

Metal Complexes with Mixed Ligands. 22. Complex Formation between Cobalt(II) – Imidazoles and Chloride Ions. A Potentiometric Study in Mixed 3.0 M (Na)ClO₄, Cl Media

WILLIS FORSLING, INGER GRANBERG and STAFFAN SJÖBERG

Department of Inorganic Chemistry, University of Umeå, S-901 87 Umeå, Sweden

Stability constants of ternary Co²⁺ complexes with ligands imidazole (L) and chloride ions were studied at 25 °C. The measurements were performed as potentiometric titrations (glass electrode) in ionic media consisting of mixtures of 3.0 M (Na)ClO₄ and 3.0 M (Na)Cl. In addition to binary complexes, CoL_n²⁺, with formation constants (log(β_n ± 3σ), n = 1, 2, 3, 4) 2.73 ± 0.01, 4.92 ± 0.01, 6.53 ± 0.03 and 7.45 ± 0.11, ternary Co²⁺–L–Cl[–] complexes were formed. Experimental data were explained with the complexes CoLCl⁺, CoL₂Cl₂, CoL₃Cl⁺ with formation constants log β₁₁₁ = 2.76 ± 0.06, log β₂₁₂ = 4.68 ± 0.05 and log β₃₁₁ = 6.96 ± 0.04, respectively. The results show that CoL₂²⁺, as well as CoL₃²⁺, form stronger complexes with a chloride ion than the hydrated Co²⁺ ion. A comparison of the results obtained in the corresponding Ni²⁺, Cu²⁺ and Zn²⁺ systems is made. Data have been analyzed with the least-squares computer program LETAGROPVRID.

The ability of the metal ions Ni²⁺, Cu²⁺, Zn²⁺ and Hg²⁺ to form mixed complexes with imidazole (C₃H₄N₂, L) and chloride ions has been demonstrated in preceding publications in this series (parts 18,¹ 13,² 15³ and 12⁴). Within the concentration range 0 ≤ [Cl[–]] ≤ 3.0 M several mononuclear species MeL_nCl_s^{(2–s)+} have been characterized. The aim of the present investigation is to determine corresponding complexes formed in the system Co²⁺ – imidazole – Cl[–].

EXPERIMENTAL

Chemicals and analysis. All solutions used were prepared and analyzed as described earlier.^{5,6} Stock

solutions of CoCl₂ were prepared by dissolving recrystallized CoCl₂ · 6H₂O (AnalaR) in water. Stock solutions of Co(ClO₄)₂ were prepared by dissolving CoCO₃ (Merck *p.a.*) in standardized HClO₄. The cobalt content of these different solutions was determined by titration with EDTA using Xylenol orange as indicator (Vogel⁷).

Apparatus. The cell arrangement and experimental details of the emf measurements are fully described earlier.⁶

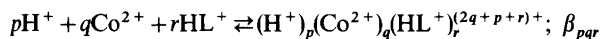
Method. The titrations were performed as potentiometric titrations at 25 °C. The titration procedures used were similar to those described in Ref. 6.

The equilibrium solutions were made to contain [ClO₄[–]] + X = 3.0 M. X is defined as the total chloride concentration. The general composition of the solutions was: B M Co²⁺, C M HL⁺, H M H⁺, X M Cl[–], ([ClO₄[–]] + X – 2B – C – H) M Na⁺ and 3.0 – X M ClO₄[–]. B and C are the total concentrations of cobalt(II) and imidazole, and H stands for the total concentration of protons, calculated over the zero level Co²⁺, HL⁺ and H₂O. The free hydrogen ion concentration, h, was determined according to the relation (1), where E₀ is

$$E = E_0 + 59.157 \log h + E_j \quad (1)$$

a constant determined in acid solution where complex formation could be neglected. The liquid junction potential E_j = –16.7 h mV was used in 3.0 M (Na)ClO₄, 3.0 M (Na)Cl as well as in mixtures of these two media. It has earlier been found by Sjöberg⁶ that within the concentration range 0 ≤ X ≤ 3.0 with [ClO₄[–]] + X = 3.0 M the concentration scale for H⁺ remains constant. No change in E₀ could be found on replacing ClO₄[–] by Cl[–] or *vice versa*.

