Ecl. Quím., São Paulo,
4: 39-46, 1979.

EQUILIBRIA IN ACETONE MEDIUM. VI*. THE COBALT(II) CHLORIDE — TRI-n-OCTYLPHOSPHINE OXIDE SYSTEM.

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MELIOS, C.; MOLINA, M.; TOGNOLLI, J. O.; ESPELETA, A. C. F. Equilíbrios em meio acetônico. VI. Sistema cloreto de cobalto(II) — Tri-n-octilfosfinóxido *Ecl. Quím.*, São Paulo, 4: 39-46, 1979.

SUMMARY: The Cobalt(II) chloride-tri-n-octylphosphine oxide (TOPO) system in anhydrous acetone, at 25.00 ± 0.05°C, has been investigated *via* spectrophotometric and conductimetric measurements. The relevant equilibria are represented generically by the equation:

$$CoCl_2 + n(TOPO) \rightleftarrows CoCl_2(TOPO)_n$$

It was found that at least four complex species are formed in this system within the fixed experimental conditions. The overall stability constants are: $\beta_1 = 1.25 . 10^4 M^{-1}$, $\beta_2 = 7.77 . 10^7 M^{-2}$, $\beta_3 = 2.87 . 10^{11} M^{-3}$ and $\beta_4 = 1.66. 10^{15} M^{-4}$. A very good compatibility between these constants and the corresponding experimental data was achieved. The results obtained in the present work are compared with those associated with other $CoCl_2$ — phosphine oxide systems, previously investigated in this laboratory. A preliminary survey on binary systems involving $CoCl_2$ and some monodentate organic ligands (*i.e.*, dimethyl sulfoxide, diphenyl sulfoxide, diphenyl sulfide, dibenzyl sulfide, triphenylphosphine sulfide, triphenylphosphine, triphenylarsine and thiophene), in the above mentioned solvent and temperature is presented.

UNITERMS: Cobalt(II) Chloride; Tri-n-octylphosphine oxide; Acetone; Spectrophotometry; Stability Constants.

INTRODUCTION

Equilibrium investigations on binary systems involving Cobalt(II) Chloride and some phenyl and benzyl-substituted phosphine oxides in acetone medium, at 25°C, have been developed in this laboratory(1, 2). In the present work the equilibria of Cobalt(II) Chloride with tri-n-octylphosphine oxide were studied in

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[*] References 1,2a,2b, 7 and 19 are to be considered as parts I-V, respectively.

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the same medium and temperature with the aim of determining both the nature and the stability constants of the complex species formed in this system. Results from an exploratory investigation on binary systems comprising the named salt and some organic monodentade ligands are also reported.

LIST OF MAIN SYMBOLS AND NOTATIONS

A, measured absorbance; b, length of the optical path (cm); BDPPO, benzyldiphenylphosphine oxide; β_n, overall stability or formation constant of $CoCl_2L_n(M^{-n})$; C_L total concentration of ligand; C_M, total concentration of $CoCl_2$; DBPPO, dibenzylphenylphosphine oxide; DBS, dibenzyl sulfide; DMSO, dimethyl sulfoxide; DPS, diphenyl sulfide; DPSO, diphenyl sulfoxide; ε, mean molar absorptivity = $= A/b.C_M(M^{-1})$; ε_n, molar absorptivity of $CoCl_2L_n(M^{-1}.cm^{-1})$; F_n, Fronaeus functions⁽³⁾; K_n, step stability constant of $CoCl_2L_n(M^{-1})$; L, ligand; [L], free ligand concentration; Λ_m measured conductance (mho); Λ_M, molar conductance ($mho.cm^2.mole^{-1}$); M, molar concentration; n, number of ligands in mononuclear complex $CoCl_2L_n$; 1:n, central group to ligand proportion in mononuclear species; R, linear correlation coefficient; TBPO, tribenzylphosphine oxide; TH, thiophene; TOPO, tri-n-octylphosphine oxide; TPAs, triphenylarsine; TPP, triphenylphosphine; TPPO, triphenylphosphine oxide; TPPS, triphenylphosphine sulfide; z, average number of ligands bound to one central group.

