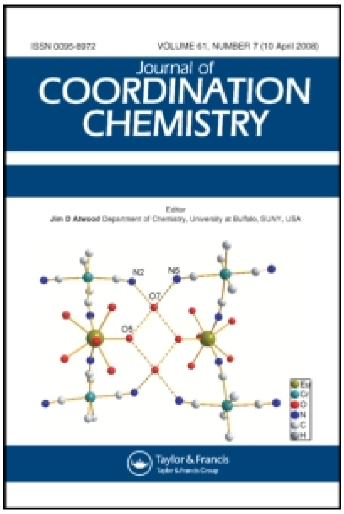

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Verhoeven, Peter , Hefter, Glenn and May, Peter M.(1990) 'Cyanide Complexes of zinc(II) and Cadmium(II) in 3 *M* NaCl Medium', Journal of Coordination Chemistry, 22: 1, 7 — 19
To link to this Article: DOI: 10.1080/00958979009408203
URL: http://dx.doi.org/10.1080/00958979009408203

J. Coord. Chem. 1990. Vol. 22. pp. 7–19
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CYANIDE COMPLEXES OF ZINC(II) AND CADMIUM(II) IN 3 *M* NaCl MEDIUM

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(Received December 6, 1989; in final form March 23, 1990)

A detailed re-investigation of the complexation of zinc(II) and cadmium(II) ions by cyanide at high pH values has been made in aqueous 3 *M* NaCl medium at 25°C using glass electrode potentiometry. Both metal ion systems gave clear evidence for the formation of ternary hydroxocyano complexes although only the Zn(II) species could be characterised quantitatively due to the lack of quantitative information for the Cd(II)–OH^- complexes in this medium. A detailed computational analysis using the ESTA suite of programs has been made, including an assessment of the effects of error propagation in these highly correlated systems by Monte Carlo simulation. Formation constants are derived for the binary H^+-, Zn(II)-, and Cd(II)–CN^- systems and ternary Zn(II)CN^-–OH^- system. For both metal ions a maximum coordination number of four was found even for the ternary systems. The absence of higher coordination number complexes was confirmed by FTIR and ^{13}C NMR spectroscopy.

Keywords: Zinc(II), cadmium(II), cyanide, hydroxide, proton, stability constants

INTRODUCTION

The extraction of gold from its ores is almost universally achieved by leaching with aerated alkaline cyanide solution.[1,2] Nowadays, this process is performed in conjunction with activated carbon (the carbon-in-pulp process) but the end product remains the same: a dilute solution of $Au(CN)_2^-$. Metallic gold is recovered from this solution either by electrolysis or by cementation with zinc dust.[1,2,3]

The latter process is also electrochemical in nature[4] with an overall reaction which may be approximated as:

$$2Au(CN)_2^-(aq) + Zn(s) \rightarrow 2Au(s) + Zn(CN)_4^{2-}(aq)$$

This process has been thoroughly developed, with an efficiency of >99% for the recovery of gold down to 0.01 mg dm^{-3}. It can also be used for the recovery of other precious metals, especially silver.[3]

The cementation of gold on zinc has been studied in detail by Nicol *et al.*[4] Whilst the detailed findings of that work are beyond the scope of the present paper, the reaction was found to be favoured by relatively high concentrations of cyanide and hydroxide ions. Zinc(II)–hydroxide and/or mixed zinc(II)–cyanide–hydroxide complexes have been invoked to explain the observed behaviour.[4] However, the characterisation of the zinc(II)–cyanide system, especially at high pH where the mixed complexes are likely to be more important, is extremely poor and considerable doubt remains as to both the number and stoichiometry of the complexes formed.[5,6]

In part, this is due to the limited range of probes with which this system can be studied. Of the more obvious techniques, the zinc amalgam electrode is attacked by cyanide,[7–9] direct spectrophotometry is probably inapplicable[10] and polarographic data are of dubious value because the reduction of Zn(II) on mercury is not fully reversible.[11] The cyanide ion-selective electrode can be used in principle but there are doubts about its performance at the necessary high cyanide concentrations.[12] Apart from the less common techniques such as calorimetry *etc.*, this leaves only the glass electrode. Unfortunately, although glass electrodes appear to perform satisfactorily in alkaline cyanide media, the accessible concentration ranges are severely limited by formation of volatile HCN, by precipitation of $Zn(CN)_2$ and/or $Zn(OH)_2$, and by the "alkaline error" of the glass electrode itself.[5,13,14]

Another difficulty in the quantitative characterisation of the $Zn(II)/CN^-/OH^-$ system is that of model selection. It is well known that in the potentiometric study of complex equilibria the accumulation of relatively minor systematic experimental errors may result in quite erroneous formation constants or even the misidentification of species especially when the complexes are strongly overlapping.[15,16] This situation is not, of course, unique to the $Zn(II)/CN^-/OH^-$ system but is exacerbated in this case by the experimental limitations referred to above and the overlapping of the complexes, *i.e.*, the similarity of the formation constants.[5]

