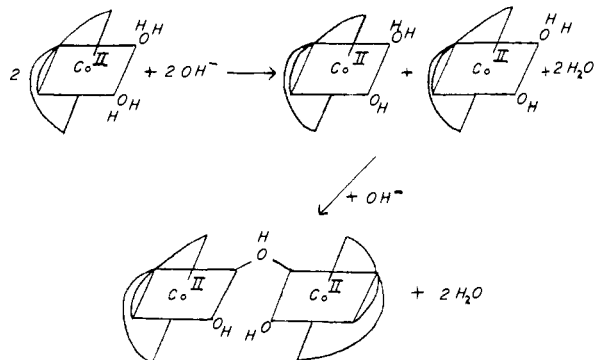
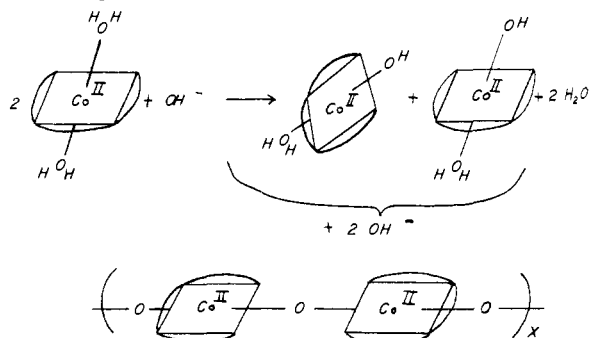


5. Stereochemistry of the Complexes.—The above data permit certain conclusions about the stereochemistry of these complexes.

It is well known that tren imposes certain stereochemical restrictions on the configuration of its complexes. Because of its tertiary amino group, tren can only coordinate in an octahedron in such a way that the coordinating groups are *cis* to each other. In the presence of hydroxide ions the following reaction presumably takes place when there are 3/2 hydroxide ions per cobalt complex.



For the trien complex, on the other hand, the trien can coordinate in such a way that the two solvated positions are either *cis* or *trans*. However, of these, the *trans* complex is the one more stable in solution. For the trien hydroxy complexes the following reaction then seems likely.



Such structural considerations also explain why $[\text{Cotren}(\text{OH})_{1/2}]_2$ should decompose H_2O_2 catalyti-

cally, whereas $(-\text{O}-\text{Cotrien}-\text{O}-)_2$ should not. The mechanism for H_2O_2 decomposition should be similar to that proposed by Wang¹² for the $[\text{Fe}(\text{III})\text{trien}(\text{OH})_2]^+$ complex, but in the cobalt amine binuclear complex the decomposition of the peroxide ions should occur through hydroxide groups *cis* to each other.

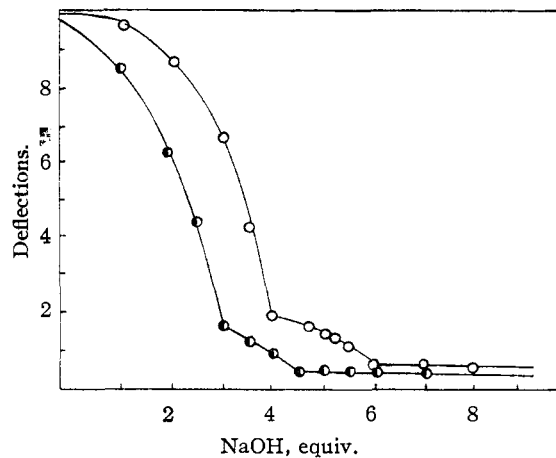


Fig. 4.—Magnetic titration of $\text{CoCl}_2 + \text{trien} \cdot 4\text{HCl}$ and $\text{CoCl}_2 + \text{tren} \cdot 3\text{HCl}$ with NaOH : O, $\text{CoCl}_2 + \text{trien} \cdot 4\text{HCl}$; ●, $\text{CoCl}_2 + \text{tren} \cdot 3\text{HCl}$.

The trien hydroxy complex on the other hand should only become oxidized since it contains no *cis* hydroxide groups in the complex. The experimental results show indeed that $[\text{Cotren}(\text{OH})_{1/2}]_2$ decomposes H_2O_2 catalytically whereas the $[\text{Cotrienhydroxy}]$ complex becomes oxidized.