Table 1. Results of LETAGROP calculations concerning equilibria

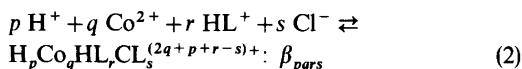


in 3.0 M (Na)ClO₄ and 3.0 M (Na)Cl media, respectively. The different β_n values are defined according to the equilibria Co²⁺ + nL ⇌ CoL_n²⁺, i.e. log β_n = log β_{pqr} - nlog K_a.

Medium	log β ₋₁₁₁ (±3σ)	log β ₋₂₁₂ (±3σ)	log β ₋₃₁₃ (±3σ)	log β ₋₄₁₄ (±3σ)	σ(Z) × 1000	Rem. ^a
3.0 M (Na)ClO ₄	-5.18(1) -5.170(8)	-10.91(1) -10.91	-17.21(3) -17.22	-24.20(11) -24.11	1.4 1.5	(1)
3.0 M (Na)Cl	-4.960(5) -4.963(3)	-10.49(1) -10.49	-16.59(6) -16.58	-23.18(19) -23.23	1.5 1.6	(1)
	log β ₁	log β ₂	log β ₃	log β ₄		
3.0 M (Na)ClO ₄	2.73	4.92	6.53	7.45		
3.0 M (Na)Cl	2.68	4.78	6.32	7.36		
3.0 M (Na)Cl	3.19	5.29	6.83	7.84		(2)

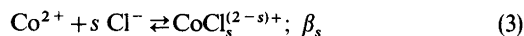
^a(1) Values calculated according to the relation β_{pqr} = β₋₁₁₁ⁿK^{n(n-1)/2} with log K = -0.571(7) (3.0 M (Na)ClO₄) and -0.563(7) (3.0 M (Na)Cl), respectively. (2) Conditional stability constants β_n defined according to the relation β_n = β_n(1+k), where k = 0.525 × 3 + 0.0078 × 3⁴ = 2.21.

We will assume the presence of four component equilibria of the general form (2). It is convenient to write complexes where -p=r as Co_qL_nCl_s^{(2q-p-s)+} with formation constants β_{nqs}. This terminology is used throughout this paper.

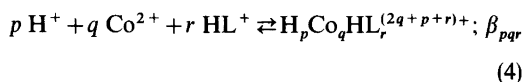


In addition to the four component equilibria in (2) we have

(i) the complex formation between Co²⁺ and Cl⁻, eqn. (3). In 3.0 M NaClO₄ medium β₁ = 0.53 M⁻¹ and β₄ = 0.0071 M⁻³ have been reported.⁸



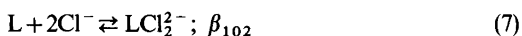
(ii) the cobalt(II) - imidazole equilibria (4) with equilibrium constants determined in this work and given in Table 1.



(iii) the proton imidazole equilibrium (5) which has been found to be dependent on the composition of the ionic medium; e.g. log K_a = -7.913 and



-7.635 in 3.0 M (Na)ClO₄ and 3.0 M (Na)Cl,⁹ respectively. It has been shown by Sjöberg⁴ that with [ClO₄⁻] + X = 3.0 M the variation in K_a(HL⁺) could equally well be explained by assuming the perchlorate ion to form complexes with the imidazolium ion or speciation between the imidazole molecule and chloride ions. The types of complexes that are formed are difficult to predict from potentiometric measurements. However, as these complexes are very weak, we can approximate the free concentration of Cl⁻ and ClO₄⁻ by the total concentrations. This means that interpretation of the four component equilibria as defined under (2) are independent of whether we assume the presence of HL⁺ - ClO₄⁻ or L - Cl⁻ complexes. However, to restrict the number of components to four, corrections for the medium dependence of K_a(HL⁺) will be made by means of the equilibria (6) and (7),



with log β₁₀₁ = -0.70 and log β₁₀₂ = -1.34. Equilibria (3)-(7) were determined in separate investigations and are assumed to be known in calculations concerning equilibria (2).