Recent developments[17] in computation procedures for estimating the effects of such errors on formation constants using Monte Carlo simulation gives us an improved ability to assess the significance of relatively minor, but possibly important, complexes in the $Zn(II)/CN^-/OH^-$ system. For comparative purposes, a study of the analogous Cd(II) system was also undertaken. The medium chosen for the present study was 3.0 *M* (NaCl), which was preferred over the less complexing perchlorate because of its relevance to commercial gold extraction operations.[18,19]

EXPERIMENTAL

Reagents

All solutions were prepared using high purity water (Millipore Milli-Q). Analytical grade reagents were used throughout without further purification. Stock solutions of 0.1 *M* carbonate-free sodium hydroxide and 0.1 *M* hydrochloric acid were prepared from commercial solutions (BDH, concentrated volumetric standards). NaOH solutions were cross-checked by titration against potassium hydrogenphthalate (Ajax, 99.8–100.2%; dried overnight at 120°C), and HCl solutions against standard NaOH. Stock solutions of metal ions were prepared from the chloride salts ($ZnCl_2$: Pronalys, >99.0%; $CdCl_2.2\frac{1}{2}H_2O$: Ajax, 79.5–81%) and standardised against EDTA (BDH, CVS) using Erio-T indicator.[20] Titration data were analysed by Gran plots,[21] using the program MAGEC,[22] for mineral acid concentration. Solutions of sodium cyanide (BDH, >97.0%) were freshly prepared just before each titration to minimise cyanide hydrolysis and analysed for CN^- by titration with standard silver nitrate solution (BDH, CVS) according to the Leibig method.[23] Sodium chloride (Ajax, >99.5%, dried overnight at 120°C) was added to all solutions to provide a constant level of chloride ion throughout the titrations.

Instrumentation

Potentiometric titrations were performed in a tall-form 50 cm^3 titration vessel,[24] thermostatted at 25 ± 0.01°C. The cell emf was measured with a digital differential electrometer to ± 0.1 mV. Glass electrodes (Metrohm, Model 6.0101.000) were calibrated externally, before and after each titration. However, in the protonation studies, the glass electrodes were also calibrated internally as described by May *et al.*[22] All potentials were measured relative to a silver/silver chloride reference electrode, consisting of a silver wire in contact with solid silver chloride and used in conjunction with a salt bridge. Titrations were carried out using a Metrohm Dosimat 655 automatic burette under control of a Hewlett-Packard calculator (HP45).[25] Continuous magnetic stirring was applied and solutions were degassed with pre-saturated high purity N_2.

Special precautions were taken to minimise volatilisation of HCN at $pH < 9$. Thus, the titration cell was carefully sealed, degassing discontinued, and stirring minimised. In this way stable potentials ($< \pm 0.1$ mV over 3 minutes) could be achieved. All other experimental details are as described previously.[24]

The cells used in the potentiometric measurements may be represented:

Reference half-cell			Salt bridge		Test solution		
Ag|AgCl	| 3.0 *M* NaCl	‖	3.0 *M* NaCl	‖	(3.0–2z) *M* NaCl, x *M* NaCN, y *M* NaOH, z *M* Cd/ZnCl$_2$	|	GE
		E_{j1}		E_{j2}			

where GE is the glass electrode, and E_{j1} and E_{j2} are liquid junction potentials (LJPs). These cells are of the constant ionic strength type and providing the ionic strength variation is minimised and x, y, z $\ll 3$ *M*, the LJPs are negligible.[26]

Infrared spectra were recorded on a Perkin-Elmer 1720X FTIR spectrometer using a specially constructed 25–50 μm cell with silicon windows. The total or analytical zinc(II) concentration, T_{Zn}, varied from 0.06–0.37 *M* and the zinc(II) to cyanide ratio, R $(=T_{CN}/T_{Zn})$, from 4 to 50. ^{13}C-NMR measurements were made at natural abundance at 75.46 MHz using a Bruker AM-300 spectrometer. Chemical shifts were measured in 5 mm tubes relative to MeOD/D_2O at 49 ppm. T_{Zn} varied from 0.19–0.76 *M* and R from 4 to 12. Both experiments were carried out at room temperature (23 ± 1°C).

Calculations and species selection

Potentiometric data were processed using the ESTA suite of programs.[27,28] Equilibrium constants are defined in terms of the generalised formation reaction (omitting charges for simplicity):

$$pM + qL + rH_2O \xrightleftharpoons{\beta_{pqr}} M_pL_q(OH)_r + rH$$

$$\beta_{pqr} = \frac{[M_pL_q(OH)_r]K^r_w}{[M]^p[L]^q[OH]^r}$$

where
$$K_w = [H^+][OH^-]$$

Model selection was based primarily on minimisation of the objective function

$$U = (N-n_p)^{-1} \sum_{n=1}^{N} n_e^{-1} \sum_{q=1}^{n_e} W_{nq}\left(Y^{obs}_{nq} - Y^{calc}_{nq}\right)^2$$

where N is the total number of experimental titration points, n_p is the total number of electrodes, n_e is the number of parameters to be optimised, Y_{nq} is either total concentration of electrode ion q or the emf of electrode q at the n^{th} titration point.