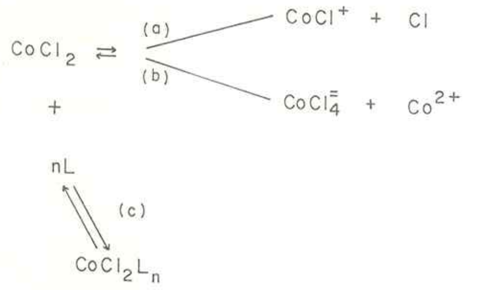
EXPERIMENTAL PART

Pure anhydrous acetone was obtained as previously mentioned⁽¹,⁴⁾. The preparation and standardization of anhydrous stock solutions of Cobalt(II) chloride was described elsewhere⁽¹,⁴⁾. Working solutions were prepared from these solutions as required. TOPO, obtained from "E. Merck", revealed and acetone-insoluble impurity. The raw product was dissolved in acetone and the resulting solution was filtered. Water was added to the filtrate until a slight turbidity appeared. After this treatment the system was slowly evaporated on a hot plate until its volume had been reduced to about half of the original, cooled and maintained overnight in the refrigerator. The precipitated crystals were filtered. Acetone and water were eliminated from the purified product through distillation at reduced pressure. The isolated substance presented m.p. 51.6-52.1°C. Some of the reported m.p's. for pure TOPO are⁽⁵⁾: 50-52°C; 50-53°C; 51-51.5°C; 52-53°C; 53°C; 54-55°C. Acetone solutions of known concentrations of this ligand were assessed by direct weighing of the anhydrous product. DMSO ("Fluka", "purissimum" grade) was used as received. Other ligands (employed only in preliminary experiments), obtained from several commercial sources, were used without further purification.

Spectrophotometric and conductimetric data were gathered with previously described equipment and procedures⁽²⁾. Measurements were all carried out at 25.00 ± 0.05°C, in acetone medium. Stability constants were determined by combining the spectrophotometric method of corresponding solutions⁽⁶⁾ which makes it possible to obtain the z and [L] pairs of values) with the computation technique of Fronaeus⁽³⁾. Computations were assisted by using a Hewlett-Packard model 9810A programmable electronic calculator.

RESULTS AND DISCUSSION

Conductivity measurements of $CoCl_2$ solutions and $CoCl_2$-TOPO mixtures (Table I) reveal that the metal salt and the complex species formed in solution are almost undissociated. In previous investigations⁽⁷⁾ it has been shown that the Λ_M value for 1.00mM solutions of $CoCl_2$ in anhydrous acetone is 9.5 ± 1.5. The mean Λ_M value given for 1:1 electrolytes (complexes) in the named solvent is 120 (range: 80-200); for 1:2 electrolytes (complexes) the value is 180 (range: 146-344)⁽⁸⁾. Thus, $CoCl_2$ is a weak electrolyte in acetone and the low conductance values sistematically found could be ascribed to equilibria (a) and/or (b) in the following scheme:



The occurence of equilibria represented by (c) — with the resulting reduction in the concentrations of the ionic species shown in (a) and/or (b) — is clearly indicated by the continuous decrease of conductance with increasing C_L (Table I). The chloride ions are not displaced from the inner coordination sphere of the complex species formed, even when TOPO is present in considerable excess. Thus, $CoCl_2$ acts as a central group and the overall stability constants for the system under consideration are defined by:

$$\beta_n = \frac{[CoCl_2\,(TOPO)_n]}{[CoCl_2]\,[TOPO]^n}$$

The constancy of absorbances as a function of time for fixed ligand and metal salt concentrations indicates that the attainment of equilibria is rapid relative to the time necessary to prepare a sample for examination. Moreover, the set of absorption spectra for different C_L/C_M ratios (at constant C_M) — covering the 500-750nm range — is analogous to the one displayed by the $CoCl_2$-TPPO system⁽¹⁾ providing further evidence of complex formation and pointing to the feasibility of a spectrophotometric study of the system.

TABLE I — Conductimetric Data for $CoCl_2$ — Phosphine Oxide Systems in Anhydrous Acetone. t = 25.00 ± 0.05°C

C_M = 1.00 mM Cell constant: 0.78 cm^{-1} Λ_m(μmho)

C_L(mM)	TOPO	TPPO*	BDPPO*	DBPPO*	TBPO*
0	11.0	11.0	11.0	11.0	11.0
1.00	5.75	9.34	6.46	5.65	5.03
2.00	4.28	7.96	5.35	3.76	2.84
3.00	3.40	6.98	4.90	3.46	2.23
4.00	2.80	6.23	4.72	2.87	1.98
5.00	2.40	5.68	4.65	3.30	1.78
6.00	2.15	5.17	4.60	3.70	—
7.00	1.98	4.72	4.52	4.06	—
11.0	1.69	—	4.05	4.30	—

