Fig. 1.—Half-wave potential shift for cadmium(II) complexes of pyrazole *vs.* log of pyrazole concentration.

TABLE I

POLAROGRAPHIC RESULTS AT 25° FOR SOLUTIONS CONTAINING 5×10^{-4} M Cd(NO$_3$)$_2$ AND 0.10 M KNO$_3$

$-\log$ [Py]	Slope log $[(i_d/i) - 1]$ $vs.$ $E_{1/2}$	$-E_{1/2}$ $vs.$ s.c.e.	$\log K_{st}$
1.226	0.034	0.580	1.52
1.100	.032	.582	1.49
1.002	.031	.585	1.49
0.874	.033	.589	1.48
.701	.033	.594	2.23
.588	.031	.600	2.19
.524	.031	.603	2.17
.302	.032	.615	2.14
.156	.033	.624	2.37
− .008	.032	.638	2.32
− .155	.032	.648	2.32
− .300	.033	.661	2.26

TABLE II

THERMODYNAMIC RESULTS FOR CADMIUM(II)–PYRAZOLE COMPLEXES

Reaction	Temp., °C.	p	$\log K_{st}$	$-\Delta G°$, kcal./mole	$-\Delta H°$, kcal./mole
Cd^{++} + Py = CdPy^{++}	0	1.1	1.76	2.20	
	25	0.94	1.50	2.04	3.94
	45	0.96	1.28	1.86	
Cd^{++} + 2Py = CdPy$_2^{++}$	0	2.0	2.73	3.41	
	25	1.8	2.18	2.97	8.10
	45	1.8	1.80	2.62	
Cd^{++} + 3Py = CdPy$_3^{++}$	0	3.1	3.21	4.01	
	25	2.8	2.32	3.17	12.14
	45	2.9	1.83	2.66	
Cd^{++} + 4Py = CdPy$_4^{++}$		No formation observed			

rents of the complex and simple metal ions shown by

$$(i_d)_c/(i_d)_s = (D_c/D_s)^{1/2} = k_c/k_s \tag{3}$$

which is obtained from the ratio of the Ilkovic equation[5] for the complex and simple metal ions. As a complex ion becomes increasingly bulky its rate of diffusion decreases. The k_c/k_s ratios for CdPy^{++}, CdPy$_2^{++}$, and CdPy$_3^{++}$ at 25° are 1.0, 0.94, and 0.83, respectively. A half-wave potential of -0.571 volt was observed for simple cadmium ion at 25° in the system described for this investigation.

The results obtained at 25° are typical of those obtained at all temperatures and are presented in Table I and Fig. 1. It is observed that the plot of $E_{1/2}$ *vs.* log [Py] is composed of three straight lines. The 1:1 complex of cadmium(II) with pyrazole predominates up to a pyrazole concentration of 0.13 M. Between 0.20 and 0.50 M the predominant species is the 1:2 complex. The highest ordered complex found, namely 1:3, exists above 0.70 M. The experimental values of p in these three areas are 0.94, 1.8, and 2.8, respectively. Similar results were found at 0 and 45° and are summarized in Table II. Included in Table II are the thermodynamic quantities, $\Delta G°$ and $\Delta H°$, which were derived from the logarithms of the stability constants in the usual manner.

Cadmium(II) usually presents a coordination number of four for monodentate groups and as high as six for polydentate groups.[6] Since pyrazole is monodentate, one might logically expect that the highest ordered complex would be 1:4. However, in view of the low

basic strength of the ligand it would seem reasonable that the steric resistance to the addition of a fourth pyrazole molecule could not be overcome. Pyrazole concentrations as high as 2.0 M produced no evidence of a 1:4 complex.

CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS

Some Mono-n-alkylamino Derivatives of Hexachlorotriphosphonitrile

BY THERALD MOELLER AND SIGRED LANOUX

The synthesis of monosubstituted pentachlorotriphosphonitriles has been of interest since de Fiquelmont[1] obtained the monoamido derivative by heating tetrachlorodiamidotriphosphonitrile with hydrogen chlo-

(5) D. Ilkovic, *Coll. Czech. Chem. Commun.*, **6**, 498 (1934).

