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Complexes from Phosphines and Nickel(II) Salts of Dibasic Oxo-Acids

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The synthesis and characterization of an orange-red, crystalline compound corresponding to the formula $[n\text{–}butyl_3P]_2NiSO_4$ *is reported. The complex is found to have planar structure, and further to be monomeric and nonionic in nitrobenzene solution. Preliminary reactions have shown that also other new complexes from phosphines and nickel salts of dibasic oxo-acids may be isolated.*

Introduction

Whereas a variety of nickel complexes of the type $[(R'R''R''')P]_2MeX_2$ (Type I-complex), Me = Ni; R', R'',R''' = alkyl, cycloalkyl, aryl; X = univalent anion, are well known and characterized, little is known about complexes from phosphines and nickel salts of dibasic oxo-acids, such as $NiSO_4$, $NiSeO_4$, $NiCO_3$, $NiSO_3$ and the like. One might assume, that if such complexes eventually could be prepared, they would correspond to the general formula $[(R'R''R''')P]_2MeY$ (Type II-complex), Me = Ni; R',R'',R''' = alkyl, cycloalkyl, aryl; Y = anion of a dibasic oxo-acid.

Complexes of this type with other transition metals than nickel are known from the literature. The compound *cis*–$[ethyl_3P]_2PtSO_4$ was prepared from the corresponding *cis* chloro compound by the reaction with Ag_2SO_4.[1] Presumably, the analogous nickel complexes can not be prepared by this method, *i.e.* by the reaction of Ag_2SO_4 and an alkylphosphine nickel halide compound, because silver salts generally destroy nickel phosphine complexes by depriving them of the phosphine.[2] Besides, to prepare for example a *cis*-planar alkylphosphine nickel-sulfate complex (a Type II-complex), the *cis*-isomer of the nickel halide complex preferably would be used. As well known, the square planar alkylphosphine nickel halide complexes usually are *trans* configurated.

Very interesting reactions also resulted in the formation of other Type II-complexes. Thus $[phenyl_3P]_2PtSO_4$ was rapidly formed on passage of SO_2 into a solution of $[phenyl_3P]_2PtO_2$.[3] The same sulfato-compound, as well as its palladium analogue $[phenyl_3P]_2PdSO_4$, could further be prepared by oxidation of phenylphosphine sulphur dioxide complexes of these metals.[3,4]

Until our recent work,[5] however, no Type II nickel complex has been prepared, even though attempts to isolate nickel sulfate complexes were made. Thus, ethanolic solutions of nickel acetate, perchlorate or chlorate and nickel bromate *or sulfate* in methanol when cooled at –80°C gave red-brown to red violet colour on addition of triethyl- or tripropylphosphine. On heating, however, the colour changes over from brown to yellow or green, and it was reported that no crystalline phosphine complexes could be isolated, and that such solutions contained only traces of nickel compounds.[2]

Results and Discussion

We wish to report the preparation and characterization of a Type II-complex, where R' = R'' = R''' = n-butyl, Me = Ni and Y = SO_4, *i.e.* $[n\text{–}butyl_3P]_2NiSO_4$. The complex was first isolated in this institute in 1966 in connection with our works in the field of homogenous catalysis. It was then used as a very active catalyst component for the di- and trimerisation of mono-olefins.[5] The complex was prepared by the addition of excess tri-n-butylphosphine to $NiSO_4 \cdot xH_2O$ (x = 6,7) in absolute ethanol. It is an orange-red, fairly air-stable crystalline compound which can be kept for hours in open air without visible decomposition. Crystals of several mm length have been isolated. On heating, the compound decomposes gradually; the decomp. range found was 211-225°C. The molecular weight is 553 (calcd. for $[(C_4H_9)_3P]_2NiSO_4$: 559,4).

The new complex is a non-electrolyte in nitrobenzene. It is quite soluble in nitrobenzene and other polar solvents, such as chloroform, acetone, methanol, ethanol, chlorobenzene and *o*-dichlorobenzene, but is almost insoluble in benzene, carbon tetrachloride, hexane and other nonpolar solvents.

The nickel complex is diamagnetic and thus[6] it is assigned a planar configuration; due to steric requirements we assume a *cis*-planar configuration of the

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(1) K. A. Jensen, *Z. anorg. u. allg. Chem.*, *229*, 225 (1936).
(2) K. A Jensen, P. H. Nielsen, and C. Th. Pedersen, *Acta Chem. Scand.*, *17*, 1115 (1963).
(3) C. D. Cook and G. S. Jauhal, *J. Am. Chem. Soc.*, *89*, 3066 (1967).
(4) J. J. Levison and S. D. Robinson, *Chem. Commun.*, 198 (1967).
(5) Brit Pat. 1.153.827, 4.9.1969.
(6) R. W. Asmussen, A. Jensen, and H. Soling, *Acta Chem. Scand.*, *9*, 1391 (1955). C.R.C. Coussmaker, M. H. Hutchinson, J. R. Mellor, L. E. Sutton, and L. M. Venanzi, *J. Chem. Soc.*, 2705 (1961).