Data treatment. In the present study, hydrolytic equilibria of the cobalt(II) ion as well as formation of mixed Co²⁺ - L - OH⁻ complexes could be neglected as long as C/B ≥ 4.

Thus it will be possible to reduce the four-component system $H^+ - Co^{2+} - HL^+ - Cl^-$ to the three-component system $L - Co^{2+} - Cl^-$ under the assumption that $-p=r$ in (2), which means that only complexes of the type $Co_nL_nCl_s^{(2q-s)+}$ are formed. With this assumption we have eqn. (8), where K_w is

$$[L]_{tot} = [L] + [LCl^-] + [LCl_2^{2-}] + \sum n\beta_{nqs}[Co^{2+}]^n[L]^n[Cl^-]^s = h - H - K_w h^{-1} \quad (8)$$

the ionic product of water. In the present study the term $K_w h^{-1}$ can be neglected. $[L]$ can be calculated from the relation (9), where K_a is the acidity constant of HL^+ in 3.0 M $(Na)ClO_4$.

$$[L] = K_a h^{-1} [HL^+] = K_a h^{-1} (C - (h - H)) \quad (9)$$

The mathematical analysis was performed with the least squares computer program LETAGROPVRID¹⁰ (version ETITR¹¹). As input to this program data in the form $[L]_{tot}$, $\log[L]$, B , and X were given. On treating the emf data the error squares sum $U = \sum ([L]_{tot}^{calc} - [L]_{tot}^{exp})^2$ was minimized. The standard deviations were defined and calculated according to Sillén.¹² The computations were performed on a CYBER 172 computer.

DATA, CALCULATIONS AND RESULTS

The analysis of data was started by making $\bar{n}(\log[L])$ plots, which are given in Fig. 1. It was found that with $C/B \geq 4$ or higher values of B ($B \geq 0.04$ M), coinciding curves were obtained, thus indicating the formation of a series of mononuclear complexes CoL_n^{2+} . With $C/B < 4$ deviations from the mononuclear \bar{n} curves were observed, probably due to the formation of mixed hydroxo Co^{2+} complexes. However, these data will not be treated in this investigation. The evaluation of binary $Co^{2+} - L$ as well as ternary $Co^{2+} - L - Cl^-$ complexes will now be given in detail.

(i) *Cobalt(II) - imidazoles in a 3.0 M (Na)ClO₄ medium.* Experimental data were collected covering the concentration ranges $0.005 \leq B \leq 0.02$ M, $0.005 \leq C \leq 0.16$ M, $-0.045 \leq H \leq 0.08$ M with $\bar{n} \leq 2.6$ and $-\log h \leq 8.7$. In each titration the quotient C/B was kept constant and had values 0.25, 0.5, 1, 2, 4, 8 and 16. Some of these experimental data are visualized in Fig. 1 in the form of a Bjerrum plot $\bar{n}(\log[L])$.