(6) B. E. Douglas, H. A. Laitinen, and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **72**, 2484 (1950).

(1) A. M. de Fiquelmont, *Ann. Chim.*, **12**, 169 (1939).

TABLE I
Properties of Pentachloroaminotriphosphonitriles

Compound	Yield, %	M.p., °C	B.p., °C. (mm.)	$n^{25}D$	Sp. gr.	P–N frequency, cm.$^{-1}$	Mol. wt.^{a}	C	H	N	P	Cl
$N_3P_3Cl_5NHCH_3$	10	69				1210, 1225	342	3.50	1.18	16.37	27.15	51.79
							333	3.63	1.21	16.74	27.48	51.85
$N_3P_3Cl_5NHCH_2CH_3$	23		105 (0.05)	1.5414	1.065 (29°)	1213	356	6.73	1.70	15.72	26.07	49.74
							346	6.36	1.65	15.78	26.40	49.59
$N_3P_3Cl_5NH(CH_2)_2CH_3$	53		137 (1.75)	1.5362	1.58 (30°)	1208, 1220, 1226	370	9.71	2.16	15.10	25.22	47.55
							384	9.79	2.30	15.30	24.99	47.50
$N_3P_3Cl_5NH(CH_2)_3CH_3$	56		110 (0.05)	1.5312	1.54 (28°)	1205, 1222	384	12.49	2.62	14.84	24.18	46.12
							383	12.49	2.65	14.31	24.61	45.96
$N_3P_3Cl_5NH(CH_2)_4CH_3$	37		115 (.05)	1.5265	1.51 (27°)	1208, 1220	398	15.07	3.04	14.06	23.32	44.50
							383	14.81	3.00	14.28	23.22	44.57
$N_3P_3Cl_5N(CH_3)_2$	41		85 (.05)	1.5377	1.63 (28°)	1203, 1217	356	6.74	1.70	15.72	26.08	49.76
							356	7.14	1.65	15.85	26.29	49.23
$N_3P_3Cl_5N(CH_2CH_3)_2$	6		97–100 (.05)	1.5287	1.54 (26°)	1200, 1210, 1220	384	12.49	2.62	14.58	24.18	46.12
							384	12.31	2.51	14.32	24.83	46.94
$N_3P_3Cl_5N[(CH_2)_2CH_3]_2$	2.2		112 (.01)	1.5218	1.47 (29°)	1210, 1220	412	17.37	3.43	13.58	22.53	42.98
							425	16.90	3.29	13.23	20.91	43.41
$N_3P_3Cl_5N[(CH_2)_3CH_3]_2$	1		130–131 (.01)	1.5148	1.36 (29°)	1205, 1218	440	21.81	4.12	12.72	21.10	40.25
							454	21.32	4.62	12.39	19.91	40.73

^{a} First line calculated; second line found.

ride at 180°. Kropacheva and co-workers[2,3] reported the preparation of corresponding pentachloro ethylenimino, piperidino, ethylglycino, and methyl-β-alanino compounds but gave neither details nor analytical data. More recently Ray and Shaw[4] prepared the dimethylamino and diethylamino compounds in excellent yields by direct aminolysis in diethyl ether. These data all suggest that aminolysis of hexachlorotriphosphonitrile is a stepwise process[5] and that the di-, tri-, tetra-, and hexasubstituted products usually obtained[4,6–9] are the result of careful control of stoichiometry or other reaction conditions.