W_{nq} is the weight of the q^{th} residual at the n^{th} point,

$$W_{nq} = \left[\sum_{p} \left(\frac{\delta(Y^{obs}_{nq} - Y^{calc}_{nq})}{\delta p} \right)^{2} \sigma_p^2 \right]^{-1}$$

where p is the optimisation parameter vector, and σ_p is the standard deviation of the titration parameters held constant during the optimisation.

Species were considered acceptable in general only if the objective function was significantly reduced (>50%) by their inclusion.

The formation function, $\bar{Z}_M$, which can be formulated as

$$\bar{Z}_M = \left[T_{CN} - A(1 - H.\beta_{011}(HCN)) \right] / T_M$$

where T represents total or analytical concentrations and

$$A = \left[(T_H - H + K_w.H^{-1}) / H.\beta_{011}(HCN) \right]$$

was also used to assist in model selection along with the standard deviations of the β values. When only mononuclear metal-ligand complexes (*i.e.*, p = 1 in the above equilibrium expression) are present, A is the free ligand concentration and $\bar{Z}_M$ can be considered as the average number of ligands bound per metal ion.

Once the most likely set of species were determined, the precision of the calculated formation constants was determined using a Monte Carlo method.[16] This procedure produces a specified number (75 in this work) of sets of simulated titration data, *i.e.*, as if the experiment were repeated by 75 independent workers. Using standard deviations which reflect realistic estimates of the experimental errors in titration parameters, random errors are introduced on each occasion into those parameters which are held constant in the calculation. This includes any auxiliary formation constants used. Optimisation of the formation constants on the simulated error-affected data is then carried out and the results for the calculated parameters over all 75 cycles is used to calculate their standard deviations. The effects of systematic errors on the formation constant calculation are thus quantified. In this way, the program identifies the best set of parameters to optimise, *i.e.*, those which give rise to the smallest standard deviations in the formation constants. The formation constants obtained are those which are least likely to be affected by systematic errors. Further details on this approach are given elsewhere.[17]

Following a number of exploratory titrations, computer simulations were also used to select concentration ranges for study in order to maximise information on difficult-to-detect complexes.

Auxiliary data

Since titrations were carried out at pH values up to 12, the formation of M(II)-hydroxy complexes in 3.00 *M* NaCl must be considered, especially for the characterisation of any mixed M(II)-CN-OH complexes. There has apparently been only one study of the zinc(II)-hydroxy complexes in 3.0 *M* NaCl.[29,30] Formation constants were reported for the simple complexes $Zn(OH)^+$ and $Zn(OH)_4^-$ and the polynuclear species Zn_2OH^{3+} and $Zn_2(OH)_6^{4-}$. The observed values were in good agreement with those determined by other workers[31,38] in 3 *M* $NaClO_4$, consistent with the relatively weak chloro-complexing of Zn(II). Consequently, the formation constants of $Zn(OH)_2^0$ and $Zn(OH)_3^-$ determined in 3 *M* $NaClO_4$ were included, without adjustment, in the present calculations. The data for the zinc(II)-hydroxy complexes are summarised in Table I.

TABLE I

Literature formation constants for Zn(II)/hydroxy complexes, 25°C.[a]

Complex	$\log \beta_{p0r}$
$ZnOH^+$	−9.25
$Zn(OH)_2^0$	−22.19
$Zn(OH)_3^-$	−31.87
$Zn(OH)_4^{2-}$	−42.61
Zn_2OH^{3+}	−7.50
$Zn_2(OH)_6^{2-}$	−57.50

[a] See text for sources and conditions.

Unfortunately, no literature data for Cd(II)-hydroxy complexes in 3.0 *M* NaCl could be found. Since Cd(II) forms much stronger chloro-complexes than Zn(II), the formation constants of $Cd(II)/OH^-$ complexes determined in 3 *M* $NaClO_4$[32–33] will not be applicable in 3 *M* NaCl. Consequently, data analysis for the $Cd(II)/CN^-$ system had to be restricted to pH ≤ 8.5 where $Cd(II)/OH^-$ species are negligible.

