

Photoreduction and Deprotonation of [Co(1,3,6,8,10,13,16,19-octa-azabicyclo[6.6.6]icosane)][BPh₄]₃ in Organic Media

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Irradiation with visible light of [Co(sep)][BPh₄]₃, (sep = 1,3,6,8,10,13,16,19-octa-azabicyclo[6.6.6]icosane) in aprotic solvents gave a divalent cobalt complex [Co(sep)][BPh₄]₂, air-oxidation of which produced a complex containing a trivalent cobalt atom and a deprotonated sep ligand.

The tetraphenylborates of metal complexes such as [Co(en)₃][BPh₄]₃, (en = ethylenediamine) and [Co(sep)][BPh₄]₃ (sep = 1,3,6,8,10,13,16,19-octa-azabicyclo[6.6.6]icosane)¹ are insoluble in water but soluble in aprotic polar solvents such as

tetrahydrofuran (THF), acetonitrile, and dimethylformamide (DMF). Solutions of these cobalt(III) complexes in THF, the least polar, showed 'tailing off' of the ligand-metal charge transfer band into the visible region (Figure 1) and broadening

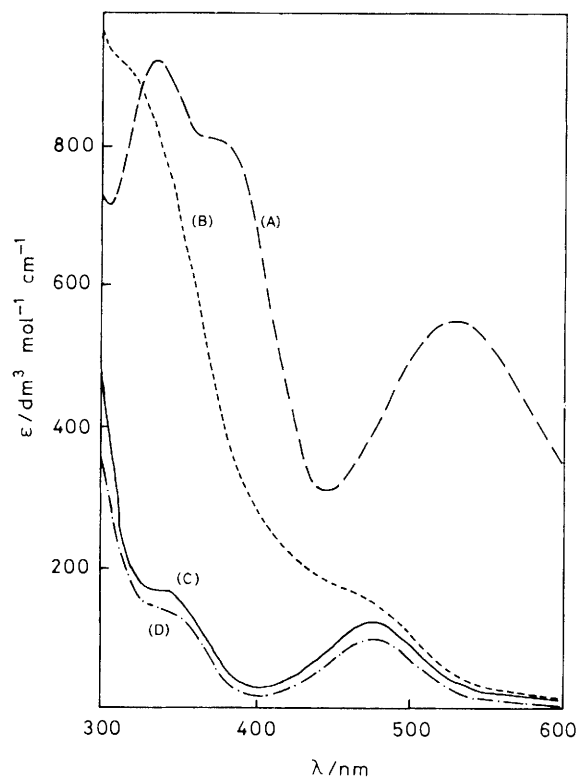


Figure 1. Electronic spectra of (A) the purple oxidised complex, (B) $[\text{Co}(\text{sep})][\text{BPh}_4]_3$ in THF, (C) $[\text{Co}(\text{sep})][\text{BPh}_4]_3$ in MeCN, and (D) $[\text{Co}(\text{sep})][\text{BPh}_4]_3$ in DMF.

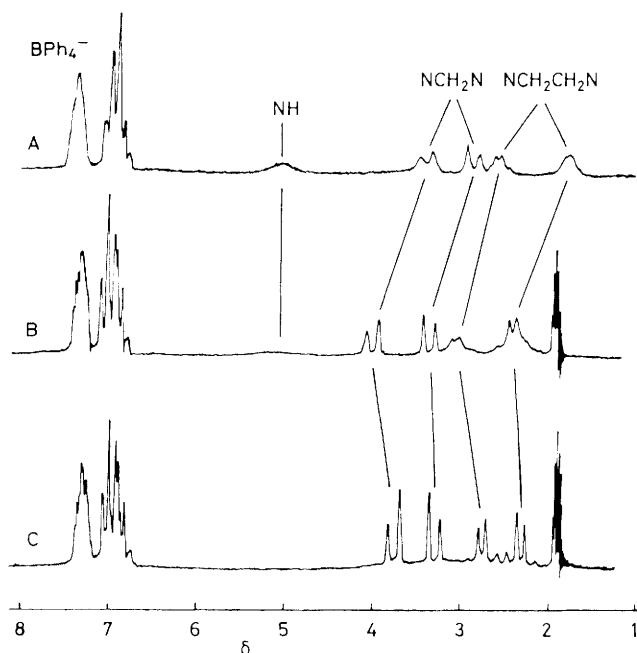


Figure 2. $^1\text{H-N.m.r.}$ spectra of (A) $[\text{Co}(\text{sep})][\text{BPh}_4]_3$ in $[\text{D}_8]\text{THF}$, (B) $[\text{Co}(\text{sep})][\text{BPh}_4]_3$ in CD_3CN , and (C) purple oxidised complex in CD_3CN .