Formation constants for the different species

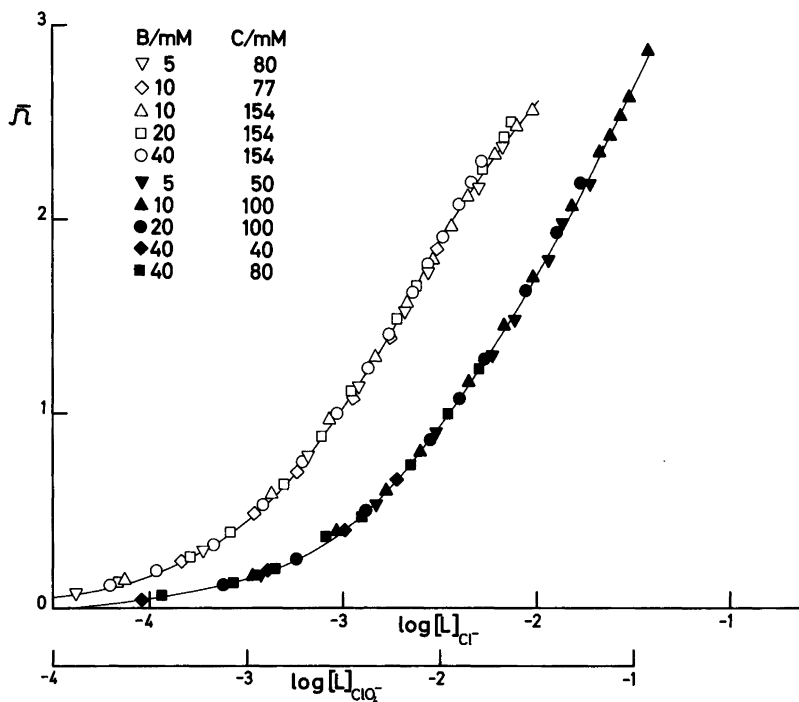


Fig. 1. Parts of experimental data plotted as curves ($\bar{n} \log[L]$). Open symbols refer to titrations in 3.0 M $(Na)ClO_4$ and filled symbols to corresponding in 3.0 M $(Na)Cl$. The full curves were calculated with β_n values given in Table 1.

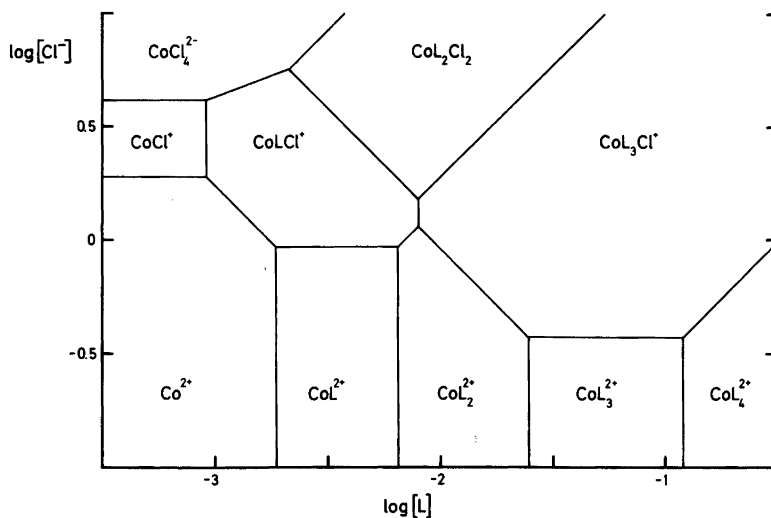
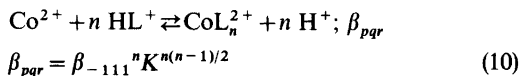


Fig. 2. Predominance area diagram for the different cobalt(II) complexes. The computer program SOLGASWATER²⁰ was used in the calculations. $\log[L] \geq -1.5$ and $\log[Cl^-] \geq 0.5$ denote extrapolated ranges.

were evaluated in a LETAGROP calculation with the result given in Table 1. Data were also analyzed with the two-parameter approximation of the type (10).



By using a special version of the LETAGROP program β_{-111} and K were calculated and the result of this calculation is also given in Table 1. From these parameters formation constant for each of the different CoL_n^{2+} complexes were calculated and were found to be in good agreement with those separately calculated (cf. Table 1).

(ii) *Cobalt(II)–imidazoles in a 3.0 M (Na)Cl medium.* To determine whether ternary species like $CoL_n Cl_s^{(2-s)+}$ exist, the medium was changed to 3.0 M NaCl. At this high chloride concentration $CoCl^+$ is the dominating complex in the absence of imidazole (cf. Fig. 2). The following concentration ranges were investigated: $0.01 \leq B \leq 0.08$ M, $0.04 \leq C \leq 0.1$ M, $-0.055 \leq H \leq 0.04$ M, $\bar{n} \leq 2.9$ with $-\log h \leq 8.4$. The quotients C/B had values 0.25, 0.5, 1, 2, 5 and 10. In this medium mononuclear $Co^{2+} - L$ species are formed too and their formation constants were evaluated in a similar way as in the perchlorate medium (cf. Table 1). It has to be pointed