Experiments are under way to determine the kinetics of this decomposition of hydrogen peroxide and to find out whether such a binuclear species is present with other metals and ligands.

Acknowledgment.—Financial support for this and continuing investigations by the Office of Ordnance Research, U. S. Army, is gratefully acknowledged.

NEW ORLEANS 18, LOUISIANA

(12) J. H. Wang, *THIS JOURNAL*, **77**, 4716 (1955).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

A Polarographic Study of Thiourea Complexes of Cadmium and Lead in Aqueous Media

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Polarographic studies of coordination complexes of thiourea with cadmium(II) ion and lead(II) ion in aqueous solution have been carried out using 0.1 *M* potassium nitrate as supporting electrolyte and Triton X-100 as maximum suppressor. Application to the data of the Hume and DeFord method of mathematical analysis showed the existence of mono-, bis-, tris- and tetrakis-coordinated species for cadmium(II) and lead(II) complexes. Their formation constants also were calculated. These results do not agree with those obtained by other workers.

Federova² reported the results of polarographic studies of thiourea complexes of cadmium(II) and

lead(II) in aqueous solution by varying the concentration of excess ligand from 0.2 to 0.8 *M* and obtaining results indicating the presence of tris-thiourecadmium(II) ion and tris-thiourealead(II) ion. His calculations of formation constants for the respective species were made according to the

(1) (a) Carroll College, Helena, Montana. (b) Xavier Jr. College, Sydney, N.S., Canada.

(2) O. S. Federova, *Sbornik Statei Obshchei Khim. Akad. Nauk S.S.S.R.*, **1**, 206 (1953).

mathematical treatment of Heyrovsky and Ilkovic.³ In this paper the Hume and DeFord⁴ method for determination of consecutive formation constants showed the existence of mono-, bis-, tris- and tetrakis-species of cadmium(II) ions and lead(II) ions in aqueous media.

Experimental

Materials and Solutions.—Reagent-grade cadmium nitrate, lead nitrate and thiourea were used without further purification. Triton X-100, Rohm and Haas Company, Philadelphia, was used as maximum suppressor. Lamp Nitrogen, General Electric Company, was used for deaeration.

For each of the metal ions a series of solutions was prepared from standard stock solutions, each containing 0.001 *M* metal ion, 0.1 *M* potassium nitrate, 0.004% Triton and thiourea in concentrations varying from 0.05 to 1.0 *M*. A similar series of solutions was prepared in which bis-thiourecadmium(II) chloride—prepared according to the method of Rosenheim and Meyer⁵—was substituted for cadmium nitrate.

Apparatus.—Current-voltage measurements were made with a Sargent Recording Polarograph, Model XXI. Sargent tubing (S-29419) was used for the capillary, which had a value of 1.97 for $m^3/t^{1/2}$ at the potential of the S.C.E. An "H" cell was employed with the solution to be examined in one arm and saturated calomel in the other arm. The two arms of the "H" cell were separated by a sintered glass disk and an agar plug 1 *M* with respect to potassium nitrate. The temperature of the cell was maintained at 25 ($\pm 0.1^\circ$), and voltage measurements were checked with an outside potentiometer (Rubicon).

Treatment of Data.—The potential measurements made along each current-voltage curve were tabulated. The current values (*i*) at these potentials and the limiting current were measured. From these data a graph of $E_{d.s.}$ versus $\log(i_d - i)/i$ was drawn for each current-voltage curve. The values obtained from the graphs for 0.0591/*n* and $E_{1/2}$ were tabulated. Thus, a series of ($E_{1/2}$)₀ values, corresponding to the various concentrations of ligand, were obtained for each thiourea-metal complex.

In a second set of graphs, values of ($E_{1/2}$)₀ were plotted against values for $\log C_x$, where C_x is the molar concentrations of ligand. From the slopes of the lines in these graphs the coordination numbers, *p*, were calculated. Since these plots indicated that the value of *p* changed with increasing concentrations of ligand, the method of DeFord and Hume⁴ was used to obtain the formation constants.

