Synthesis of Cobalt Complexes Containing Iminophosphino Ligands. Reactivity and Structure of [LCo(SO₂)]ClO₄·C₂H₅OH (L = N,N'-Bis[o-(diphenylphosphino)benzylidene]-o-phenylendiamine)

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(Received September 4, 1987)

The coordinating ability of quadridentate Schiff bases towards transition metal ions as well as the reactivity of their planar cobalt(II) complexes have been for a long time the subject of intensive study. In particular the cobalt complexes of the quadridentate Schiff base (**1a** and **1b**), when reduced to mononegative species are found to behave as strong nucleophilic reagents to activate small molecules or organic substrates [1].
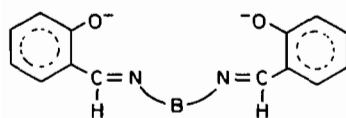
B = —CH₂-CH₂—: Salen, **1a**
B = —(C₆H₄)—: Salophen, **1b**

The related uncharged iminophosphino ligands **2a** and **2b** (**2a** = N,N'-bis[o-diphenylphosphino)benzylidene]ethylenediamine, en=P₂; **2b** = N,N'-bis[o-(diphenylphosphino)benzylidene]o-phenylendiamine, o-PDA=P₂) with analogous skeleton but a softer donor atom set, should be able to stabilize low oxidation states in transition metal complexes, thus developing a different reactivity.
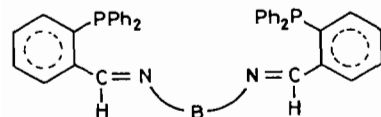
B = —CH₂CH₂—: en=P₂, **2a**
B = —(C₆H₄)—: o-PDA=P₂, **2b**

With this in mind we have investigated the complexes of 3d metal ions with the above ligands and have found that the cobalt complexes (**2a** and **2b**) undergo a spontaneous redox process when reacted with SO₂ gas.

The ligand en=P₂ was prepared by condensation of the *o*-diphenylphosphino-benzaldehyde with ethylendiamine as described by Rauchfuss *et al.* [2]; the ligand *o*-PDA=P₂ has not been isolated, the complexes being prepared by template reactions.

When SO₂ gas is bubbled through a solution of Co(ClO₄)₂·6H₂O and en=P₂* (or *o*-diphenylphosphino-benzaldehyde and *o*-phenylendiamine, ratio 2:1) in methylene chloride/ethanol solution, at 50 °C, a deep red solution is formed. After evaporation of the solvent, red crystals of formulae [(en=P₂)Co-(SO₂)]ClO₄ or [(*o*-PDA=P₂)Co(SO₂)]ClO₄ precipitate.

The air sensitive, solid compounds are diamagnetic. Their IR spectra show a strong band at 1180 cm⁻¹, a pair of bands at 1030 and 1010 cm⁻¹ and a band of medium intensity at 540 cm⁻¹, which are respectively assigned to the asymmetric stretching, to the symmetric stretching and to the bending vibrations of the coordinated SO₂ [4].

The *o*-PDA=P₂ derivative has been investigated by diffraction analysis. The crystals are triclinic, space group P$\bar{1}$, with *a* = 15.258(9), *b* = 12.278(6), *c* = 11.908(6) Å, α = 76.12(4), β = 83.42(4), γ = 75.17-(4)°, *Z* = 2. Data collection was carried out on a Philips PW 1100 automatic diffractometer using the ω−2θ scan technique and graphite monochromated Mo Kα radiation within 2θ ≤ 40°. Full-matrix least-squares refinement converged at *R* and *R*_w both of 0.071 for the 1466 absorption corrected reflections having *I* ≥ 3σ(*I*).

The molecular structure consists of discrete complex cations [(*o*-PDA=P₂)Co(SO₂)]⁺ and ClO₄⁻ anions, with solvating ethanol molecules interspersed in the lattice. In the cation (Fig. 1) the metal atom is surrounded in a distorted square pyramidal mode by the phosphorus and the nitrogen atoms of the *o*-PDA=P₂ ligand in the basal plane and by the SO₂ group at the apex. The distortion of the square pyramid from the limit geometry is evidenced by the values of the basal angles (161.0(5), 165.3(5)°), probably mainly dictated by the short bite of the *o*-phenylendiamine fragment (N1—Co—N2 = 81.1(7)°).