RESULTS AND DISCUSSION

Dissociation constants for water and HCN

The dissociation constants of water and HCN are required for the quantification of the $M(II)/CN^-/OH^-$ systems. The values obtained at $I = 3.0$ *M* (NaCl) and 25°C are given in Table II. The pK_w value was determined from strong acid-strong base titrations (*i.e.*, $x = z = 0$ in the cell) and falls within the spread of literature values (13.96–14.20) reported at this ionic strength.[34–38] The present value is in especially good agreement with the values reported for 3 *M* NaCl medium (Table II). The pK_a of HCN was determined in the usual way ($z = 0$ in cell(1)). No other data have been reported in this medium although the value is in reasonable agreement with the value of 9.48 reported by Persson in 3 *M* ($NaClO_4$).[9] Both values differ significantly from the result of 8.81 reported by Gáspár and Beck,[39] also in 3 *M* ($NaClO_4$); it may be noted that the pK_a (HCN) values of these authors show an unusual dependence on ionic strength and are probably incorrect.[40]

TABLE II

Dissociation constants for H_2O and HCN in 3 *M* (Na)Cl at 25°C.

Constant	Value	Std. devn.	No. titns.	No. data pts.	Literature values
pK_w	13.989	0.002	5	250	13.91,[a] 14.03,[35] 13.96[36]
$pK_a(HCN)$	9.220	0.005	6	465	[b]

[a] Interpolated from data in ref. [34]. [b] No previous data reported for this medium but see text.

The Zn(II)/CN⁻/OH⁻ System

Twenty titrations were performed yielding 1032 data points for this system. Total initial cyanide and zinc(II) concentration varied between 2–80 m*M* and 4–20 m*M* respectively. Solution pH typically ranged from 6 to 12 during the course of a titration. The data obtained are summarised in the form of a $\bar{Z}_M$ *vs* pA plot in Figure 1. The "curl-backs" in Figure 1 are characteristic of the formation of mixed hydroxo-complexes.[5] Nevertheless, model selection commenced with the simple mononuclear binary complexes $Zn(CN)_q^{2-q}$ for which there is unequivocal chemical evidence (q = 2, 3, 4).[9,10] Further species were accepted into the model only if the unweighted objective function was significantly reduced (>50%) by their inclusion. Initial estimates of the formation constants of the mixed complexes were obtained by applying the equation of Sharma and Schubert[41] to the simple cyano- and hydroxo-complexes.

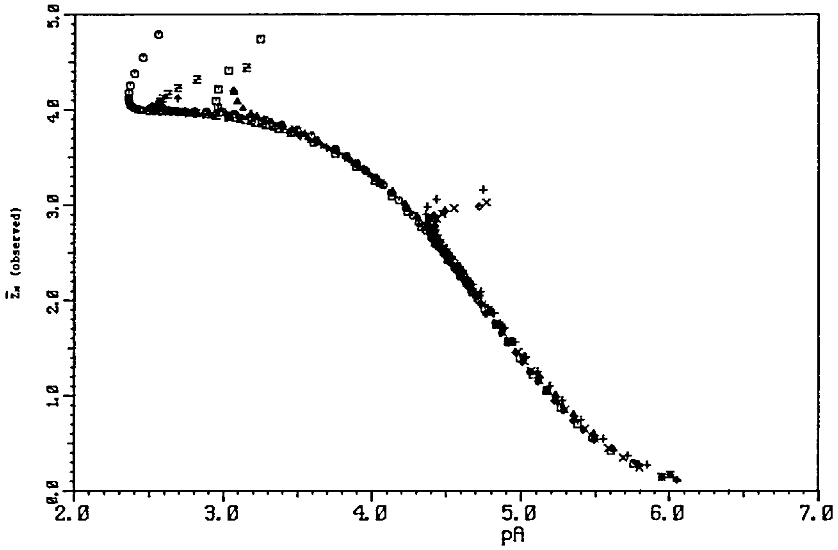

FIGURE 1 Observed formation function $\bar{Z}_M$ for the Zn(II)/CN⁻ system plotted against pA, covering the pH range 6 to 12.

The final model and the "best" estimates of the formation constants for the Zn(II)/CN⁻/OH⁻ system are summarised in Table III. As explained above, the "best" formation constants are those which are calculated using the best set of optimised parameters as determined by the Monte Carlo simulations. Also included in Table III are the formation constants reported for this system in 3 *M* ($NaClO_4$) by Persson[9] which will be discussed later. Evidence for $ZnCN^+$ was marginal on the stated criteria which is reflected in the relatively large standard deviation for β_{110}. However, its inclusion considerably improved the agreement between the observed and calculated $\bar{Z}_M$ plots at low free cyanide concentrations. A number of previous workers have also experienced difficulties in detecting $ZnCN^+$.[5,9,13] This largely arises from experimental difficulties (precipitation of $Zn(CN)_2$ and volatilisation of HCN) in the region where $ZnCN^+$ is likely to predominate[9] but also, as pointed out by Beck,[6] because $K_1(ZnCN^+) < K_2(Zn(CN)_2{}^0)$ (an unusual situation).