Reliability of Data.—The $E_{1/2}$ values were not corrected for *iR*-drop across the cell. The error encountered here was generally less than 1.0 mv. The presence of liquid junction potentials of unknown magnitude at the saturated potassium chloride -1.0 *M* potassium nitrate interface and at the 1.0 *M* potassium nitrate -0.1 *M* potassium nitrate interface also was neglected. But, since the errors incurred by neglecting liquid junction potentials are approximately the same for each $E_{1/2}$ determination, the net error should approximate zero when the difference between the ($E_{1/2}$)₀ and the ($E_{1/2}$)₀ values is taken. In any given experiment the half-wave potential resulting from a graph of $E_{d.s.}$ vs. $\log(i_d - i)/i$ could be estimated to 0.5 mv.

The errors in diffusion current values due to probable concentration values may be of the order of $\pm 2\%$. DeFord and Hume⁴ have ascribed errors of $\pm 4\%$, $\pm 5\%$, $\pm 80\%$ and $\pm 15\%$ to determinations of K_1 , K_2 , K_3 and K_4 , respectively, in their work with the thiocyanate complexes. Since the methods employed in this investigation of the thiourea complexes are similar to those employed by those authors, it is reasonable to assume that the possible errors incurred in this study are of the same order of magnitude.

Results and Discussion

The experimental data for the individual polarographic measurements are given in Tables I and

(3) J. Heyrovsky and D. Ilkovic, *Coll. Czech. Chem. Comm.*, **7**, 198 (1935).

(4) D. D. DeFord and D. N. Hume, *This Journal*, **73**, 5321 (1951).

(5) A. Rosenheim and V. J. Meyer, *Z. anorg. Chem.*, **49**, 13 (1906).

II. The data in Table I were obtained using a solution of 0.001 *M* cadmium nitrate. Similar results were obtained when 0.001 *M* bis-thiourea cadmium(II) chloride was used instead of cadmium nitrate.

TABLE I

Molarity of ligand	$-E_{1/2}$ (v.)	i_d (μ a.)	$F_0(X)$	$F_1(X)$	$F_2(X)$	$F_3(X)$	$F_4(X)$
0.0000	0.579	8.76	1.00
.050	.590	8.52	2.39	27.7	74
.100	.598	8.40	4.66	36.6	126
.150	.608	8.16	10.5	63.0	260
.200	.615	8.16	16.8	79.1	275
.250	.623	8.12	32.2	125	404
.300	.629	8.12	50.7	166	472
.400	.640	7.96	128	317	731
.500	.649	7.88	253	504	960	1818	3636
.600	.657	7.88	492	818	1324	2122	3537
.700	.665	7.84	908	1296	1817	2523	3504
.800	.673	7.80	1638	2046	2528	3096	3870
.900	.678	7.72	2445	2716	2991	3267	3630
1.000	.683	7.64	3620	3619	3595	3544	3544

TABLE II

Molarity of ligand	$-E_{1/2}$ (v.)	i_d (μ a.)	$F_0(X)$	$F_1(X)$	$F_2(X)$	$F_3(X)$	$F_4(X)$	$F_5(X)$
0.000	0.388	9.48	1.00
.050	.389	9.72	1.09	0.18	3.52
.100	.392	9.64	1.39	3.85	38.5
.150	.392	9.40	1.41	2.73	18.2
.200	.394	9.12	1.63	3.17	15.8
.250	.398	9.28	2.19	4.77	19.1
.300	.401	8.92	2.86	6.19	20.6	32	107	..
.400	.409	8.40	5.89	12.2	30.6	49	123	..
.500	.416	8.16	10.4	18.8	37.5	53	106	..
.600	.423	7.96	18.8	29.6	49.4	64	107	..
.700	.429	7.80	29.4	40.6	58.0	67	96	..
.800	.437	7.68	57.5	70.6	88.3	96	120	..
.900	.442	7.48	83.3	91.4	102	101	112	..
1.000	.447	7.48	125	124	124	113	113	..

A plot of the half-wave potentials (Table I) versus $\log C_x$ (concentrations of excess ligand) is given in Fig. 1. The slopes of the various parts of the line in Fig. 1 indicate the presence of thiourea complexes varying from the mono-species at low concentrations of ligand, to the tetrakis-form at higher concentrations.

