regions. The latter maximum could be considered as the 325 mμ band of the salicylaldehyde[6] shifted toward longer wave lengths owing to the formation of the benzoylhydrazone. This band can be ascribed to the existence of a chelate enol ring stabilized through hydrogen-bond formation and enol resonance.[7]

Beside showing a very strong absorption band in the ultraviolet region below 250 mμ, the spectra of the ligand molecules of type II show a maximum at 336 mμ. This band presumably can be related to the band at 310 mμ ascribed to the enol form of benzoylacetone.[6]

The spectra of the complexes of type I show four absorption bands at *ca.* 260, *ca.* 280, *ca.* 360 and 400–410 mμ. The band at *ca.* 410 mμ may be identified as the characteristic band of covalent nickel chelates, which is due to the presence of a chelate ring of which the metal is a member.[8] The intensity of this band (of $\epsilon \simeq 10^4$) is that of an allowed transition.[9]

The main features of the absorption spectra of type II complexes consist of two absorption bands in the 340 and 400–410 mμ regions. The former, of smaller intensity, is lacking in the complex with triethylphosphine. The band at 406–410 mμ can be recognized as that of the Ni chelates with dsp^2 covalent structure.

Table I shows that the molecular extinction coefficient of the nickel band maximum at 400–410 mμ increases from the values 9,000–11,600 for the complexes of the type I, to values 21,100–23,900 for the complexes of the type II. Hence the position of the aromatic nucleus, adjacent to the chelate ring in the complexes of type I, attached by a C–C bond in the complexes of type II, influences the chromophoric grouping responsible for this band, *i.e.*, the chelate ring containing the nickel atom. This fact can be related to the existence in the chelate ring of the complexes of a completely conjugated resonance which interferes with the resonance of the aromatic nucleus when the two rings are condensed. Thus a "crossed resonance" of the type already studied for some copper chelates[10] is produced. This "cross conjugation"[11] implies the participation of a nickel atom in the π-bond system of the coördinate ring.

The absence of an hyperchromic effect in the maxima at 326–336 mμ of the spectra of ligands of type II can be explained keeping in mind that the chromophore possibly responsible for such maxima is not a completely conjugated system. In fact it is obvious that the hydrogen atom which completes the enol ring in the ligand molecules is incapable of forming double bonds.

These results therefore are consistent with the concept of π-bond character of the coördinate links between nickel and donor atoms in the above complexes.

The hyperchromic and bathochromic effects caused by the presence of a chlorine atom in the molecules of both ligands and complexes must be noticed. The substitution of ethylamine and triethylphosphine for ammonia produces only a little hypsochromic shift of the band at about 400 mμ. This fact is in accordance with the assumption that this band is due to the presence of a chelate ring including the nickel atom.

Acknowledgment.—We are indebted to the Italian "Consiglio Nazionale delle Ricerche" (C.N.R.) for the financial support of this work.

PALERMO, ITALY

[6] A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry," Edward Arnold Publishers, Ltd., London, 1954, pp. 128, 223.

[7] L. N. Ferguson, "Electron Structures of Organic Molecules," Prentice-Hall, Inc., New York, N. Y., 1952, p. 216.

[8] *Cf.* H. A. McKenzie, D. P. Mellor, J. E. Mills and L. N. Short, *J. Proc. Roy. Soc. N.S. Wales*, **78**, 70 (1944); A. E. Martell and M. Calvin, ref. 1; K. Sone, THIS JOURNAL, **75**, 5207 (1953).

[9] *Cf.* R. J. P. Williams, *J. Chem. Soc.*, 137 (1955).

[10] M. Calvin and R. H. Bailes, THIS JOURNAL, **68**, 949 (1946); *cf.* A. E. Martell and M. Calvin, ref. 1, p. 164.

[11] L. N. Ferguson, ref. 7, p. 43.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES]

The Gluconate Complexes. IV. The Cadmium–Gluconate System

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Cadmium in varying concentrations of gluconate has been investigated polarographically from *p*H 2 to 14. A number of complexes are formed. Those which were identified and studied have a ratio of cadmium to gluconate of 1:2 (*p*H 5 to 8), 2:3 (*p*H 13 to 14), and 2:1 (*p*H 13 to 14). Half-wave potentials and dissociation constants are given.

Although it is known that gluconic acid forms complexes with many metal ions, no previous description of the cadmium–gluconate system is available. The complexes do not give spectra suitable for study, therefore this investigation is entirely polarographic. As in most supporting electrolytes, cadmium in gluconate solutions gives well-defined, reversible polarograms which are subject to thermodynamic interpretation.