out that these constants are not "true" stability constants but rather "conditional" constants as it is assumed that no chloride ions take part in the complex formation. However, it is possible to calculate new conditional constants β'_n which are corrected for the binary $Co^{2+} - Cl^-$ equilibria through the relation (11), where $k = \beta_{011}[Cl^-] + \beta_{014}[Cl^-]^4$

$$\beta'_n = \beta_n(1 + k) \quad (11)$$

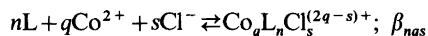
k is a constant provided $[Cl^-]$ remains constant during the titrations.

The values of β'_n from 3.0 M (Na)Cl medium are given in Table 1. As can be seen from this table the values of the β'_n constants are usually greater than those in the perchlorate medium, thus indicating that $CoL_n Cl_s^{(2-s)+}$ complexes are also formed.

(iii) *Cobalt(II)–imidazoles in mixtures of 3.0 M NaClO₄ and 3.0 M (Na)Cl.* In order to determine the compositions and stabilities of ternary $Co^{2+} - L - Cl^-$ complexes, it is necessary to perform measurements in media containing varying amounts of chloride ions e.g. $[ClO_4^-] + X = 3.0$ M.

Experimental data were collected by performing titrations both at constant X -values ($X = 0, 1.5, 2$ and 3 M) and at defined \bar{n} -values ($\bar{n} = 0.5, 1, 1.5$ and 2.0) where solutions 3.0 M in (Na)ClO₄ were titrated

Table 2. Results of LETAGROP calculations concerning formation of ternary $\text{Co}^{2+} - \text{L} - \text{Cl}^-$ complexes. The formation constants are defined according to the equilibrium



When no $3\sigma(\log \beta_{pqr})$ is given, the formation constant has not been varied. R denotes a rejected complex ($\beta_{n1s} \leq 0$).

No. of titr./ No. of points	CoCl ⁺	CoLCl ⁺	CoL ₂ Cl ₂	CoL ₃ Cl ⁺	CoL _n Cl _s ^{(2-s)+}	n, s	U	σ(L)	
	log(β ₀₁₁ ± 3σ)	log(β ₁₁₁ ± 3σ)	log(β ₂₁₂ ± 3σ)	log(β ₃₁₁ ± 3σ)	log(β _{n1s} ± 3σ)				
10/215	-0.28	2.76(6)	4.68(5)	6.06(4)	—		11.0	0.23	
		2.60(15)	4.68	6.96	1.93(25)	1,2	10.5	0.22	
		2.69(8)	4.68	6.96	1.30(26)	1,3	10.4	0.22	
		2.69	4.68(5)	6.96	R	2,1	11.0	0.23	
		2.69	4.68	6.96(11)	4.77-6.05	3,2	11.0	0.23	
		2.69	4.68	6.93(5)	7.53-7.88	4,1	10.8	0.22	
		2.69	4.68	6.95(4)	6.65-7.30	4,2	11.0	0.23	
		-0.27(4)	2.76(3)	4.68	6.96	—		11.0	0.23

with solutions 3.0 M in (Na)Cl or *vice versa*, thus giving $0 \leq X \leq 3.0$ M. 10 titrations including 215 titration points were performed.

In the calculations formation constants for binary $\text{Co}^{2+} - \text{Cl}^-$, and $\text{L} - \text{Cl}^-$ as well as for the different CoL_n^{2+} species, ($n = 1, 2, 3$ and 4) obtained in the 3.0 M (Na)ClO₄ medium were assumed to be known and were not varied in the calculations.