Λ_m (acetone) < 0.4 μmho; Λ_m (phosphine oxides) < 0.4 μmho
* — ref. 2

The spectra associated with the $CoCl_2$-TOPO system made clear that the 640-665nm range would be the most appropriate for investigation. The spectrophotometric measurements were carried out at 660nm. The ε *vs.* C_L curves were obtained for two fixed C_M (1.00 and 1.50mM); C_L values were allowed to vary within the 0-6.00mM range. In such conditions, the range of ε data was 285 (ε_o value)-533 $M^{-1}.cm^{-1}$ (useful range for stability constants evaluation: 300-445$M^{-1}.cm^{-1}$). Table II lists the ε values interpolated from the ε *vs.* C_L curves, the corresponding z and [L] data as well as the Fronaeus'function (F_o) derived by graphical integration of de z/[L] *vs.* [L] curve as recommended by AHRLAND(9). A linear relationship, with positive slope, between F_3 and [L] was found (R = 0.9996) indicating that the system comprises four complex species in the experimental range studied.

TABLE II — $CoCl_2$- Tri-n-Octylphosphine Oxide System in Anhydrous Acetone. Concentration Variables and Fronaeus'Function. t=25.00±0.05°C.

ε*	[L], mM	z	F_o	zcalc.**
300	0.0110	0.137	1.147	0.137
305	0.0146	0.182	1.200	0.183
310	0.0183	0.228	1.256	0.228
315	0.0219	0.273	1.314	0.273
320	0.0255	0.318	1.375	0.318
325	0.0292	0.364	1.439	0.363
330	0.0328	0.409	1.505	0.409
335	0.0365	0.454	1.575	0.454
340	0.0401	0.500	1.648	0.499
345	0.0437	0.545	1.725	0.545
350	0.0474	0.590	1.805	0.590
355	0.0510	0.636	1.889	0.636
360	0.0546	0.681	1.976	0.681
365	0.0583	0.727	2.068	0.727
370	0.0619	0.772	2.164	0.772
375	0.0655	0.817	2.264	0.818
380	0.0692	0.863	2.369	0.863
385	0.0728	0.908	2.479	0.909
390	0.0765	0.953	2.594	0.954
395	0.0801	0.999	2.715	0.999
400	0.0837	1.04	2.840	1.04
405	0.0874	1.09	2.972	1.09
410	0.0910	1.13	3.110	1.13
415	0.0946	1.18	3.254	1.18
420	0.0983	1.22	3.405	1.22
425	0.102	1.27	3.563	1.27
430	0.106	1.32	3.729	1.31
435	0.109	1.36	3.902	1.35
440	0.113	1.41	4.083	1.40
445	0.117	1.45	4.272	1.44

* — Interpolated values.

** — Values calculated from β_n given in Table III.

TABLE III — $CoCl_2$- Tri-n-Octylphosphine Oxide System in Anhydrous Acetone. Overall and Step Stability Constants. t = 25.00 ± 0.05°C

	n				
	0	1	2	3	4
β_n	1.00	$1.25.10^4$	$7.77.10^7$	$2.87.10^{11}$	$1.66.10^{15}$
$\log\beta_n$	0	4.10	7.89	11.46	15.22
K_n	1.00	$1.25.10^4$	$6.22.10^3$	$3.69.10^3$	$5.78.10^3$
$\log K_n$	0	4.10	3.79	3.57	3.76

The very good agreement between the experimental and calculated z values (Table II) confirm the compatibility between the computed stability constants (Table III) and the experimental data; furthermore this agreement furnishes an evidence pointing to the absence of polynuclear species within the experimental limits fixed for the present work.

Two features (at least) should be stressed in connection with the stability constants quoted in Table III: a) an unusual stability sequence is depicted, as $K_4 > K_3$, b) no linear relationship between log K_n and (n-1) is found. Such behaviour is essentially in common with the one observed for similar systems(1, 2).

A comparison of the stability constants obtained in the present work with those secured for analogous $CoCl_2$-phosphine oxide systems(1, 2) shows that when β_1 and β_2 values are considered, the following relative basicity order holds:

TBPO > DBPPO > TOPO > BDPPO > TPPO .... (1)

On the other hand, taking into account the β_3 and β_4 values, the sequence is:

TOPO > DBPPO > BDPPO > TPPO .... (2)

TBPO is not included in this last sequence because only the order of magnitude of β_1 and β_2 could be obtained for the $CoCl_2$-TBPO system(2). The conductimetric data given in Table I are in satisfatory agreement with sequences (1) and (2), providing further support regarding the reliability of the formation constants evaluated in the present work. In concern with the data listed in Table I, it is perhaps worth noting that the more pronounced the decrease of conductance as a function of C_L, the more stable the system.