This suggestion is supported, in the present investigation, by the ready synthesis of mono-n-alkylamino derivatives by the direct reaction of hexachlorotriphosphonitrile with the amine or its hydrochloride in a 1:2 mole ratio in a diethyl ether–water system. For water soluble, nonvolatile amines, the procedure involves the direct addition of an aqueous solution of the amine to an ether solution of the triphosphonitrile and results in yields of 37–56%. For water-insoluble amines, dropwise addition of an ether solution of the amine to a heterogeneous mixture of water and an ether solution of the triphosphonitrile gives the products but only in 1–2% yield. For volatile amines, treatment of a mixture of an aqueous solution of the amine hydrochloride and an ether solution of the triphosphonitrile with 1 N sodium hydroxide near 0° gives the products in 6–23% yield. Unavoidable loss of amine reduces the yield in each case.

(2) A. A. Kropacheva, L. E. Mukhina, N. M. Kashnikova, and V. A. Parshina, *Zh. Obshch. Khim.*, **31**, 1036 (1961).

(3) A. A. Kropacheva and L. E. Mukhina, *ibid.*, **31**, 2437 (1961).

(4) S. K. Ray and R. A. Shaw, *J. Chem. Soc.*, 872 (1961).

(5) T. Moeller and S. Lanoux, *J. Inorg. Nucl. Chem.*, **25**, 229 (1963).

(6) L. F. Audrieth, *Rec. Chem. Progr.*, **20**, 57 (1959).

(7) M. Becke-Goehring, K. John, and E. Fluck, *Z. anorg. allgem. Chem.*, **302**, 103 (1959).

(8) R. A. Shaw, B. W. Fitzsimmons, and B. C. Smith, *Chem. Rev.*, **62**, 247 (1962).

(9) S. G. Kokalis, K. John, T. Moeller, and L. F. Audrieth, *J. Inorg. Nucl. Chem.*, **19**, 191 (1961).

Data relating to the synthesis and properties of the pentachloro-n-alkylaminotriphosphonitriles are summarized in Table I. Monosubstitution has little effect upon the P–N stretching frequency of hexachlorotriphosphonitrile, as may be expected.[9] All of the compounds except the dimethylamino derivative undergo decomposition on standing for a month. Several are particularly irritating to the skin and eyes. Caution in handling them is advised. Only typical syntheses are described.

Experimental

Measurements.—Infrared spectra were measured with a Perkin–Elmer Model 21 instrument with sodium chloride optics, using 1% solutions in carbon tetrachloride. The specific gravity pipet was calibrated against purified water and benzene.

Materials.—Hexachlorotriphosphonitrile, obtained from Hooker Chemical Co., was purified by sublimation under vacuum. It melted at 112°. The amines were either Eastman White Label products that were used without further purification or substances that had previously been repeatedly distilled.

Pentachloromethylaminotriphosphonitrile.—Sodium hydroxide (300 ml. of 1 N) was added over a 3-hr. period to a vigorously stirred two-phase mixture containing 21.4 g. (0.32 mole) of methylamine hydrochloride dissolved in 150 ml. of water and 50 g. (0.14 mole) of hexachlorotriphosphonitrile dissolved in 400 ml. of diethyl ether. The reaction vessel was maintained below 10° during reaction and then allowed to warm to room temperature. The ether layer was removed and dried over calcium chloride. Evaporation gave a mixture of product and unreacted hexachlorotriphosphonitrile. The former was removed by sublimation.

Modifications of this procedure gave the ethylamino and dimethylamino derivatives.

Pentachloro-n-propylaminotriphosphonitrile.—An aqueous solution of 20 g. (0.34 mole) of n-propylamine was added to 200 ml. of a solution of 50 g. (0.14 mole) of hexachlorotriphosphonitrile over a 2-hr. period and with vigorous stirring. The ether layer was removed and dried over calcium chloride. Evaporation of the ether left an oily residue, which was converted to the pure product by fractional distillation at *ca.* 5 mm. pressure.

Modifications of this procedure gave the n-butylamino, n-amylamino, and diethylamino derivatives.

Pentachlorodi-n-propylaminotriphosphonitrile.—One hundred

ml. of a solution of 30.3 g. (0.30 mole) of d-*n*-propylamine in diethyl ether was added over a period of 11 hr. to 400 ml. of a vigorously stirred ether solution of 50 g. (0.14 mole) of hexachloro-triphosphonitrile. The oil obtained after drying the solution over calcium chloride, evaporating, and removing the unreacted hexachloro compound was purified by fractional distillation at 0.01 mm. pressure.