and up-field ^1H n.m.r. shifts of the methylene protons of both the NCH_2N and $\text{NCH}_2\text{CH}_2\text{N}$ moieties (Figure 2), compared with the MeCN and DMF solutions. These phenomena are

probably caused by the closer approach of the positive and negative ions in the ion pair.

In an attempt to study the Raman spectra in aprotic solvents of the tetraphenylborate of $[\text{Co}(\text{sep})]^{3+}$, a very stable cryptate complex ion of cobalt(III),¹ the solution was subjected to laser radiation at 488.0 and 514.5 nm. Rapid bleaching of the solution was observed and a massive amount of a white precipitate deposited when THF was used as the solvent. Elementary analyses, electronic and i.r. spectra, as well as the magnetic moment ($4.28 \mu_B$ at 24°C)¹ proved that the precipitate was the bivalent cobalt complex $[\text{Co}(\text{sep})][\text{BPh}_4]_2$. From the residual solution, biphenyl and phenol could be isolated as the main products, indicating that the phenomenon was a photo-assisted reduction of the Co^{III} complex by the tetraphenylborate anion. The fact that the photoreduction was not observed in aqueous solution and that it was much slower in DMF seems to show that again close approach of the cation and the anion is essential to the reaction.

The bivalent complex, which appears colourless owing to the weakness of the ligand field band,¹ is soluble in MeCN. When the solution is exposed to air, it gradually assumes a purple colour, and upon addition of THF precipitates a purple complex. Magnetic moment, elemental analysis, and i.r., and $^1\text{H-n.m.r.}$ spectra described below indicate that it is a diamagnetic cobalt(III) complex with a deprotonated anionic sep ligand. The purple complex showed an absorption band at 530 nm ($\epsilon 547 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) in addition to two near-u.v. bands at λ 335 ($\epsilon 932$) and 380 (807) nm (Figure 1). We have prepared a purple complex, which gives the same elemental analysis and i.r. and $^1\text{H-n.m.r.}$ spectra, by a different route, *i.e.*, by the deprotonation of $[\text{Co}(\text{sep})][\text{BPh}_4]_3$ with 1,8-diazabicyclo[5.4.0]undec-7-ene, a superbase, in THF. This confirms the above constitution. However we have not observed deprotonation of $[\text{Co}(\text{en})_3][\text{BPh}_4]_3$ under the same conditions, nor have we observed its photoreduction.

The $^1\text{H-n.m.r.}$ spectrum of the deprotonated purple complex is shown in Figure 2. Compared with $[\text{Co}(\text{sep})][\text{BPh}_4]_3$, the chemical shifts of the methylene protons of NCH_2N and $\text{NCH}_2\text{CH}_2\text{N}$ have both shifted towards higher magnetic field by *ca.* 0.2 p.p.m. While the coupling pattern of the NCH_2N methylene group was similar (*i.e.* an AB quartet), that of the $\text{NCH}_2\text{CH}_2\text{N}$ ethylene group showed a better defined pair of AB quartets. Moreover, the amino-NH proton resonances had disappeared. From these spectral features, we concluded that the deprotonated purple complex still has D_3 symmetry¹ and that the negative charge produced by deprotonation is delocalized over the six nitrogen atoms co-ordinated to the cobalt ion.

It seems noteworthy that the photoreduction is caused by visible light at 488.0 and 514.5 nm, since electron transfer is usually induced only by u.v. light. This may be accounted for either in terms of a shift of the charge transfer band (due to the close approach of the complex ion to the tetraphenylborate anion as described above) or in terms of labilization of the d-electron by a d-d transition.

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