Experimental

The polarographic equipment and methods used have been described previously.[1] The purification and preparation of solutions of gluconic acid and sodium gluconate also have been described.[1] A stock solution of cadmium perchlorate was prepared by dissolving cadmium hydroxide in perchloric acid and standardized electrolytically. Conductivity water was used throughout. The ionic strength was adjusted to

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[1] R. L. Pecsok and R. S. Juvet, Jr., THIS JOURNAL, **77**, 202 (1955).

1.0 with sodium perchlorate or potassium nitrate except where otherwise indicated. Sufficient time was allowed for equilibrium to become established (3-4 hr. at *p*H 10-11). In alkaline solutions, it is necessary to add the sodium gluconate before the sodium hydroxide in order to prevent precipitation. The temperature was maintained at 25.0 ± 0.1° by a water thermostat.

The half-wave potential of cadmium in nitrate or perchlorate media of ionic strength 1.0 was found to be −0.583 v. *vs.* the saturated calomel electrode (used throughout this study). The half-wave potentials were determined graphically on the recorded polarograms, and were reproducible to ±2 mv. The reversibility was tested by measuring the difference, $E_{3/4}$-$E_{1/4}$, which was no more than 2 mv. from the theoretical value of 28 mv. for a 2 electron reduction.[2]

Results and Discussion

The general reaction for the reduction of the cadmium–gluconate complexes at the dropping mercury electrode is assumed to be

$$\text{complex} + x\text{H}^+ + \text{Hg} + 2\text{e}^- = \text{Cd(Hg)} + p\text{GH}_4^- \quad (1)$$

or the equivalent in basic solution

$$\text{complex} + \text{Hg} + 2\text{e}^- = \text{Cd(Hg)} + p\text{GH}_4^- + x\text{OH}^- \quad (2)$$

from which it follows[3] that

$$(E_{1/2})_c - (E_{1/2})_s = 0.0296 \log K(k_s/k_c) - 0.0296(p) \log (\text{GH}_4^-) - 0.0296(x) \log (\text{OH}^-) \quad (3)$$

where K is the dissociation constant of the pertinent complex. The symbols follow those previously described.[1] (GH_4^-) represents the free gluconate ion concentration

$$(\text{GH}_4^-) = (\text{GH}_4^-)_{\text{total}}/[1 + (\text{H}^+)/K_\text{A}]$$

where the subscript "total" indicates the free ion plus the acid and lactones, and K_A is the dissociation constant of gluconic acid, 2.75×10^{-4}.

Several series of solutions were prepared, all containing 2.14×10^{-4} *M* cadmium, at either constant *p*H or constant concentration of gluconate, the other being varied. The discussion of the results can be divided conveniently into regions of *p*H units in which the several species are predominant and the polarographic behavior is similar. Below *p*H 2 no complexing is detectable, and the addition of gluconic acid does not affect the half-wave potential.

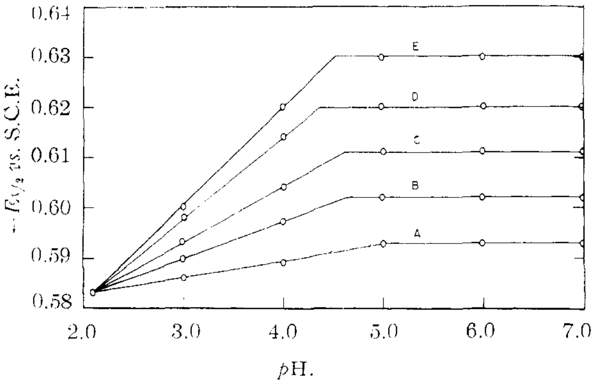

Fig. 1.—Effect of *p*H on the polarographic $E_{1/2}$ potential obtained with solutions 2.14×10^{-4} *M* Cd(II) and various sodium gluconate concentrations at ionic strength 1.0: A, 0.080 *M;* B, 0.200 *M;* C, 0.300 *M;* D, 0.500 *M;* E, 0.700 *M* sodium gluconate.

***p*H 2 to 5.**—The half-wave potentials are plotted *vs.* *p*H (constant concentration of gluconate) in Fig. 1. As the *p*H or gluconate concentration is decreased, the degree of complexing becomes vanishingly small and the half-wave potentials approach that of the aquo-cadmium ion. Furthermore equation 3, in which it is assumed that a large excess of ligand is present, is no longer valid. The calculated values of the dissociation constant for the 1:2 complex (*vide infra*), included in Table I, likewise show deviations from the average value obtained at higher *p*H. There is probably a mixture of a 1:1 and a 1:2 complex present in this *p*H region. However, the change in half-wave potential is too small to warrant exact interpretation.

