

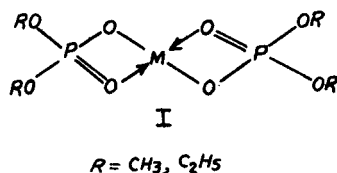
Bis(di-*n*-butoxyphosphato)cobalt(II) & Its Complexes with Lewis Bases

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Bis(di-*n*-butoxyphosphato)cobalt(II) has been prepared by a solvolytic reaction of tri-*n*-butylphosphate with cobalt(II) chloride. It has been assigned a tetrahedral geometry on the basis of magnetic moment, electronic and IR spectral data. It readily dissolves in strong Lewis bases like pyridine, γ -picoline, *n*-butylamine, etc. An investigation of these solutions on the basis of conductance, IR and electronic spectra indicates the presence of $\text{Co}[\text{O}_2\text{P}(\text{O}-n\text{-C}_4\text{H}_9)_2]_2 \cdot 2\text{B}$ (B = Lewis base) species. The dissociation constants of octahedral species have been measured in benzene. The solid adducts could be isolated in the case of pyridine and isoquinoline.

It has been established that triethyl- and trimethyl phosphates react with divalent and trivalent metal halides yielding tetrahedral (I) and octahedral chelates respectively¹⁻⁴. The volatile alkyl halides are produced in the reaction.



It has also been observed that tetrahedral chelates of Co(II)⁵ and Ni(II)⁶ have a tendency to enhance their coordination number from 4 to 6. The present paper deals with the isolation and characterization of the chelate, $\text{Co}[\text{O}_2\text{P}(\text{O}-n\text{-C}_4\text{H}_9)_2]_2$. Since butoxy is a bulkier group than methoxy or ethoxy groups, an attempt has also been made to study acceptor capability of the former in relation to strong nitrogen donors.

Materials and Methods

Bis(di-n-butoxyphosphato)cobalt (II) — Anhydrous cobalt(II) chloride (6.5 g) and tri-*n*-butylphosphate (27 g) were taken in nitrobenzene (100 g) and refluxed at 170-80° for 40 hr. The vapours evolved were cooled and the liquid (9.0 g) collected. This colourless liquid was identified as *n*-butyl chloride on the basis of its boiling point (77.5°) and IR spectral data. The reaction was considered complete when no more of butyl chloride evolved. The deep-blue solution containing the reaction product was shaken 4 to 5 times with equal amounts of water in a separating funnel. The aqueous layer had a pink colour which on evaporation gave a blue viscous mass. It was crystallized (3 to 4 times) from CH_2Cl_2 and kept *in vacuo* over P_2O_5 for a fortnight. The analytical⁷ data suggest the composition, $\text{Co}[\text{O}_2\text{P}(\text{O}-n\text{-C}_4\text{H}_9)_2]_2$ (Found: Co, 11.9; P, 12.7. Required: Co, 12.4; P, 13.0%).

The Lewis bases were kept over solid NaOH and distilled before use.

The complexes of the blue compound with pyridine and isoquinoline were prepared according to known procedures⁵. The electronic spectra of the chelates and the dissociation constants of the complexes

in situ were measured at $25^\circ \pm 0.1^\circ$, spectroscopically.

Results and Discussion

The electronic spectrum of $\text{Co}[\text{O}_2\text{P}(\text{O}-n\text{-C}_4\text{H}_9)_2]_2$, $\text{Co}(\text{TBP})_2$, reveals a band at 626 nm (16.0 kK) ($\epsilon=200$ litre mole⁻¹ cm⁻¹) having shoulders at 599, 578 and 562 nm and a band at 1275 nm (7.8 kK) ($\epsilon=20$ litre mole⁻¹ cm⁻¹). The high molar extinction coefficients of these bands indicate the existence of four coordinated tetrahedral Co(II) species. The bands at 16.0 and 7.8 kK may, therefore, be assigned to ${}^4T_1(P) \leftarrow {}^4A_2(v_3)$ and ${}^4T_1(F) \leftarrow {}^4A_2(v_1)$ transitions respectively. The v_3 transition is known to possess a multiple structure usually on the high energy side^{2,8}. The ligand field parameters, D_q and B' , have been computed using the relationships given by Jørgensen⁹ and the values obtained (10 $D_q=4.55$ kK; $B'=8.75$ kK) indicate tetrahedral stereochemistry. In accordance with the usual practice¹⁰, v_3 transition energy has been assumed to correspond with the centre of the multiple band (i.e. 17.2 kK in the present case).

The infrared spectrum of the chelate shows a band at 1170 cm⁻¹ attributable to coordinated P=O. Free P=O absorbs at 1270 cm⁻¹ in tri-*n*-butylphosphate. The lowering in $\nu(\text{P}=\text{O})$ also corroborates structure of type (I). A magnetic moment value of 4.71 BM at room temperature is also compatible with the tetrahedral geometry.

As reported earlier⁵ in the case of bis(dimethoxy/diethoxyphosphato)cobalt(II), it was possible to enhance the coordination number of Co(II) from 4 to 6 without breaking the chelate ring. In view of the fact that the present chelate carries a more bulky group, it may be of interest to study its acceptor properties.

$\text{Co}(\text{TBP})_2$ dissolves exothermally in various strong nitrogen donors like pyridine, γ -picoline, isoquinoline, etc., giving pink solutions. This indicates that Co(II) has attained hexacoordination. This can occur in several ways (Eqs. 1-3).