TABLE III

"Best" estimates of the formation constants for the Zn(II)/CN$^-$/OH$^-$ System; 3 *M* (Na)Cl, 25°C.

Complex	log β_{pqr}[a]	Lit.[b]	Lit.[c]
$ZnCN^+$	4.98 ± 0.08	5.34 ± 0.11	5.19 ± 0.02
$Zn(CN)_2{}^0$	10.19 ± 0.03	11.03 ± 0.01	11.04 ± 0.02
$Zn(CN)_3{}^-$	14.54 ± 0.04	16.68 ± 0.05	16.65 ± 0.01
$Zn(CN)_4{}^{2-}$	18.62 ± 0.04	21.57 ± 0.11	21.49 ± 0.02
$Zn(CN)_3OH^{2-}$	4.08 ± 0.04		
$Zn(CN)_2OH^-$	0.71 ± 0.06		

[a] Present work; errors are standard deviations; 20 titrations/1032 data points; $T_{CN} = 2\text{–}820 \times 10^{-4}$ *M*; $T_{Zn} = 4\text{–}190 \times 10^{-4}$ *M*; $R = 3\text{–}14$; weighted objective function based on residuals in emf's, OBJE = 200; unweighted objective function based on residuals in total analytical concentrations, OBJT = 2.5×10^{-8}. [b] Ref. [9], 3 *M* ($NaClO_4$); errors are "subjectively estimated maximum errors". [c] Data of ref. [9] recalculated as described in text; errors are standard deviations.

There has been considerable controversy in the literature regarding the existence of higher order (coordination number > 4) complexes of Zn(II) in cyanide media.[5,9,10] Whilst some higher order complexes of Zn(II) are well characterised both in the solid state and in solution,[42] no such species appear to exist among the halide or pseudohalide complexes.[43] Although many of the reports of higher order complexes in the Zn(III)/CN$^-$/OH$^-$ system, such as the early polarographic studies,[44] can be discounted because of the instrumental inadequacies and limited theoretical understanding at the time, claims for higher order complexes have persisted. Most recently, Marsicano *et al.*[5] have reported formation constants for the five coordinate species $Zn(CN)_5{}^{3-}$ and $Zn(CN)_3(OH)_2{}^{3-}$. However, in the present study, inclusion of such species did not significantly improve the fit between the experimental and calculated data.

Even so, it was thought worthwhile to investigate the possible existence of higher order complexes spectroscopically. FTIR spectra at T_{CN}/T_{Zn} ($=R$) ratios from 4 to 50 show only the presence of $Zn(CN)_4{}^{2-}$ at 2150 cm^{-1} and free CN$^-$ at 2080 cm^{-1} consistent with previous studies by Ashurst *et al.*[45] and Penneman *et al.*[46] The ^{13}C-NMR studies supported these findings. Sharp peaks were observed when one species predominated. Peaks were assigned to $Zn(CN)_4{}^{2-}$ and free CN$^-$ at 165.58 and 147.22 ppm respectively.[47] The exchange rate between the free and complexed cyanide is reasonably fast and only a broad population-averaged shift was observed at high T_{CN}/T_{Zn}. However, the observed shifts were always consistent with the presence of only $Zn(CN)_4{}^{2-}$ and CN$^-$.[47] Taken in combination with the potentiometric data, the spectroscopic evidence strongly argues against cyanide complexes of Zn(II) with coordination number >4.

The Cd(II)/CN$^-$/OH$^-$ System

The data for this system (17 titrations, 825 data points) are summarised in the form of a $\bar{Z}_M$ *vs* pA plot in Figure 2. Again the "curl-backs" are indicative of the presence of mixed Cd(II)/CN$^-$/OH$^-$ species. However, as noted above, the absence of satisfactory formation constants for the Cd(II)/OH$^-$ complexes in 3 *M* (NaCl) lead us to restrict computational analysis to data obtained at pH ≤ 8.5. As a consequence, only the formation constants of the simple $Cd(CN)_q^{2-q}$ complexes could be