Table I gives the values for the DeFord-Hume functions $F_0(X)$, $F_1(X)$, $F_2(X)$, $F_3(X)$ and $F_4(X)$. These $F_j(X)$ values are plotted against C_x in Figs. 2 and 3.

The formation constants for the lead(II) complexes of thiourea were determined in the same manner as those for the cadmium(II) complexes. The data from the polarographic curves are given in Table II. A plot of the half-wave potentials versus $\log C_x$ is given in Fig. 4 and those of the DeFord-Hume functions in Figs. 5 and 6.

Discussion

The slopes of the graph in Fig. 1 indicate the presence of mono-, bis-, tris- and tetrakis-thiourea cadmium(II) complexes in varying concentrations of ligand. In a previous work on these complexes, Federova² reported a K_3 value of 833. The

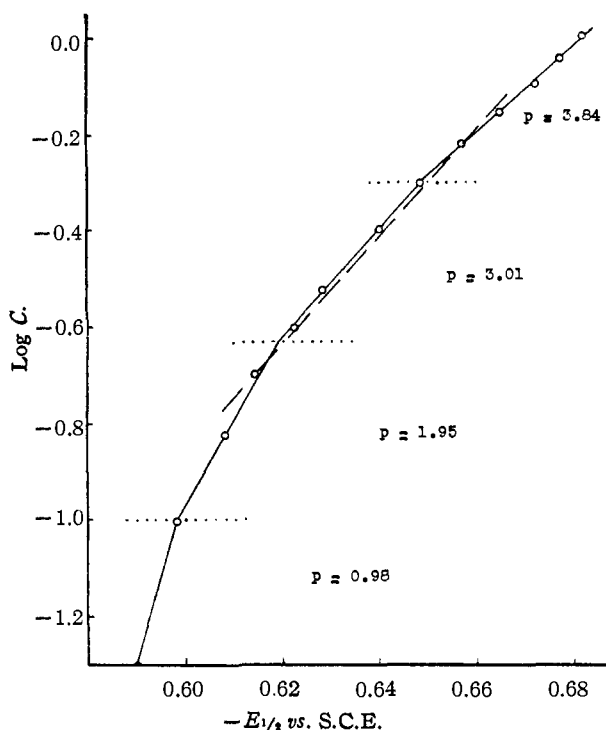


Fig. 1.—Polarographic data for 0.05–1.0 *M* ligand concentration with 0.001 *M* $\text{Cd}(\text{NO}_3)_2$.

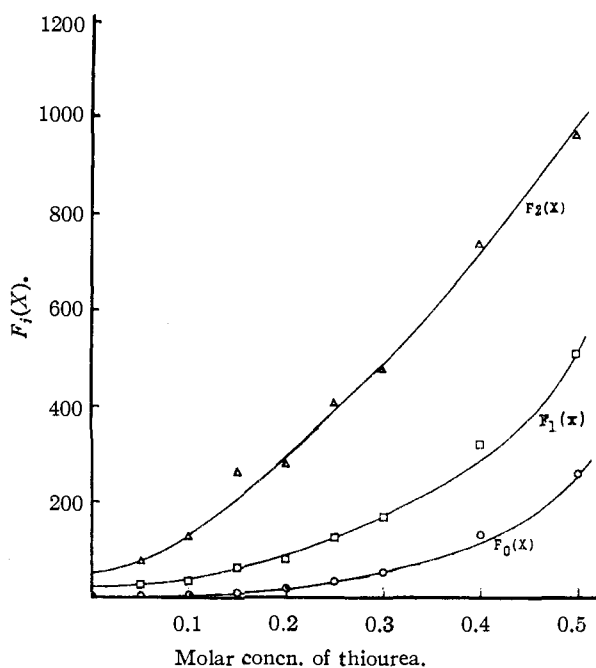


Fig. 2.—DeFord-Hume function vs. molar concentration of thiourea in 0.001 *M* $\text{Cd}(\text{NO}_3)_2$.