***p*H 5 to 8.**—Above *p*H 5 the conditions of equation 3 are fulfilled, and it can be seen from Fig. 1 that a definite complex predominates. Since the half-wave potential is independent of *p*H in this region, the reduction does not involve hydrogen ion. For solutions containing more than 0.2 *M* gluconate, the half-wave potential changes by 59 mv. per tenfold change in gluconate concentration and the number of gluconates per cadmium in the complex is 1.8 ± 0.14. Therefore $p = 2$ and $x = 0$ in this region, and the formula of the complex is $\text{Cd(GH}_4)_2$. In Table I are computed values for $pK_{1:2}$ as defined by

$$pK_{1:2} = \frac{(E_{1/2})_c - (E_{1/2})_s}{-0.0296} + \log \frac{(i_d)_s}{(i_d)_c} - 2 \log \frac{(\text{GH}_4^-)_{\text{total}}}{1 + (\text{H}^+)/K_\text{A}} \quad (4)$$

TABLE I

HALF-WAVE POTENTIALS OF THE CADMIUM–GLUCONATE SYSTEM BELOW *p*H 8

*p*H	$(\text{GH}_4^-)_{\text{total}}$, *M*	$(\text{GH}_4^-)_{\text{free}}$, *M*	$-E_{1/2}$, v. *vs.* S.C.E.	$pK_{1:2}$
2.90	0.200	0.036	0.585	2.91
2.90	.500	.090	.596	2.69
2.90	.700	.126	.593	2.33
3.00	.200	.043	.589	2.92
3.00	.300	.064	.593	2.83
3.00	.500	.108	.598	2.49
3.00	.700	.152	.600	2.39
3.40	.200	.082	.592	2.51
4.00	.200	.147	.597	2.25
4.00	.300	.221	.604	2.10
4.00	.500	.368	.614	2.09
4.00	.700	.515	.620	2.04
5.00	.200	.194	.599	2.08
5.00	.300	.290	.610	2.07
5.00	.500	.483	.621	2.12
5.00	.700	.677	.630	2.12
6.00	.200	.200	.599	2.05
6.00	.300	.300	.610	2.06
6.00	.500	.500	.621	2.09
6.00	.700	.700	.630	2.08
6.31	.050	.050	.590	
6.50	.080	.080	.593	
6.83	.100	.100	.597	
7.10	.300	.300	.610	2.06
7.04	.500	.500	.621	2.09
7.00	.700	.700	.530	2.11

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[2] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishing Co., New York, N. Y., 1952.

[3] R. L. Pecsok and R. S. Juvet, Jr., THIS JOURNAL, **78**, 3967 (1956).

The average value of $pK_{1:2}$ is 2.10 with a mean error of ±0.05.

pH 8 to 12.—The half-wave potentials are plotted *vs.* pH (constant gluconate concentration) in Fig. 2, and *vs.* concentration of gluconate (constant pH) in Fig. 3. From the latter, it is seen that the ratio of Cd:G remains constant at 1:2; but from the former, it is apparent that in this region the complex is becoming hydroxylated (or the gluconate bound in the complex is losing hydrogen ions from the secondary hydroxyl groups). Furthermore, solutions in this region required several hours to reach equilibrium, and the data were not exactly reproducible as in the other regions. For these reasons, the nature of the complexes and their constants were not determined.

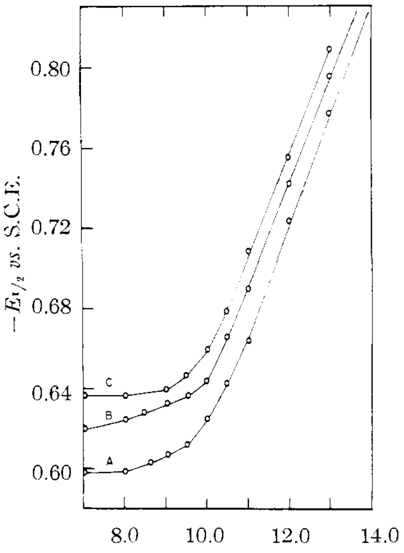

Fig. 2.—Effect of pH (above 8.00) on polarographic $E_{1/2}$ potential obtained with solutions 2.14 × 10^{-4} M Cd(II) and various sodium gluconate concentrations and constant ionic strength 1.0: A, 0.200 M; B, 0.500 M; C, 0.900 M sodium gluconate.