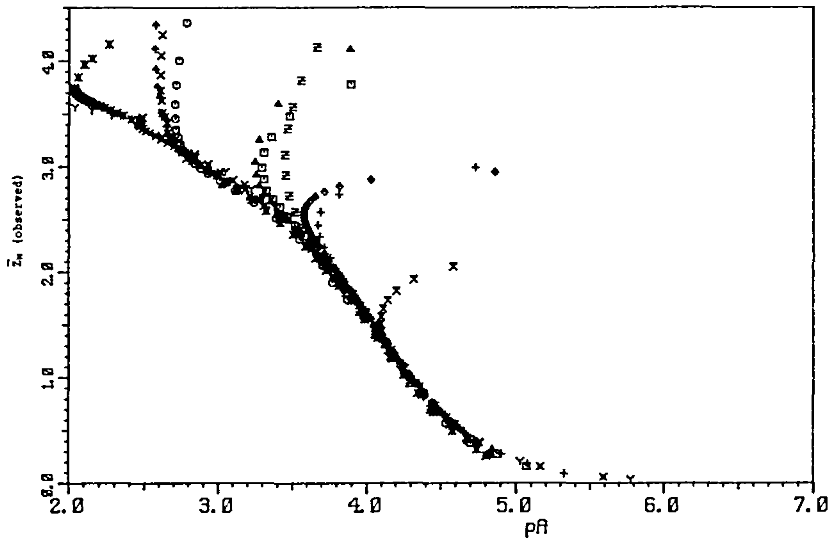

FIGURE 2 Observed formation function $\bar{Z}_M$ for the Cd(II)/CN$^-$ system plotted against pA, covering the pH range 6 to 12 but see text.

determined. The "best" values are listed in Table IV along with the data reported by Persson[9] in 3 *M* (NaClO$_4$) which will be discussed below. Attempts to simultaneously obtain $\beta_{por}(Cd_p(OH)_r^{2p-r})$ and $\beta_{pqr}(Cd_p(CN)_q(OH)_r^{2p-q-r})$ from the higher pH data were unsuccessful because of the high degree of correlation between the various formation constants.

TABLE IV
"Best" estimates of the formation constants for the Cd(II)/CN$^-$ system; 3 *M* (Na)Cl, 25°C.

Complex	log β_{pqr}[a]	Lit.[b]	Lit.[c]
CdCN$^+$	4.34 ± 0.02	5.62 ± 0.01	5.68 ± 0.01
Cd(CN)$_2^0$	8.50 ± 0.02	10.84 ± 0.03	10.87 ± 0.04
Cd(CN)$_3^-$	12.10 ± 0.03	15.72 ± 0.02	15.75 ± 0.05
Cd(CN)$_4^{2-}$	14.45 ± 0.06	19.20 ± 0.12	19.09 ± 0.06

[a] Present work; errors are standard deviations; 17 titrations/825 data points; $T_{CN} = 9\text{–}820 \times 10^{-4}$ *M*; $T_{Cd} = 4\text{–}200 \times 10^{-4}$ *M*; $R = 2\text{–}11$; OBJE (weighted) = 33; OBJT = 2.0×10^{-8}. [b,c] As for Table III.

Comparisons with Previous Studies

Zn(II)/CN$^-$

As noted in the Introduction, the Zn(II)/CN$^-$ system has been investigated on numerous occasions. The available data have been reviewed in depth quite recently by Marsicano *et al.*[5] and so will not be considered in detail here. However, it is emphasised that no previous studies have been made in NaCl media and, with one exception,[9] none has been made at high ionic strength.

TABLE V
Previous studies of the formation constants of cadmium(II)-cyanide complexes in aqueous solution.[a]

Year	Temp.[b] (°C)	Medium (M)	$CdCN^+$	$Cd(CN)_2^0$	$Cd(CN)_3^-$	$Cd(CN)_4^{2-}$	$Cd(CN)_6^{4-}$	Method	Reference
1903	21	Variable				16.85		Cd metal electrode	Euler[48]
1929	RT	Variable			18.9			Polarography	Pines[49]
1931	25	Variable			17.73			Cd metal electrode	Masaki[50]
1943	25	Variable				18.36		Re-interpretation	Leden[51]
1932	14	Variable				17.6–19.3		Cd metal electrode	Britton and Dodd[52]
1936	RT	Variable				18.3		Cd metal electrode	Ferrel *et al.*[8]
1943	25	$3(NaClO_4)$	5.48	10.60	15.23	18.78		Cd amalgam electrode	Leden[51]
1944	25	$3(NaClO_4)$	5.54	10.60	15.26	18.84		Re-interpretation	Leden[53]
1950	25	0 corr.				18.24		Cd amalgam electrode	Hirata[54]
1952	RT[c]	Variable				Evidence	Evidence	Polarography	Prytz and Osterud[55]
1953	25	0 corr.				16.04		Cd amalgam electrode	Suzuki[56]
1955	25	Variable	5.18	9.60	13.92	17.11		Cd metal electrode	Flengas[57]
1955	25	$3(NaClO_4)$	5.48	10.62	15.18	18.76		Re-interpretation	Rossotti and Rossotti[4]
1960	RT[c]	Variable		No evidence $Cd(CN)_q$ for $q > 4$ at $R \leqslant 5.6$				Raman spectroscopy	Chantry and Plane[58]
1961	RT[c]	Variable		No evidence $Cd(CN)_q$ for $q > 4$ at $R \leqslant 44$				IR spectroscopy	Penneman and Jones[59]
1964	RT[c]	Variable			Evidence	Evidence		Raman spectroscopy	Griffith[60]
1965	30	$0.1(NaClO_4)$	5.8	11.1				Solvent extraction	Hellwege and Schweitzer[61]
1966	25	$3(NaClO_4)$	5.48	10.60	15.15	18.30		Re-interpretation	Gerding[62]
1971	RT[c]	Variable	No evidence $Cd(CN)_q$ for $q > 4$ at $R \leqslant 10$					IR spectroscopy	Ashurst *et al.*[45]
1971	25	$3(NaClO_4)$	5.62	10.83	15.72	19.20		Glass electrode	Persson[9]
1971	25	0 corr.	6.01	11.12	15.65	17.92		Glass electrode	Izatt *et al.*[63]
1985	25	$0.1(KNO_3)$	5.76	10.75	15.72			Ag-Ion selective electrode	Yuchi *et al.*[64]