The different LETAGROP calculations showed that the "best" explanation of the experimental data was obtained with the ternary complexes CoLCl^+ , CoL_2Cl_2 and CoL_3Cl^+ . The complexes CoLCl_2 , CoLCl_3^- , CoL_2Cl^+ , CoL_3Cl_2 , CoL_4Cl^+ and

CoL_4Cl_2 were also tested, one at a time. However these species were either rejected in the calculations or their formation constants came out with large standard deviations. The results of these calculations are summarized in Table 2.

In order to visualize the amounts of the different Co^{2+} species in this system a predominance area diagram has been constructed and is given in Fig. 2. It is seen from the diagram that the ternary $\text{Co}^{2+} - \text{L} - \text{Cl}^-$ species are predominating at high chloride concentration levels ($\leq 60\%$ of *B* cf. Fig. 3).

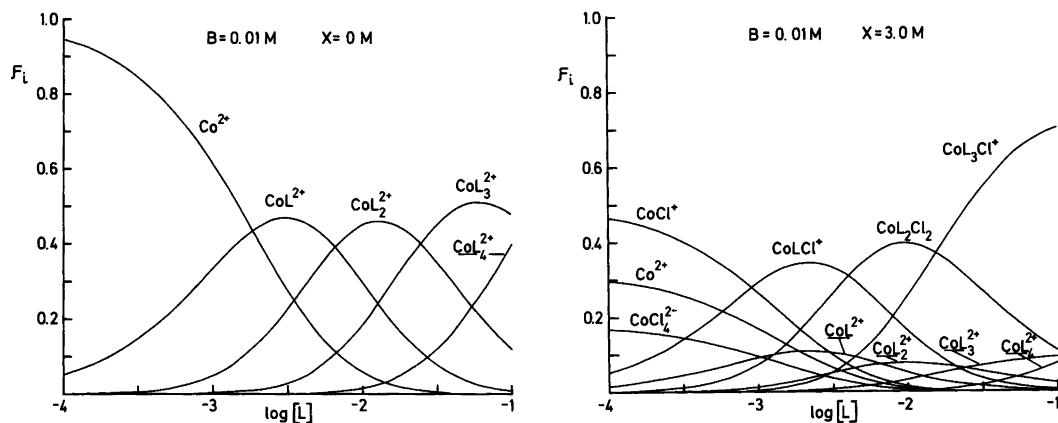


Fig. 3. Distribution diagrams $F_i(\log[\text{L}])_{B,X}$ for the different cobalt(II) complexes.

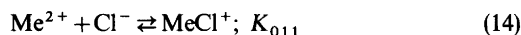
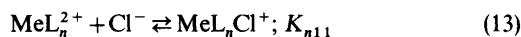
DISCUSSION

The present investigation has shown that in addition to the binary CoL_n^{2+} complexes, $n=1, 2, 3$ and 4, experimental data were explained with the ternary complexes CoLCl^+ , CoL_2Cl_2 and CoL_3Cl^+ . These ternary species are all formed in significant amounts and do, in fact, predominate at high chloride concentrations ($X \gtrsim 1 \text{ M}$, cf. Fig. 2).

The similarities between the Co^{2+} system and the earlier investigated Ni^{2+} , Cu^{2+} and Zn^{2+} systems are striking. The species MeLCl^+ , MeL_2Cl_2 and MeL_3Cl^+ are all found to be the most stable ternary complexes in these systems. This is an indication that coordination numbers 2 and 4 (with respect to $\text{L} + \text{Cl}^-$) are favoured.

To characterize the stability of the different mixed complexes, the difference $\Delta \log K_n$ given by the relation (12) has been calculated. K_{n11} and K_{011} are defined according to the equilibria (13) and (14).

