. Chem.* (in press).
2. L. M. Venanzi, *J. Chem. Soc.* 1958, 719.
3. F. A. Cotton, R. D. Barnes and E. Bannister, *J. Chem. Soc.* 1960, 2199.
4. C. Udovich, J. Takemoto and K. Nakamoto, *J. Coord. Chem.* 1971, **1**, 89.
5. A. H. Maki, N. Edelstein, A. Davison and R. H. Holm, *J. Am. Chem. Soc.* 1964, **86**, 4580.
6. B. R. McGarvey, *Can. J. Chem.* 1975, **53**, 2498.
7. R. K. Poddar and U. Agarwala, *Inorg. Nucl. Chem. Lett.* 1973, **9**, 785.

Polyhedron Vol. 2, No. 7, pp. 673–675, 1983
Printed in Great Britain.

0277–5387/83 $3.00 + .00
Pergamon Press Ltd.

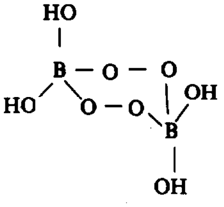
On the nature of the peroxoborate ion in solution

CHRISTOPHER J. ADAMS* and IAN E. CLARK
Unilever Research Laboratory, Port Sunlight, Bebington, Wirral, Merseyside, L63 3JW, England

(*Received* 19 *October* 1982; *accepted* 10 *December* 1982)

Abstract—The Raman spectra of alkaline lithium metaborate solutions containing H_2O_2 reveal lines attributable to a peroxoborate anion, $B(OH)_3OOH^-$, in equilibrium with $B(OH)_4^-$ and H_2O_2. There is no evidence for the formation of peroxoboric acids at low pH.

Sodium perborate is in widespread use as a bleaching agent in fabric washing products, but the chemistry of perborates has not been much investigated. There has recently been a determination of the crystal structure of the commercial material "sodium perborate tetrahydrate", showing that it contains dinuclear anions with double peroxo bridges (I),[1] and is therefore better formulated as $Na_2[B_2(O_2)_2(OH)_4].6H_2O$.



(I)

However, the nature of peroxoborate species in solution has remained elusive. Potentiometric titrations[2] and polarographic studies[3] suggest that alkaline perborate solutions display an equilibrium involving a hydroperoxotrihydroxoborate anion (II).

$$B(OH)_4^- + H_2O_2 \rightleftharpoons B(OH)_3(OOH)^- + H_2O$$

(II)

$$\text{giving } K = \frac{[B(OH)_3(OOH)^-]}{[B(OH)_4^-][H_2O_2]}$$

as *ca.* 25 mol^{-1} dm^3 at 25°C. Other potentiometric investigations have been interpreted in terms of the formation of higher perborates in alkaline solution containing two or more peroxide groups for each boron atom[4]. In acid solutions, the formation of peroxoboric acids has been postulated to explain the drop in pH when hydrogen peroxide is added to boric acid solutions[2].

We set out to use Raman spectroscopy to identify and characterise the peroxoboron species in aqueous solution and to monitor changes in the position of equilibrium with changes in solution composition. It soon became clear that solution concentrations of about 1 mol dm^{-3} were needed to facilitate the observation of spectra, and so the lithium borate/H_2O_2 system was chosen for investigation.

EXPERIMENTAL

Preparation of materials

Lithium metaborate, $LiB(OH)_4.6H_2O$, and sodium perborate tetrahydrate, $Na_2[B_2(O_2)_2(OH)_4].6H_2O$ were prepared from AnalaR reagents. Hydrogen peroxide, Na_2H_2EDTA, boric acid, and hydrochloric acid (all AR Grade) and lithium hydroxide (GPR) were used without further purification.

Preparation of solutions

The solutions were made up by dissolving lithium metaborate in the required concentration of hydrogen peroxide, and adding HCl or LiOH to adjust the pH. All the solutions contained EDTA (1×10^{-4} mol dm^{-3}) to inhibit the metal-catalysed decomposition of H_2O_2. The pH and H_2O_2 content were checked before and after measurement of spectra.

Raman spectra

The filtered solutions were contained in a quartz cell which had been cleaned with aqua regia. Sodium perborate was finely ground and packed into a glass capillary. The spectra were excited at 5145 Å by an Ar^+ laser and were recorded at room temperature (23 ± 1°C) using a Spex Ramalog 5M spectrometer.

RESULTS AND DISCUSSION

The Raman shifts and relative intensities measured in our experiments are listed in Table 1, and partial representative

---

*Author to whom correspondence should be addressed.