[a] Data presented as log β_{1q0}, units of β_{1q0} M^{-q}; $R = T_{CN}/T_{Zn}$. [b] RT = room temperature. [c] Presumed.

The most fruitful comparison which can be made with the present data are the formation constants reported by Persson[9] in 3 *M* ($NaClO_4$) using a combination of Zn(Hg) (at low cyanide concentrations) and glass electrode potentiometry (Table III). As would be expected, the present formation constants in the more strongly complexing NaCl medium are lower than those obtained in $NaClO_4$. Interestingly, the divergence between the two data sets increases with increasing coordination number. Table III also lists the formation constants which have been obtained by recalculating Persson's data using the ESTA programs (Persson's constants were obtained graphically[9]). The values are in good agreement but the present constants have significantly lower standard deviations than Persson's subjectively estimated errors (Table III).

Cd(II)/CN⁻

Although the Cd(II)/CN^- system has been less frequently investigated than the Zn(II) system, a considerable body of data exists. As these data have not been reviewed previously they are collected together into Table V.

The data reported for the Cd(II)/CN^- system are generally in much better agreement than for the Zn(II)/CN^- system. There is a general consistency not only with respect to the number and stoichiometry of the complexes present but also, with a few exceptions, the magnitudes of the formation constants. Unlike $ZnCN^+$, the $CdCN^+$ complex is readily quantified. More importantly, except for the early polarographic study of Prytz and Osterud,[55] there have been no reports of complexes higher than $Cd(CN)_4{}^{2-}$. A detailed critique of the data of Prytz and Osterud is given elsewhere.[47]

Again, as shown in Table V, no data have previously been reported in NaCl media and the most apposite comparison is the study of Persson[9] (Table IV). The latter are generally in good agreement with the early study of Leden[51,53] under the same conditions (Table V) except for $\beta_{140}(Cd(CN)_4{}^{2-})$, presumably as a result of the attack of the Cd(Hg) electrode in high cyanide concentrations.[9]

Unlike the Zn(II)/CN^- complexes the present values of $\beta_{1q0}(Cd(CN)_q^{2-q})$ differ significantly from Persson's values[9] as a result of the very much stronger chloride complexing of Cd(II).[31] As for Zn(II) the difference between the two data sets increases with increasing cyanide coordination.

The effect of increased chloro-complexing of the metal ion is also reflected in the relative values of the cyano-formation constants. Interestingly, in non-complexing perchlorate media Persson[9] found a mixed order with $\beta_{1q0}(Cd(CN)_q^{2-q}) > \beta_{1q0}(Zn(CN)_q^{2-q})$ for $q = 1$ and 2 but the opposite for $q = 3$ and 4 (see Persson's data in Tables III and IV). The same order was found by Izatt *et al.*[63] at $I = 0$. This is unusual but does not appear to have been commented on previously. A possible explanation is a change in (overall) coordination number.[43] This usually occurs earlier for the smaller Zn(II) ion than for Cd(II), a fact which may explain why $K_1(ZnCN^+) < K_2(Zn(CN)_2{}^0)$. Alternatively, it may be that the addition of the "soft" CN^- ligands to the "borderline" Zn(II) ion (in Pearson's hard–soft Lewis acid-base theory[65]) enhances its interaction[65] with subsequent CN^- ligands more than does CN^- bound to the already "soft" Cd(II) ion.

In the present study, because $\beta_n(CdCl_n^{2-n}) \gg \beta_n(ZnCl_n^{2-n})$[31] all the "apparent" values of $\beta_{1q0}(Cd(CN)_q^{2-q})$ are less than the analogous Zn(II) formation constants.

