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Reaction of Co(II) and Tri n-Butyl Phosphate

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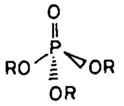
Abstract

$CoCl_2 \cdot 6H_2O$ reacts with excess tri n-butyl phosphate (TBP), neat, yielding a deep blue solution, typical of Co(II) tetrahedral complexes. Compound I, composed of two chlorides and two TBPs as ligands, is believed to be present in this medium. Removal of excess TBP at low pressure and 180 °C yielded compound **II** where Co(II) maintained a tetrahedral geometry and the TBPs rearranged to bidentate DBPs with the rupture of one O–R bond from each TBP. Spectroscopic and physical properties of compound **II** were obtained and are consistent with the proposed structure.

Introduction

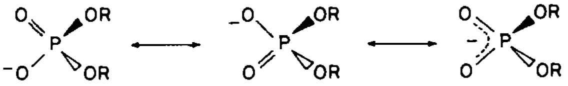
TBP (tri n-butyl phosphate) has been used to extract metal ions such as Ce^{4+}, Th^{4+}, Sm^{3+}, etc. from a mixture containing several Ln^{3+} ions [1a,b,c,e] (Ln = lanthanide or rare earth elements).



R = n-C_4H_9

TBP

The role of TBP in the extraction processes was studied and it was concluded that the TBP molecule merely solvated the metal ions to be extracted [2]. This implies that the interaction between the dipole of TBP and the charged metal ions should be weak, albeit still stronger than that with ethers or ketones [1d]. In the solvation, TBP could behave as a monodentate ligand, by using the ketonic oxygen as the donor site, or as a multidentate ligand, by using more than one oxygen atom as the donor site. In an attempt to differentiate these cases we found another mode of reaction of TBP, due to the extreme conditions in our reactions, involving cleavage of one R group from the TBP molecule to yield the DBP (di n-butyl phosphate) anion which behaves as a bidentate ligand.



R = n-C_4H_9

DBP

The product thus formed in this work was studied and characterized as $[Co\{O_2P(OC_4H_9)_2\}_2]$ or abbreviated as $[Co(DBP)_2]$ (**II**).

Experimental

$CoCl_2 \cdot 6H_2O$ (0.24 g, 1.0 mmol) was added to 30 ml of TBP** to yield a deep blue solution which remained unchanged after refluxing for 4 h. Excess TBP was removed by low pressure distillation (app. 2 mm Hg) at 180 °C. The deep blue solid (**II**) was obtained after 16 h of distillation. It was washed with CH_3CN and dried *in vacuo* at room temperature. The dry product was recrystallized by first dissolving it in a minimum volume of ethyl acetate then slowly adding CH_3CN (without agitation) until a deep blue solid precipitated. The mixture was left standing for some time to allow further precipitation. The product was then filtered and washed several times with CH_3CN and dried *in vacuo* at room temperature. The yield was 0.38 g (80%, based on **II**).

Compound **II** does not contain chloride as it showed a negative result when the sodium fusion method was employed. The molecular weight is 462 (calc. 477)†. *Anal.* Calc. for $[Co\{O_2P(OC_4H_9)_2\}_2]$: Co, 12.37. Found: Co, 11.33%.

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**$CoCl_2 \cdot 6H_2O$ when dissolved in absolute C_2H_5OH in the presence of TBP shows an identical electronic absorption spectrum to that obtained from the solution without TBP. These observations showed that in the presence of a solvent like alcohol the interaction between TBP and metal ions was too weak to cause any chemical changes.

†Molecular weight (M_r) was obtained by the freezing point depression method in benzene the accuracy of which as checked with naphthalene and camphore showed M_r 126 and 149 (calc. 128 and 153), respectively.

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Melting points were determined on the Tottoli melting point apparatus by Buchi. Electronic absorption and infrared spectra were obtained from a UV–Vis Spectrophotometer Beckman Model 26 and an Infrared Spectrophotometer Jasco A-302. Conductivity data was measured using a Radiometer Conductivity Meter CDM 83. Elemental analysis for the Co content of the samples was determined on an Atomic Absorption Spectrophotometer Perkin-Elmer 305B.