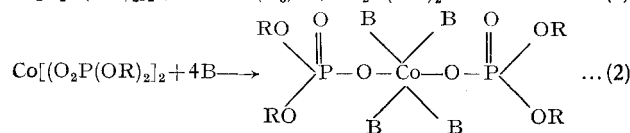
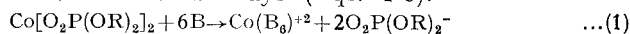
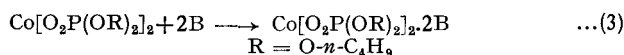


TABLE 1 — ELECTRONIC SPECTRA AND DISSOCIATION CONSTANTS OF THE COMPLEXES

Base	ν_1 (kK)	ν_3 (kK)	Dq (kK)	B' (kK)	Charge reduction	Dissociation constan $\times 10^{-3}$
Water	8.6 (4.6)	18.6 (2.4)	0.96	0.80	1.0	2.1
Pyridine	8.3 (3.45)	20.2 (15.8)	0.96	0.87	1.0	0.26
Isoquinoline	9.3 (4.3)	20.6 (28.1)	1.0	0.86	1.1	4.1
β -Picoline	8.8 (4.1)	19.9 (22.2)	0.98	0.81	1.3	6.1
γ -Picoline	8.7 (3.8)	20.0 (25.1)	1.0	0.80	1.2	98.0
BuNH ₂	9.3 (4.8)	21.0 (31.1)	1.05	0.84	1.1	2.1
<i>m</i> -Toluidine	8.9 (3.0)	19.8 (19.1)	1.0	0.80	1.0	3.7
Amylamine	8.5 (4.2)	19.6 (28.1)	0.98	0.83	1.2	8.5

Values in parentheses are the extinction coefficients of the bands.

Dissociation constants in the case of aniline, α -picoline, quinoline and piperidine are of the order of 10^4 .



To a solution of $\text{Co}(\text{TBP})_2$ in CH_2Cl_2 , the addition of any of the above mentioned bases does not alter the conductance of the solution. This rules out the possibility of the formation of ionic species such as those represented by Eq. (1). Further, IR spectral analysis of a concentrated solution of $\text{Co}(\text{TBP})_2$ in pyridine or water does not reveal a band at 1270 cm^{-1} [due to free $\text{P}=\text{O}$ in $\text{OP}(\text{O}-n-\text{C}_4\text{H}_9)_3$] indicating that the four-membered chelate ring is not ruptured in these solutions. In view of this the possibility of the formation of octahedral species of the type given by Eq. (2) is ruled out. It is thus evident that the chelate ring is not ruptured while the metal ion enhances its coordination number from 4 to 6. Eq. (3), therefore, represents the true mode of reaction.

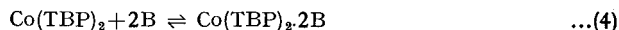
The electronic spectra of $\text{Co}(\text{TBP})_2$ in several Lewis bases has been scanned in the visible and near IR regions (Table 1). The low extinction coefficients categorically point out the formation of octahedral Co(II) complexes in solution. It may be mentioned that the absorption corresponding to the transition ν_2 [${}^4T_{1g}(F) \leftarrow {}^4A_{2g}(F)$] has not been observed. On the basis of the transition energies of ν_1 and ν_3 , various ligand field parameters have been estimated¹⁰ and are also summarized in Table 1.

From the value of $10 Dq$ in the mixed ligand field in the case of $\text{Co}(\text{TBP})_2 \cdot 2\text{H}_2\text{O}$, the Δ_{oct} value for $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ comes out to be 9.0 kK assuming $\Delta_t \approx \frac{4}{9} \Delta_{\text{oct}}$ on the basis of the rule of average environment¹¹. This is in excellent agreement with the reported value of 9.2 kK ¹⁰ for $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$. This further supports the octahedral disposition of ligands in $\text{Co}(\text{TBP})_2 \cdot 2\text{H}_2\text{O}$ and other similar complexes.

It is surprising to note that the formation of pink solution could not be detected in the case of aniline, *N,N*-dimethylaniline, α -picoline and quinoline. In these cases a violet solution was obtained even in the pure base indicating that the formation of octahedral species does not occur in these cases. This observation has been further substantiated by a study of the electronic spectra which reveals that the 16 kK band is not displaced, instead it

is only slightly diminished in intensity and the appearance of a new band has not been observed. The dissociation constants of the complexes are extremely high ($>10^4$), thus lending support to the observation that a complete conversion of tetrahedral into octahedral species is not favoured even in the pure Lewis bases in spite of the large mass effect.

Only two solid complexes, viz. $\text{CoTBP} \cdot 2\text{B}$ ($\text{B} =$ pyridine/isoquinoline) could be obtained in the present case compared to $\text{Co}[\text{O}_2\text{P}(\text{OC}_2\text{H}_5)_2]_2$, where a number of solid complexes could be isolated⁵ (Found: Co, $9.3/7.9$; P, $9.5/8.0$. Required: Co, $9.3/8.0$; P, $9.8/8.4\%$). These are pink crystalline solids and lose the base molecules on exposure to air. The actual decomposition of the pink solid sets in on warming to 50° . These observations collectively suggest that the octahedral species formed as a consequence of reaction (3) are highly unstable and can only be stabilized in the presence of a large excess of the Lewis base. It will, therefore, be advisable to represent reaction (3) as an equilibrium represented by Eq. (4).



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