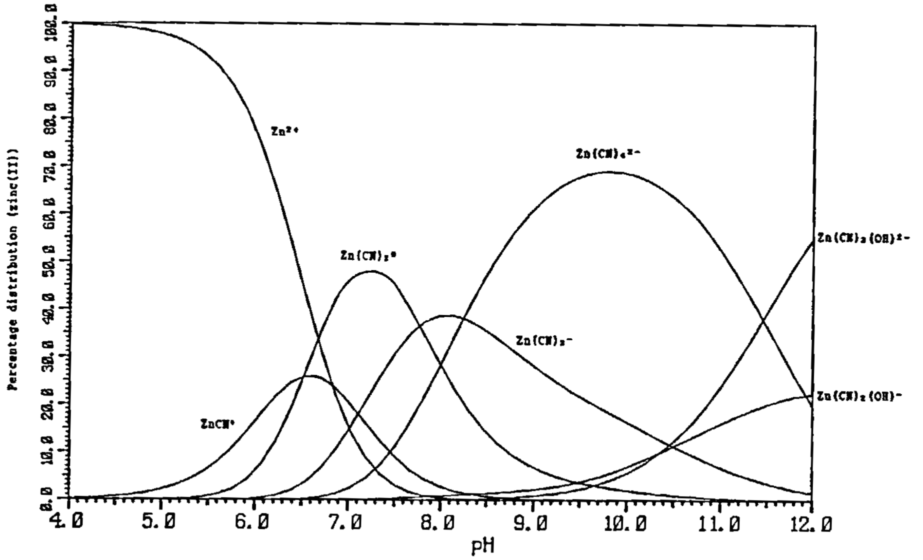

FIGURE 3 Speciation of Zn(II) in the Zn(II)/CN^-/OH^- system as a function of pH for $T_{Zn} = 1 \times 10^{-3}$ *M* and $T_{CN} = 4 \times 10^{-3}$ *M* using the formation constants given in Table III.

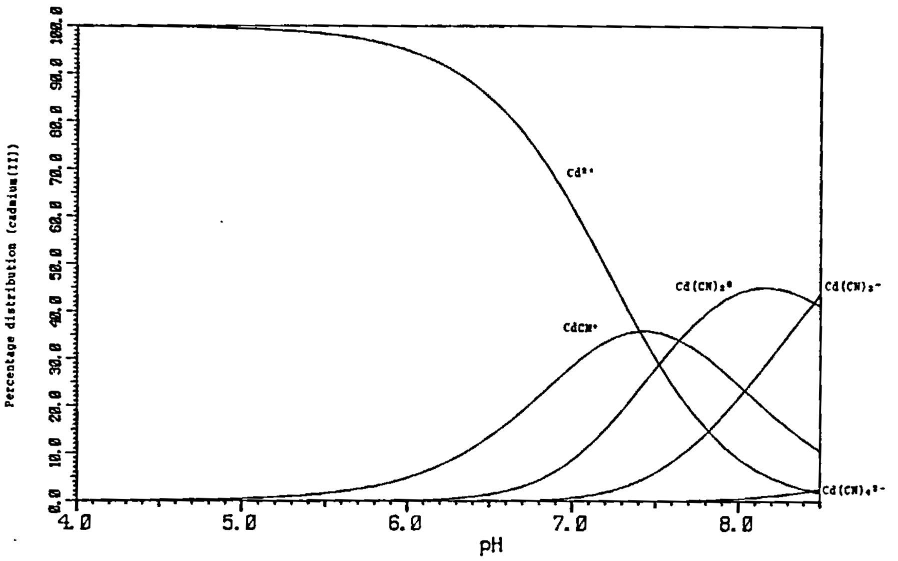

FIGURE 4 Speciation of Cd(II) in the Cd(II)/CN^- system at low pH values (see text) for $T_{Cd} = 1 \times 10^{-3}$ *M* and $T_{CN} = 4 \times 10^{-3}$ *M* using the formation constants given in Table IV.

Speciation and its Implications

Typical speciation curves for the Zn(II) and Cd(II) cyanide systems are shown in Figures 3 and 4. It must be remembered that the presence of only the simple $Cd(CN)_q^{2-q}$ complexes is purely a function of the restricted pH range: the existence of mixed complexes being clearly indicated by the "curl-backs" in Figure 2 (see also above). Figure 3 demonstrates the importance of the mixed $Zn(CN)_q(OH)_r^{2-q-r}$ complexes, which predominate at pH > 11.5 (at least under the conditions of Figure 3; the predominance range depends on the total concentrations of the interacting species) and remain significant down to pH $\simeq$ 9.0. The positive identification and characterisation of the mixed $Zn(CN)_q(OH)_r^{2-q-r}$ complexes in this work is consistent with the implication of such complexes in the cementation of gold and zinc in alkaline cyanide media.[4] The present study suggests that increased rates of zinc dissolution at high pH and high $[CN^-]$ are likely to be related to the formation of the mixed complexes rather than the $Zn_p(OH)_r^{2p-r}$ complexes, as has been suggested previously, which do not appear to be important at least up to pH = 12.0.

One interesting feature of both the Zn(II) and Cd(II) systems is the considerable overlap of many of the complexes and the fact that many of them are never predominant. This is, of course, also reflected in the absence of plateaux in the $\bar{Z}_M$ plots (Figures 1 and 2) and is one of the reasons why exact quantification of this system is so difficult.

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