Results and Discussion

Compound **II** exhibits a broad melting point range, 258–261 °C. The compound is stable *in vacuo*; if exposed to the atmosphere it slowly absorbs moisture and turns to a pink liquid. It dissolves with decomposition in H_2O, CH_3OH and C_2H_5OH yielding pink solutions. It also dissolves very well in other organic solvents including TBP, with one exception, CH_3CN, in which it dissolves only slightly. Conductivity at infinite dilution (Λ_0) in DMF was 22.5 S cm^2/eq which is well below the normal range of 65–90 S cm^2/eq for the 1:1 electrolyte in DMF [3].

The infrared spectrum of **II** shows absorption bands at 2950(s), 1460(m), 1375(w), 1180(s) (P=O str.), 1030(s) (P–O–C bending), and 735(w) cm^{-1} (Nujol mull). The band at 1180 cm^{-1} can be assigned to the P=O stretching mode (ν(P=O)). In free TBP this mode appears at 1270 cm^{-1}. Lowering of this band indicates that this O atom is used as the donor site to the metal ion. The lowering of ν(P=O) was also observed in the case of $R = CH_3$ where ν(P=O) would reduce in the range 23–76 cm^{-1} (from free ligand) depending on the types of metal [4a]*. The band at 1030 cm^{-1} which is assigned to the P–O–C (aliphatic) bending mode is also similar to the previously reported value at 1060 cm^{-1} [5].

The electronic absorption spectrum shows absorption peaks (in acetone) at 540(sh), 560(sh), 575(sh) and 600 nm which correspond to 18 520, 17 860, 17 400 and 16 700 cm^{-1}, respectively. No significant spectral shift was observed in several solvents such as CCl_4, acetone, TBP, and DMF (see Fig. 1). Apart from the deep blue color which is typical for many tetrahedrally Co(II) complexes, the absorption peak found in the range 18 000–16 000 cm^{-1} may be assigned to ν_3 ($^4A_2 \rightarrow {}^4T_1(P)$) transition in the energy diagram of tetrahedral Co(II) complexes. Tetrahedral Co(II) complexes normally exhibit three spin allowed transitions of which the first two lie in the near infrared region and the other in the visible region, *i.e.* ν_1($^4A_2 \rightarrow {}^4T_2$) usually not detectable for its very, low energy, ν_2($^4A_2 \rightarrow {}^4T_1(F)$) in the region 10 000–4500 cm^{-1}, and ν_3($^4A_2 \rightarrow {}^4T_1(P)$) in the region 18 500–13 800 cm^{-1} [6, 7].

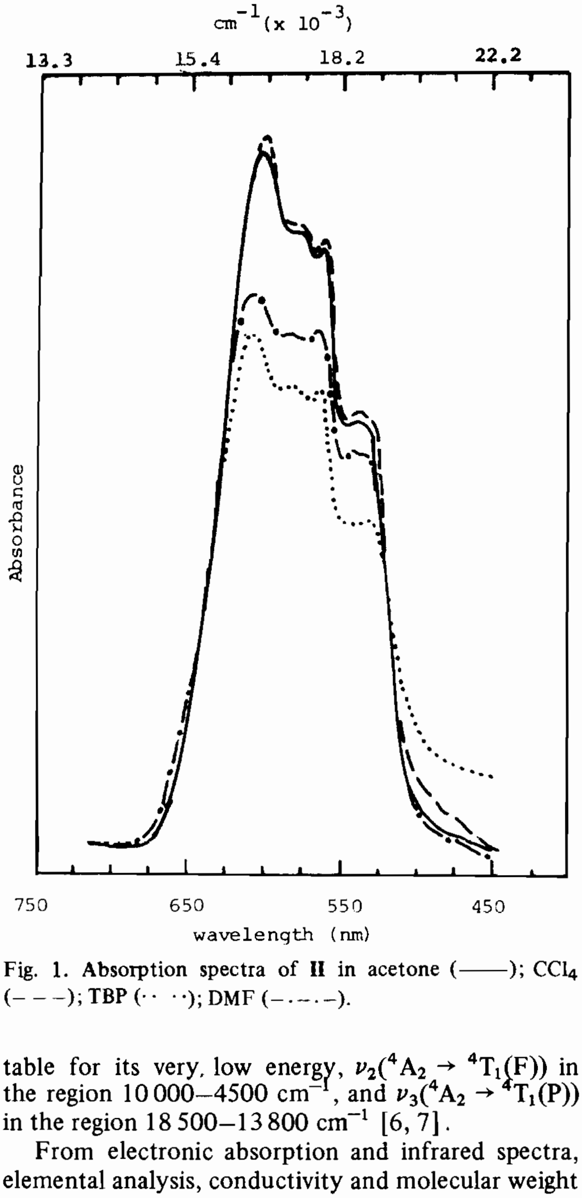
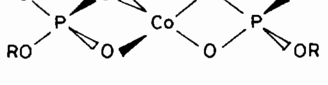