$$\Delta \log K_n = \log K_{n11} - \log K_{011} \quad (12)$$



Positive values of $\Delta \log K_n$ indicate that the mixed complex is more stable compared with the binary. To show the stabilities of the different MeLCl^+ and MeL_3Cl^+ complexes ($\text{Me}^{2+} = \text{Co}^{2+}$, Ni^{2+} , Cu^{2+} , Zn^{2+}), corresponding $\Delta \log K_n$ values have been calculated and the results are given in Table 3. As can be seen $\Delta \log K_1$ as well as $\Delta \log K_3$ are positive in all systems, thus showing that MeL_2^{2+} and MeL_3^{2+} form stronger complexes with chloride ions than the hydrated metal ions. This finding is also in accordance with the known tendency^{4,9,13-15} of different Me^{2+} -imidazole complexes to form stronger hydroxo complexes than the hydrated metal ions. These results seem to indicate that coordinated imidazole ligands enhance the affinity

for the anions Cl^- and OH^- . The same tendency is also valid for mixed $\text{Me}(\text{imidazole})$ - (nitrilotriacetate)⁻ complexes as shown in a survey by Sigel.¹⁶ In these systems ($\text{Me} = \text{Co}^{2+}$, Ni^{2+} , Cu^{2+} , Zn^{2+}) $\Delta \log K_1$ is close to zero ($-0.04 \geq \Delta \log K_1 \geq 0.16$) indicating that the greater the size of the anions the less pronounced is the stability of the mixed complexes, probably due to steric hindrance. This hypothesis is supported by the stability of ternary Cu^{2+} -imidazole-L complexes,¹⁷ where L denotes (among others) glycinate, aspartate, and malonate. In all these systems negative $\Delta \log K$ values were obtained.

As stressed by Sigel,¹⁸ the presence of an aromatic N-ligand is most important for the high stability of a ternary complex. This observation was attributed to π back-bonding from the metal ion to the aromatic N-ligand. It seems that this hypothesis should be valid in the different Me^{2+} -imidazole- Cl^- and Me^{2+} -imidazole- OH^- systems discussed. However, it is important to realize that other factors leading to the formation of mixed ligand complexes comprise statistical reasons as well as the neutralization of charge in the ternary complexes. In the present system the uncharged complex CoL_2Cl_2

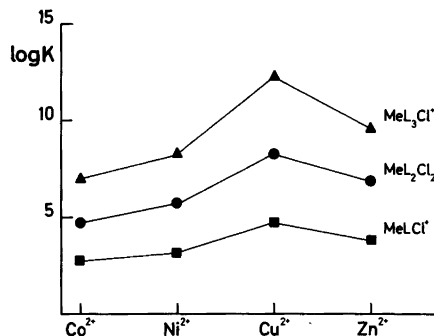
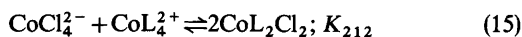


Fig. 4. $\log K$ defined according to the equilibria $\text{Me}^{2+} + n \text{L} + s \text{Cl}^- \rightleftharpoons \text{MeL}_n\text{Cl}_s^{(2-s)+}$ with $\text{Me}^{2+} = \text{Co}^{2+}$, Ni^{2+} , Cu^{2+} and Zn^{2+} .

Table 3. Comparison of binary MeCl^+ and ternary MeL_nCl^+ complexes. For definition of $\Delta \log K_n$, $n=1, 3$, see text.

Me^{2+}	$\log K_{011}$	$\log K_{111}$	$\log K_{311}$	$\Delta \log K_1$	$\Delta \log K_3$	Ref.
Co^{2+}	-0.28	0.03	0.43	0.31	0.71	This work
Ni^{2+}	-0.48	-0.21	-0.10	0.27	0.38	1
Cu^{2+}	0.00	0.10	0.28	0.10	0.28	2
Zn^{2+}	-0.19	0.55	0.83	0.74	1.02	3



is formed. According to the equilibria (15) K_{212} should have a statistical value of 4, *e.g.* $\log K_{212} = 0.6$. The experimental value of $\log K_{212}$ is 4.06, a value much higher than expected from statistical reasons. The difference may partly be attributed to the neutralization of charge in CoL_2Cl_2 . It is also of interest to note that the overall constants (defined in Table 2) for the different ternary $\text{Me}^{2+} - \text{L} - \text{Cl}^-$ complexes in the Co^{2+} -, Ni^{2+} -, Cu^{2+} - and Zn^{2+} -systems all follow the Irving-Williams¹⁹ series (*cf.* Fig. 4).

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