broken line in Fig. 1 has a slope which corresponds to a coordination number of 3 and the calculation of the formation constant by using $E_{1/2}$ values obtained in this work for solutions between 0.2 and 0.8 *M* with respect to thiourea gives a K_3 value in fair agreement with that of Federova.² Application of the DeFord and Hume⁴ method shows the presence of mono-, bis-, tris- and tetrakis-coordi-

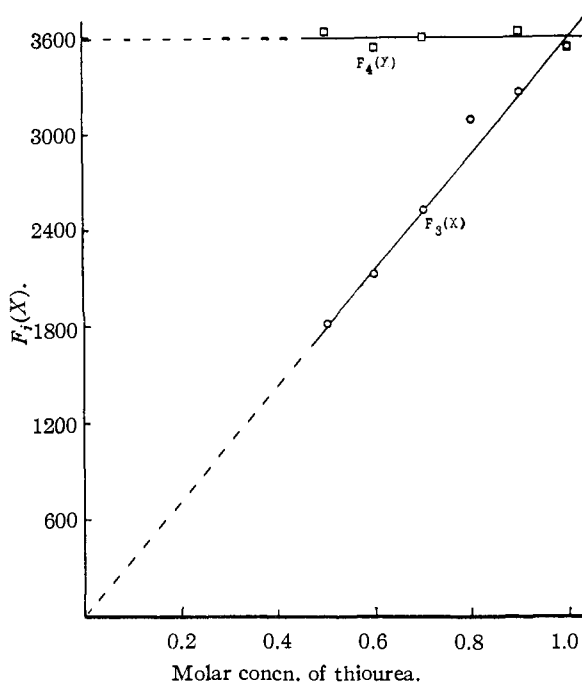


Fig. 3.—DeFord-Hume function vs. molar concentration of thiourea in 0.001 *M* $\text{Cd}(\text{NO}_3)_2$.

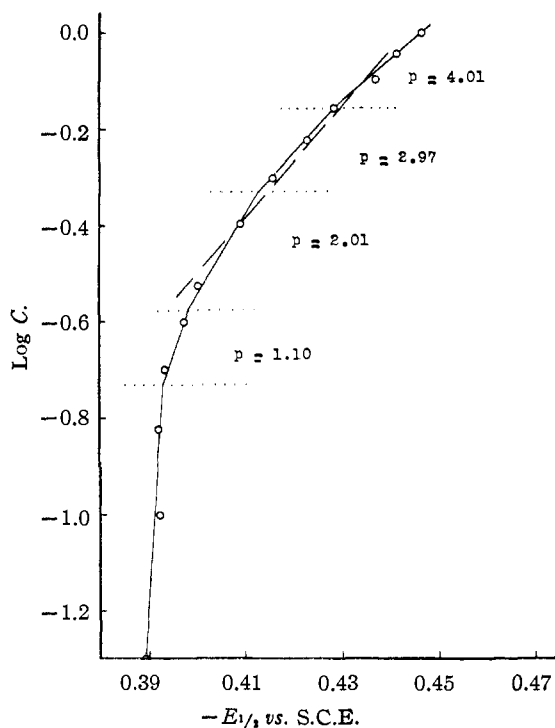


Fig. 4.—Polarographic data for 0.05–1.0 *M* ligand concentration with 0.001 *M* $\text{Pb}(\text{NO}_3)_2$.

nated species, with formation constants of 24 (± 1), 51 (± 3), 40 (± 32) and 3590 (± 540), indicating that this K_3 value has little significance. The portion of the curve (Fig. 1) which has a slope corresponding to a coordination number of 3 is probably due to an overlap of the bis- and the tetrakis-forms.