Fig. 1. Absorption spectra of **II** in acetone (——); CCl_4 (– – –); TBP (· · · ·); DMF (–·–·–).

From electronic absorption and infrared spectra, elemental analysis, conductivity and molecular weight data, the structure of **II** can be proposed as follows.



R = n-C_4H_9

II

A compound of this type has been reported with the formula $[Co\{O_2P(OC_2H_5)_2\}_2]$ and it exhibited a similar pattern of electronic absorption peaks: 18 200(sh), 17 200(sh), 16 700(sh) and 16 100 cm^{-1} [8].

When Co(II) was first added to excess TBP the initial complex formed is likely to be in the form of **I** as follows.

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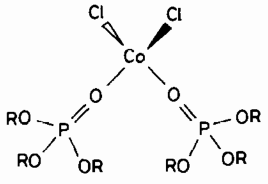
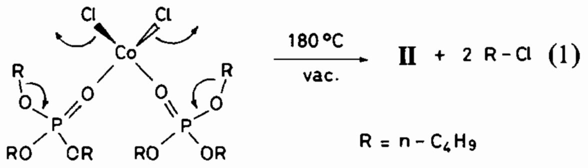
*Also in a similar system of Co–phosphetanic acid complex by Emsley *et al.*, [4b].



I

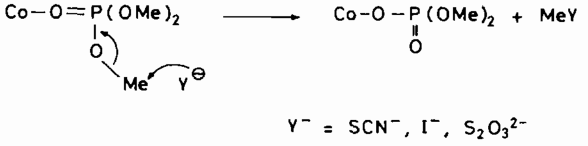
R = n-C_4H_9

The geometry of **I** is probably a tetrahedral one as judged from its deep blue color. Compound **I** dissolves very well and does not ionize in TBP, as a result very low conductivity is shown in this medium*. When excess TBP was removed by low pressure distillation (2 mm Hg) at 180 °C for 16 h, **I** could be transformed into **II** by the mechanism involving cleavage of both Co–Cl and O–C bonds as follows.



I

A similar reaction involving cleavage of the O–C bond in Co–O=P–O–R has been reported recently by Jackson and McGregor [9] where the reactions between $[(NH_3)_5CoOP(OMe)_3]^{3+}$ and nucleophiles Y^- were studied in D_2O (or Me_2SO-d_6) at 35 °C as shown in the following reaction.



However in the case of Y^- = Cl^- a different result was obtained

$$Co{-}O{=}P(OMe)_3 + Cl^- \rightarrow Co{-}Cl + OP(OMe)_3$$

The different behavior of Cl^- was rationalized as due to its poorer nucleophile property than the others.

In our studies that led to the proposed mechanism of reaction (1), though it may seem to contradict the work mentioned above, there are some other factors involved that may help reaction (1) to take place such as: (a) the driving force from the chelate effect due to the rearrangement of the monodentate ligand TBP to the bidentate ligand DBP, (b) the high temperature (180 °C) at which the reaction was carried out, and (c) the gaseous nature of the product n-C_4H_9Cl which was immediately removed from the system while maintaining the low pressure; reaction (1), therefore, will always lean to the right-hand side leading to the formation of **II**.

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*At the same concentration in TBP, I has a much lower conductivity than $(Bu)_4NI$.