

Cobalt(II) chloride complexes with some phosphine oxides: compatibility between structural data for the solid complexes and their stability constants in acetone medium

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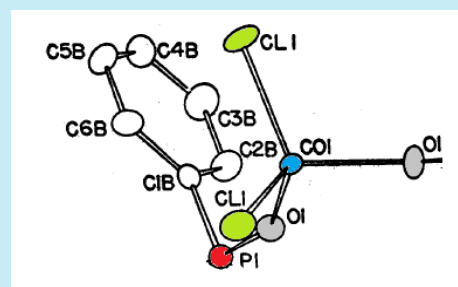
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ABSTRACT: Binary complexes of general formula CoCl_2L_2 , where L = triphenylphosphine oxide (TPPO), benzyldiphenylphosphine oxide (BDPPO), dibenzylphenylphosphine oxide (DBPPO) and tribenzylphosphine oxide (TBPO) were considered concerning X-ray structural data for the complexes in the solid state and their stability constants in acetone solution. Compatibility between structural data and stability constants are pointed out. Previous investigations showed that in acetone medium, with CoCl_2 as reference acceptor, the following basicity order is obeyed: $\text{TBPO} > \text{DBPPO} > \text{BDPPO} > \text{TPPO}$. This sequence is supported by X-ray diffraction data of the solid complexes and by electrolytic conductance values for these complexes both in acetone and in nitromethane media.



1. Introduction

First attempts made to correlate variations in bands assigned as carbonyl stretching frequencies in the infrared region for solid metal ion complexes with the stability constants of these same complexes in solution date back to early 1950s.

In some cases, very good correlations were found¹; on the other hand, complexes comprising the same oxygen donors showed no correlation at all¹.

So far as we know, correlations between X-ray structural data for the solid complexes and their stability constants in solution have not been reported. Very recently, an attempt to correlate bond lengths (in solids) and stability constants (in solution) involving organometallic complexes has been published². However, the work is quite restricted (explicitly, only two solid complexes – and these are not directly comparable – are

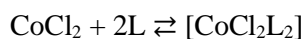
considered). Furthermore, the goal stated by the authors² namely, to establish correlations between solid structures and their corresponding thermodynamic data in solution was certainly not achieved.

The present article deals with X-ray data for the solid complexes of general formula CoCl_2L_2 , where L = triphenylphosphine oxide (TPPO), benzyldiphenylphosphine oxide (BDPPO), dibenzylphenylphosphine oxide (DBPPO) or tribenzylphosphine oxide (TBPO) as well as with formation constants of these complexes in acetone medium, at 25 °C.

2. Materials and methods

Solid complexes, appropriate for X-ray examination were prepared as previously described³. Equipment used for collection of X-ray diffraction data, measurements of diffraction

intensities, solution and refinement of the diffraction data were already described^{4,5}. Spectra in the visible region and absorbances at fixed wavelengths have been gathered as described elsewhere⁶. Stability constants for the equilibria:



$$\text{and hence: } \beta_2 = \frac{[\text{CoCl}_2\text{L}_2]}{[\text{CoCl}_2][\text{L}]^2}$$

were determined at 25 °C in acetone medium by combining the spectrophotometric method of the corresponding solutions with the Fronaeus' computation technique⁶.

3. Results and discussion

Relevant results from both X-ray examination and stability constants given in Table 1 indicate that in acetone medium, and with CoCl₂ as a reference acceptor the following basicity order holds^{7,8}: TBPO > DBPPO > BDPPO > TPPO.

Table 1: Main bond (Å) and angles (°) for the coordination sphere of the complexes and their stability constants in acetone medium.

Ligand	Co-O ₁	Co-O ₂	P-O ₁	P-O ₂	O-Co-O	Ref.	logβ ₂	Ref.
TPPO	1.997	2.001	1.500	1.498	100.04	9	6.82	6
BDPPO	1.977	1.977	1.513	1.513	100.25	5	7.31	7, 8
DBPPO	1.974	1.974	1.529	1.529	103.07	5	8.06	7
TBPO	1.937	1.920	1.505	1.547	104.98	4	8.10	7

These results are in line with the X-ray data for the solid complexes, i.e., the stronger the donor, the shorter the Co-O distances (stronger coordination) and the greater the P-O lengths. The sole exception is one of the P-O distances concerning the TBPO complex. The reason for this is unknown. The above basicity sequence has been further confirmed by conductivity data of the complexes both in acetone¹⁰ and in nitromethane³ (in this last solvent, only data for the BDPPO, DBPPO and TBPO complexes are available).

In a previous investigation⁸, no simple correlation was found between the Co-O stretching frequencies (infrared) of the solid complexes and their stability constants in acetone solution.

4. Conclusions

The basicity sequence for the phosphine oxides considered herein has been substantiated both by X-ray diffraction data of the corresponding cobalt(II) solid complexes and by their stability constants in acetone medium. The aim of this article is also to foster other people in searching possible connections between the structure of solid complexes (even in solution, through X-ray scattering and diffraction data; see *e. g.* ref. 11) and their stability constants in liquid media.

6. References

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