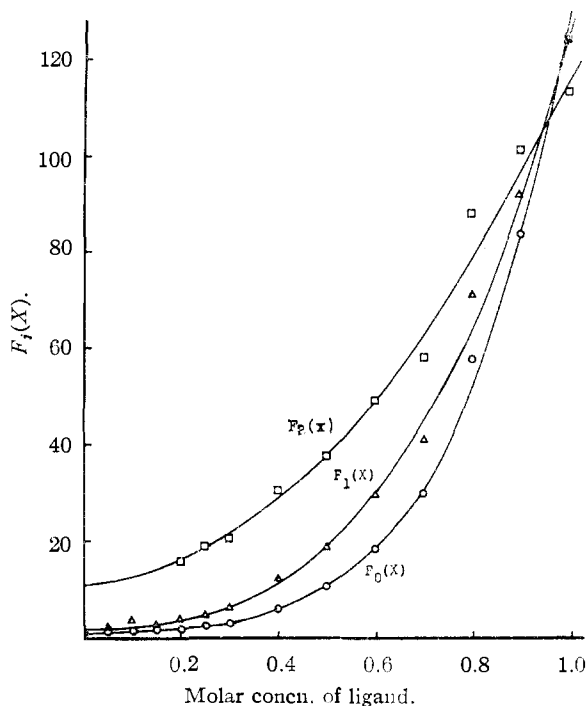


Fig. 5.—DeFord-Huene function *vs.* molar concentration of thiourea in 0.001 *M* $\text{Pb}(\text{NO}_3)_2$.

The graph of the $F_j(X)$ function *versus* concentration of ligand (Fig. 3) is a straight line with a slope of zero, indicating that thiourea, within the range of concentrations up to 1.0 molar, does not form any more highly coordinated complexes with cadmium(II) than the tetrakis-species.

The broken line, Fig. 4, has a slope which corresponds to a coordination number of 3 for the lead(II) ion. As in the case of the cadmium complexes, the formation constant, K_3 , was calculated by the Heyrovsky and Ilkovic method from data in this work and found to be 76.9, which is in good agreement with the value reported by Federova,² but, as shown above, appears to have no significance. Application of the DeFord and Huene⁷ method shows the contributing species to be the mono-, bis-, tris- and tetrakis-thiourea lead(II) ions with formation constants of 4 (± 0.08), 11 (± 0.6), 9.5 (± 7.6) and 110 (± 16), respectively. Again, the apparent presence of the tris-species as is indicated in Fig. 4 is probably due to an overlap of the bis- and tetrakis-forms.

The values of $F_3(X)$ for the cadmium(II) and the lead(II) complexes of thiourea were calculated,

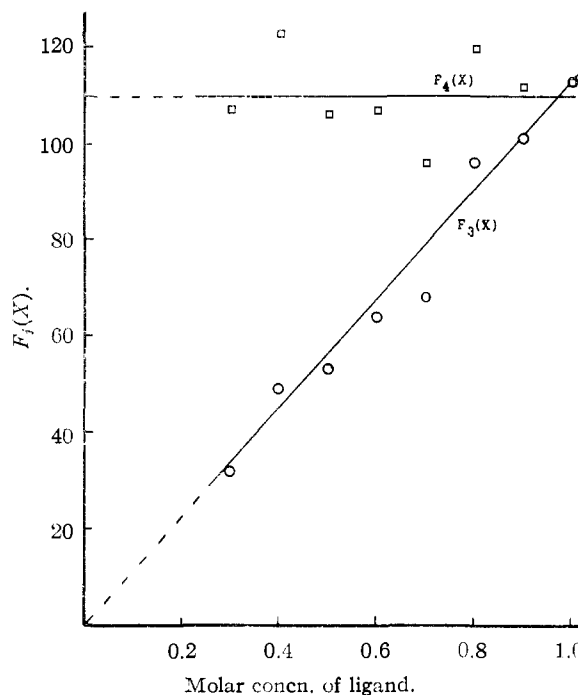


Fig. 6.—DeFord-Huene function *vs.* molar concentration of thiourea in 0.001 *M* $\text{Pb}(\text{NO}_3)_2$.

giving points approximating a straight line which if extrapolated would give K_3 values equal to zero. Since this extrapolation is uncertain, values of the limiting slopes of $F_2(X)$ were estimated to be 40 for the cadmium complex and 9.5 for the lead complex, giving K_3 values between 0 and 40, and 0 and 9.5, for the respective complexes. These values are in good agreement with K_3 values derived by assigning upper limits to $F_3(X)$ intercepts, Figs. 3 and 6.

The stability constants presented herein are not true thermodynamic values. In each case the activity coefficients were assumed to be unity. If, however, at some future date activity coefficient data for these ions become available, then the true thermodynamic constants could be readily calculated.

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