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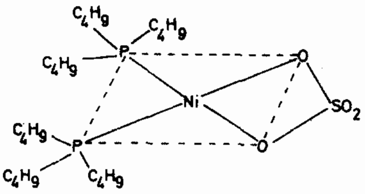

Thus its structure would be related to that of *cis*–$[(c{-}C_6H_{11})_2P(CH_2)_3P(c{-}C_6H_{11})_2]NiBr_2$.[7]

The presence of the sulfato group can be seen from the infrared spectrum. Strong bands (nujol) assigned to this group[*] were found at 1260, 1160 (shoulder) and 1157, 912 (shoulder) and 910, and 657 cm^{-1}. In addition, a medium band was found at 611 cm^{-1} and a weak band at 578 cm^{-1}. A comparison between these bands and the sulfatobands of the Type II-complex $[Ph_3P]_2PtSO_4$,[3] where the SO_4 group acts as a bidentate ligand, (1279, 1165 and 1150, 880 and 871 and 650 cm^{-1}) shows reasonable correspondence. However, there is some uncertainty whether or not the bands at 912 and 910 cm^{-1} are attributable to the sulfato group. We found that liquid butylphosphine absorbs at 905 (shoulder) and 899 cm^{-1} and $[n{-}butyl_3P]_2NiCl_2$ at 903 cm^{-1}. It then follows, that the 912 cm^{-1} bands may be due to other absorptions than those from the sulfato group.

It is most likely that other complexes analogous to $[n{-}butyl_3P]_2NiSO_4$ can be prepared. For example, it is to be expected that $[n{-}propyl_3P]_2NiSO_4$ can be prepared as easy as the butylphosphine complex. The Taft σ^*- values of $n{-}C_3H_7$ and $n{-}C_4H_9$ are close (–0.11 and –0.13 respectively) and the bond strength of Ni–P should be of the same order in the two complexes. Furthermore, from steric considerations, the smaller tripropylphosphine groups compared to the tributylphosphine groups, probably would be advantageous for the stability of the complex.

Preliminary tests have shown that if tri-n-octylphosphine is added to $NiSO_4 \cdot 6H_2O$ in abs. ethanol, the alcohol solution turns red, and if a mixture of tricyclohexylphosphine and $NiSO_4 \cdot H_2O$ in chlorobenzene is stirred at room temperature, the solution will be violet-red, a colour very similar to that of $[(c{-}C_6H_{11})_3P]_2NiCl_2$. A distinct colour change towards violet-red also was obtained by treating $[n{-}butyl_3P]_2NiSO_4$ with excess tricyclohexylphosphine in acetone. A crystalline, brick-red complex was further isolated from the reaction of tricyclohexylphosphine and $NiSO_4 \cdot 6H_2O$ in acetone. Other preliminary tests showed that an orange-coloured solution was formed when tri-n-butylphosphine was added to $NiSeO_4 \cdot 6H_2O$ in ethanol, and a yellow to yellow-orange solution was obtained from nickel sulfite and $n{-}butyl_3P$ in ethanol.

Experimental Section

Preparation. All operations were carried out under nitrogen; the solvents and liquid reagents were dried and distilled twice under nitrogen before use. To a stirred mixture of 13.15 g $NiSO_4 \cdot 6H_2O$ (Merck p.a.) in 75 ml abs. ethanol were added 25 ml tri-n-butylphosphine. Immediately after the phosphine addition, a faint orange-red colour indicated formation of a complex. After stirring for 6 hours at room temperature, unreacted solid nickel sulfate was filtered off. The filtrate — nickel complex dissolved in ethanol and tri-n-butylphosphine — was evaporated to about half of its volume under reduced pressure, and the product precipitated. After standing overnight at +4°C, an orange-red solid was isolated in a Schlenk-type glassfilter vessel. The complex was purified by washing it four times with 20 ml pentane followed by (rapid) pipette decantation. The first two pentane decantates were pale green and not quite clear due to undissolved, but finely devided nickel sulfate. The elemental analysis showed that traces of impurities were well removed by this method. Yield 3,65 g. From the mother liquid, another 0.83 g of purified complex were isolated. Total yield 4.48 g, (16%) (calcd. from the nickel sulfate).

Elemental analysis. The C and H analysis were performed at the Alfred Bernhardt microanalytical laboratory/Elbach-Germany, and the nickel analysis at the analytical division of this institute. Found: C, 51.52; H, 9.48; Ni, 10.5; Calcd. for $C_{24}H_{54}NiO_4P_2S$: C, 51.53; H, 9.73; Ni, 10.49.

Decomposition range. A Mettler FP 1 automatic melting point apparatus was used. The decomp. range is the range given from the instrument from 5 different measurements. The heating rate was 2°C pro minute, and closed tubes were used. Butylphosphine was given off gradually, and a definite melting or decomposition point could not be determined. The decomposition range was dependent of the heating rate.

Molecular weight. The molecular weight was determined by the cryoscopic method. Nitrobenzene was used as the solvent, and the measurements were performed under nitrogen.

Magnetic moment. The determination of magnetic susceptibility was made at room temperature by the Faraday method. The compound was diamagnetic, $\chi = -0.63 \times 10^{-6}$, max. 5% relative.

Conductance measurements. These were done at 20°C with $5 \times 10^{-3}\,M$ and $1 \times 10^{-3}\,M$ solutions of the complex in nitrobenzene under an atmosphere of nitrogen, a type GM 4249/01 Philips conductivity measuring bridge, PR 9500, being used. The complex was a non-electrolyte.

Infrared spectra. The IR-spectra were obtained using a Perkin Elmer 457 grating infrared spectrofotometer.

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(*) For a general discussion of infrared spectra of coordinated sulfate, see ref. (8).

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(8) K. Nakamoto, « Infrared Spectra of Inorganic and Coordination Compounds », Wiley, N. Y. 1963, Section III - 4.