The protonation constants of the involved phosphine oxides follow the order (10–12):

TOPO > TBPO > DBPPO > BDPPO > TPPO .... (3)

It can be seen hat this order and sequence (2) move in the same direction. With the presently available data no satisfactory explanation can be advanced for sequence (1). In addition to steric and inductive effects — together with possible changes in the mode of formation of the complex species as the number of coordinated ligands is increased — solvation effects should play an important role in explaining stability behaviour, especially if non-aqueous or aqueous-organic media are considered(13–15). As specific interactions involving solvents, acceptors and donors are more clearly reflected in enthalpy and entropy changes(13–16), a convincing explanation could probably be offered when such thermodynamic data become available.

Preliminary experiments on binary systems of $CoCl_2$ and some other ligands (*i.e.*, DMSO, DPSO, DPS, DBS, TPPS, TPP, TPAs and TH) have been performed. Conductimetric data associated with most of these systems are shown in Table IV. Very weak or no interaction was observed for the systems incorporating DPSO, DPS, DBS and TH. This conclusion is supported by both spectrophotometric and conductimetric data. The system with TPPS could not be conveniently investigated owing to the very low solubility of this ligand in acetone. Conductimetric data for the DMSO system indicated extensive interaction; this was confirmed by the absorption spectra of solutions with C_L/C_M ratios ranging from 0:1 to 50:1, at constant C_M. A quantitative spectrophotometric investigation seemed feasible but several difficulties arose in attempts at determining β_n values through spectrophotometric measurements. The ε *vs.* C_L curves presented unusual features suggesting that complex species other than $CoCl_2L_n$ should be formed. The solid complex $CoCl_2(DMSO)_3$ has been isolated(17). A significant amount of interaction is also found to occur between $CoCl_2$ and TPP; this is clearly apparent from spectrophotometric and conductimetric measurements. The solid complex $CoCl_2(TPP)_2$ is already known(18). No evidence of complex formation between the metal salt and TPAs could be gathered from spectrocospic measurements; extensive interaction is however pointed out by the corresponding conductimetric data.

TABLE IV — Conductimetric Data for Binary Systems Involving $CoCl_2$ and Organic Unidentate Ligands in Anhydrous Acetone. t = 25.00 ± 0.05°C

C_M = 1.00 mM Cell constant : 0.78 cm^{-1}

Λ_m(μmho)

C_L(mM)	DMSO	DPSO	DPS	DBS	TPP	TPAs	TH
0	11.0	11.0	11.0	11.0	11.0	11.0	11.0
1.00	9.14	12.3	11.2	—	10.2	6.45	11.2
3.00	7.28	12.1	11.3	11.2	8.40	6.32	10.5
5.00	6.15	12.1	—	11.0	8.30	3.99	11.7
10.0	5.67	12.2	10.7	11.4	6.40	8.14	11.2
15.0	5.37	12.4	11.2	11.8	4.40**	—	11.7
20.0	4.74	12.6	12.6	12.8	3.70	11.2*	11.2
25.0	—	—	—	—	—	13.2	—
50.0	4.61	13.3	—	—	—	—	10.8

Λ_m(acetone) < 0.4 μmho
* — Value for C_L = 19.5 mM
** — Value for C_L = 15.6 mM

The quantity of available data on $CoCl_2$ complex systems in acetone(1, 2, 7, 19–21) indicate the following stability orders:

pyridine, pyrazole >> TPP .... (4)
(N >> P)
phosphine oxides > DMSO >> sulfides ~ TH .... (5)
(O >> S)
$CoCl_4^=$ > $CoBr_4^=$ > $CoI_4^=$ .... (6)
(Cl^- > Br^- > I^-)

Sequences (4)-(6) strongly suggest that $CoCl_2$ in acetone can be considered as tipe(a) or "hard" LEWIS acid according to the classifications of AHRLAND(22) and PEARSON(23), respectively.

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RESUMO: O sistema cloreto de cobalto (II) — tri-n-octilfosfinóxido (TOPO) foi investigado em acetona anidra, a 25,00 ± 0,05°C, através de dados espectrofotométricos e condutométricos. Concluiu-se que os equilíbrios relevantes envolvidos nesse sistema podem ser representados genericamente pela equação:

$$CoCl_2 + n(TOPO) \rightleftarrows CoCl_2\ (TOPO)_n$$

Encontrou-se que esse sistema encerra pelo menos quatro espécies complexas nas condições experimentais fixadas. As constantes acumulativas de estabilidade são: $\beta_1 = 1{,}25 . 10^4 M^{-1}$, $\beta_2 = 7{,}77 . 10^7 M^{-2}$, $\beta_3 = 2{,}87 . 10^{11} M^{-3}$ e $\beta_4 = 1{,}66 . 10^{15} M^{-4}$. Alcançou-se muito boa compatibilidade entre essas constantes e os dados experimentais que as originaram. Os resultados obtidos no presente trabalho são comparados com os associados a outros sistemas $CoCl_2$-fosfinóxidos, previamente estudados neste laboratório. Dados preliminares referentes a sistemas do $CoCl_2$ com alguns ligantes orgânicos monodentados (*i.e.*, dimetilsulfóxido, difenilsulfóxido, difenil sulfeto, dibenzil sulfeto, sulfeto de trifenilfosfina, trifenilfosfina, trifenilarsina e tiofeno), investigados no mesmo solvente e à mesma temperatura, são apresentados.

UNITERMOS: Cloreto de cobalto(II); Tri-n-octilfosfinóxido; Acetona; Espectrofotometria; Constantes de Estabilidade.

REFERENCES

1. M., MOLINA; C., MELIOS; A. C., MASSABNI and T., TAKAKI — *J. Coord. Chem.*, **7:** 133 (1978).
2. a) M., MOLINA, C., MELIOS; A. C., MASSABNI and H., YAMANAKA — Proc. IV. Int. Symp. Solute-Solute-Solvent Interactions, Vienna, 1978, pp. 211-213.
   b) Idem, *Eclét. Quím.*, **3:** 17 (1978).
3. S., FRONAEUS — Dissertation, Lund (1948); *Acta Chem. Scand.*, **4:** 74 (1950); **5:** 139 (1951).
4. M., MOLINA; C., MELIOS and H., YAMANAKA — *Eclét. Quím.*, **3:** 113 (1977).
5. J., GOFFART and G., DUYCKAERTS — *Anal. Chim. Acta*, **38:** 529 (1967) and references quoted therein.
6. F. J. C., ROSSOTTI and H., ROSSOTTI — "The Determination of Stability Constants", Mc Graw Hill, New York, 1961, p. 281.

7. C., MELIOS; M., MOLINA; J. O., TOGNOLLI and M. A., PRATO — An. I Simp. Bras. Eletroquím. e Eletroanal., São Paulo, 1978, pp. 93-97.

8. W. J., GEARY — *Coord. Chem. Rev.*, **7:** 81 (1971).

9. S., AHRLAND — *Acta Chem. Scand.*, **3:** 783 (1949).

10. Z. A., SHEKA; M. A., ABLOVA and K. B., YATSIMIRSKII — *Russ. J. Inorg. Chem.*, **14:** 1465 (1969).

11. M., SENEGACNIK; C., KLOFUTAR; S., PALJK and L., SMREKAR — *J. Inorg. Nucl. Chem.*, **32:** 1659 (1970).

12. R., SHANKER and K. S., VENKATESWARLU — *ibid*, **32:** 229 (1970) and references quoted therein.

13. F. J. C., ROSSOTTI — in "Modern Coordination Chemistry", J. Lewis and R. G. Wilkins (Eds.), Interscience, New York, 1960, pp. 64-67.

14. M. T., BECK — "The Stability of Complexes in Solution" — M. T. P. Int. Rev. Sci. (*Inorg. Chem.*, ser. 1), **9:** 1972, p. 26.

15. M., MOLINA, M., ANGST; E. K., GARCIA and C., MELIOS — *J. Inorg. Nucl. Chem.*, **34:** 3215 (1972).

16. V., GUTMANN — "Coordination Chemistry in Non-Aqueous Solutions", Springer, Vienna, 1968, pp. 12-18.

17. F. A., COTTON and R., FRANCIS — *J. Am. Chem. Soc.*, **82:** 2986 (1960).

18. J. C., PIERRARD; J., RIMBAULT and R. P. HUGEL — *J. Inorg. Nucl. Chem.*, **39:** 1625 (1977) and references quoted therein.

19. C., MELIOS; M., MOLINA; H., YAMANAKA and J. O., TOGNOLLI, Proc. IV Int. Symp. Solute-Solute Solvent Interactions, Vienna, 1978, pp. 208-210.

20. M., DE MORAES, M., MOLINA; C., MELIOS and J. O. TOGNOLLI, Res. Comunic., VIII Sem. Quím., CCFN — Araraquara, 1978.

21. D. A., FINE — *J. Am. Chem. Soc.*, **84:** 1139 (1962).

22. S., AHRLAND — *Structure and Bonding*, **1:** 207 (1966).

23. R. G., PEARSON — *J. Am. Chem Soc.*, **85:** 3533 (1963).

Recebido para publicação em 5-02-1979.