pH 13 to 14.—Solutions of cadmium, sodium gluconate and sodium hydroxide were polarographed. The data indicate that two complexes exist, one in solutions having less than 0.05 M gluconate, and another in solutions having greater than 0.05 M gluconate. Above 0.05 M gluconate, the ratio of Cd:G is 2:3 and the ratio of Cd:OH is 2:5. For calculation of the dissociation constant of this complex, equation 3 becomes

$$pK_{2:3} = \frac{(E_{1/2})_c - (E_{1/2})_s}{0.0296} - \log\frac{(i_d)_s}{(i_d)_c} - 1.5 \log (\mathrm{GH_4^-}) - 2.5 \log (\mathrm{OH^-}) \quad (5)$$

Values of $pK_{2:3}$ are shown in Table II, the average value being 10.25 ± 0.64. This value applies to solutions with an ionic strength of 1.0. A number of solutions were used in which the ionic strength was not adjusted to 1.0, but estimated on the basis of the concentration of the various species present. The maximum deviation in $pK_{2s:3}$ was 0.05 log unit at ionic strength 0.1.

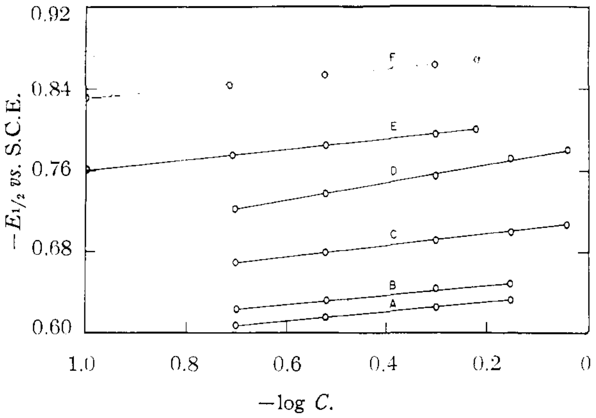

Fig. 3.—Effect of total sodium gluconate concentration on polarographic $E_{1/2}$ potential obtained with solutions 2.14 × 10^{-4} M Cd(II) and various pH at constant ionic strength 1.0: A, pH 9.00; B, pH 10.00; C, pH 11.00; D, pH 12.00: E, pH 13.00; F, 0.90 M sodium hydroxide.

TABLE II

HALF-WAVE POTENTIALS OF THE CADMIUM–GLUCONATE SYSTEM ABOVE pH 8

($NaGH_4$), M	($NaGH_4$), M	(NaOH), S.C.E.	$-E_{1/2}$, v. *vs.* $pK_{2:1}$	$pK_{2:3}$
0.010	0.500	0.786	8.70	
.010	0.700	.797	8.70	
.010	1.00	.807	8.67	
.020	0.500	.790	8.72	
.020	0.700	.800	8.67	
.020	1.00	.814	8.75	
.030	0.500	.794	8.80	
.030	0.700	.802	8.64	
.030	1.00	.814	8.66	
.050	1.00	.818	8.70	
.050	0.100	.748		10.48
.050	.200	.772		10.43
.050	.300	.784		10.27
.050	.500	.798		10.16
.050	.700	.808		10.07
.100	.100	.763		10.29
.100	.200	.784		10.37
.100	.300	.799		10.29
.100	.500	.812		10.24
.100	1.00	.830		
.200	0.100	.777		10.19
.200	.200	.800		10.27
.200	.300	.812		10.23
.200	.500	.827		10.17
.200	.700	.836		10.15
.400	.100	.792		10.20
.400	.200	.813		10.17
.400	.300	.826		10.25
.400	0.500	.841		10.20
.400	1.00	.859		10.22
.800	0.010	.733		10.209
.900	0.100	.815		10.40
	1.00	No red.		
	2.00	0.85		
	3.00	.86		
.10	1.00	.84		
.10	2.00	.85		
.10	3.00	.86		

Below 0.05 *M* gluconate, the coefficient of the log (GH_4^-) term in equation 5 must be changed from 1.5 to 0.5. The values of $pK_{2:1}$ are also listed in Table II with an average value of 8.70 ± 0.05.

Solutions Containing More than 1 *M* Sodium Hydroxide.—In 3 *M* sodium hydroxide, the half-wave potential of cadmium is independent of gluconate concentration over a wide range: 0.01 to 1.0 *M* gluconate. A small wave is apparent in 1 to 3 *M* sodium hydroxide even in the absence of gluconate, although precipitates are present. Increasing the gluconate concentration decreases the amount of precipitate and increases the height of the wave, but does not change the half-wave potential, which becomes constant at a value of −0.86 v. in 3 *M* sodium hydroxide. These results indicate that cadmium forms a slightly soluble hydroxy complex (cadmiate) in high concentrations of hydroxide ion. No definite species can be identified in this region.

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