Interestingly the title compound represents the first cobalt complex containing a η¹-pyramidal SO₂ unit. As a matter of fact, as far as we know, only a cobalt complex displaying a tetrahedral geometry with coplanar sulphur-bound M—SO₂ group has been reported [5]. The η¹-pyramidal attachment mode of the SO₂ in the title compound, which is a square pyramidal d⁸ system (with the (z², σ*) orbital filled),

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*When the reaction is carried out under a nitrogen atmosphere, the complexes [(en=P₂)Co(H₂O)](ClO₄)₂ and [(*o*-PDA=P₂)Co(H₂O)](ClO₄)₂ have been respectively isolated [3].
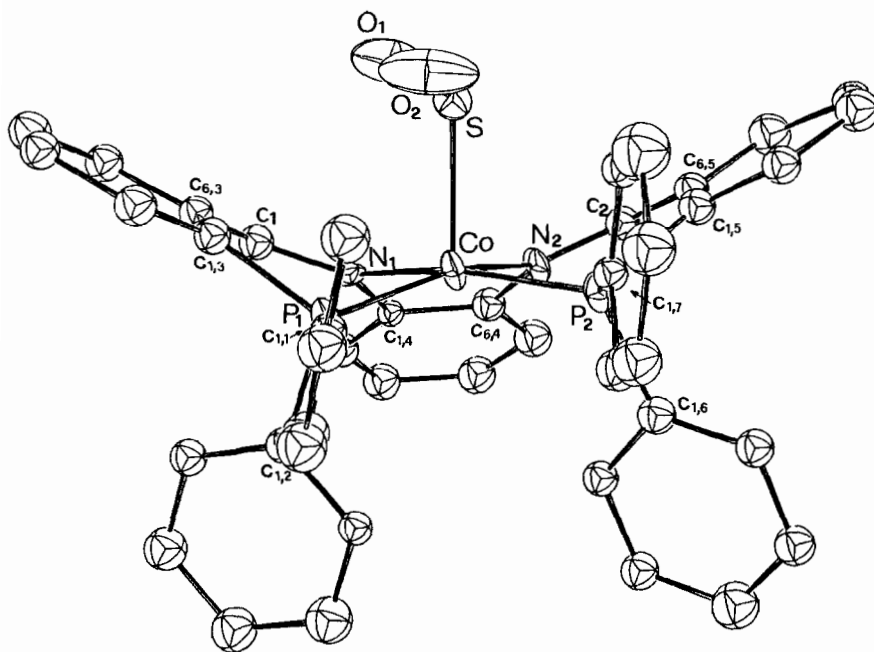
Fig. 1. Perspective view of the complex cation $[(o\text{-}PDA{=}P_2)Co(SO_2)]^+$. Ortep drawing with 30% probability ellipsoids. Selected bond distances (Å) and angles (°): Co–P1 2.232(7), Co–P2 2.218(7), Co–N1 1.993(17), Co–N2 1.966(18), Co–S 2.261(6), S–O1 1.40(2), S–O2 1.39(2) Å, P1–Co–N2 161.0(5), P2–Co–N1 165.3(6), Co–S–O1 109.1(9), Co–S–O2 110.5(8), O1–S–O2 114.2(15)°.

is not surprising, on the basis of the molecular orbital model proposed [6], which accounts for the geometry of the M–SO$_2$ moiety (linear or bent) in terms of the number of d electrons and the transition metal coordination polyhedron. The M–S bond distance (2.261(6) Å), somewhat longer than the sum of covalent radii (2.18 Å) and dramatically longer than the value reported for the other known Co–SO$_2$ complex (2.021(8) Å) [5], is in agreement with the trend of the η^1-pyramidal mode showing M–S bond distances longer than those associated to the η^1-planar one [4].

When the complex $[(o\text{-}PDA{=}P_2)Co(SO_2)]ClO_4$ is dissolved in methylene chloride under a stream of nitrogen, SO$_2$ is rapidly removed and after addition of n-butanol and solvent evaporation, red–brown crystals of analytical formula $[(o\text{-}PDA{=}P_2)CoCl]\cdot$ $ClO_4\cdot CH_2Cl_2$ are obtained. This latter complex is air-stable, 1:1 electrolyte in CH$_2$Cl$_2$ and paramagnetic with μ_{eff} = 2.13 BM at room temperature. The reflectance spectrum of the compound with two bands at 25 000 and 6665 cm^{-1} is closely related to that of the low-spin square pyramidal $[Co(pnnp)Br]^+$ complex [7], where pnnp is PPh$_2$(CH$_2$)$_2$N(CH$_3$)(CH$_2$)$_2$-N(CH$_3$)(CH$_2$)$_2$PPh$_2$.

Finally the same compound can be easily prepared by reaction of $o\text{-}PDA{=}P_2$ with CoCl$_2\cdot6H_2O$ and (NBu$_4$)ClO$_4$.

Even if, at this stage of our investigation, we are unable to fully explain the mechanism of the process

here reported, the obtained results suggest the following pathway:

(i) interaction of SO$_2$ with $[CoL]^{2+}$ to form the intermediate species $[LCo(SO_2)]^{2+}$;

(ii) immediate reduction to $[LCo(SO_2)]^+$;

(iii) removal, under nitrogen, of SO$_2$ to form $[LCo]^+$;

(iv) reaction of the intermediate strong nucleophilic species $[LCo]^+$ with CH$_2$Cl$_2$ to form $[LCoCl]^+$.

Further studies on the mechanism of these reactions and the detection of the redox agents involved are under investigation.

References

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