The di-*n*-butylamino derivative was prepared similarly.

Contribution from the Department of Chemistry
and the Laboratory for Nuclear Science of the
Massachusetts Institute of Technology,
Cambridge 39, Massachusetts

The Formation Constants of Copper, Cadmium, and Zinc Fluoride Complexes

By Štefica S. Mesarić and David N. Hume

A number of previous workers[1-3] using a variety of methods have found evidence for weak complex formation between fluoride and copper(II), cadmium, and zinc ions in aqueous solution. Indications of weak complex formation with these metal ions were also observed in the course of a survey of the polarographic behavior of a number of cations in fluoride-containing supporting electrolytes, and because of the particular applicability of the polarographic method[4] to weakly complexing systems, we have undertaken to examine several of them in some detail.

Experimental

The general technique utilized was that used in previous investigations.[5] The particular modifications necessary for the application to fluoride media (plastic apparatus, Tygon coated capillary, etc.) have been described.[6] The capillary employed had an $m^{2/3}t^{1/6}$ value of 1.67 mg.$^{2/3}$ sec.$^{1/6}$. Measurements were carried out at constant ionic strength (1.0 M for copper and 2.0 M for cadmium and zinc) in mixtures of sodium perchlorate and sodium fluoride. The pH was maintained at 5.0 ± 0.2 and the temperature at 25 ± 0.1°. The reduction waves of millimolar copper, zinc, and cadmium in both the sodium perchlorate and sodium perchlorate–sodium fluoride mixtures were well defined and showed good linearity with slopes close to the theoretical value when log $[(i_d - i)/i]$ was plotted against E. Addition of a maximum suppressor was found to be unnecessary.

(1) I. Leden, Dissertation, Lund, 1943.
(2) S. Ahrland and K. Rosengren, *Acta Chem. Scand.*, **10**, 727 (1956).
(3) (a) R. E. Connick and A. D. Paul, *J. Am. Chem. Soc.*, **80**, 2069 (1958); (b) A. D. Paul, Thesis, University of California, Berkeley, 1955 (UCRL 2926).
(4) D. D. DeFord and D. N. Hume, *J. Am. Chem. Soc.*, **73**, 5321 (1951).
(5) D. N. Hume, D. D. DeFord, and G. C. B. Cave, *ibid.*, **73**, 5232 (1951).
(6) Š. S. Mesarić and D. N. Hume, *Inorg. Chem.*, **2**, 788 (1963).

Results

The results are summarized in Tables I–III. The conventional plot of $F_0(X)$ in each instance was linear, indicating the presence only of the free metal ion and the monofluoro complex. The value of β_1 for the forma-

Table I
ANALYSIS OF $E_{1/2}$ DATA FOR COPPER IN FLUORIDE MEDIUM

(F⁻), M	$E_{1/2}$ *vs.* s.c.e.	$F_0(X)$
0.00	+0.021	1.00
.01	.020	1.08
.05	.017	1.37
.10	.012	2.01
.20	.012	2.18
.30	.007	2.99
.40	.004	3.76
.80	.001	5.98

Table II
ANALYSIS OF $E_{1/2}$ DATA FOR CADMIUM IN FLUORIDE MEDIUM

(F⁻), M	$E_{1/2}$ *vs.* s.c.e.	$F_0(X)$
0.00	−0.559	(1.000)
.05	− .563	1.37
.10	− .566	1.72
.15	− .568	2.01
.20	− .569	2.19
.30	− .573	2.97
.50	− .575	3.48
.60	− .577	4.06

Table III
ANALYSIS OF $E_{1/2}$ OF ZINC IN FLUORIDE MEDIUM

(F⁻), M	$E_{1/2}$ *vs.* s.c.e.	$F_0(X)$
0.00	−0.999	(1.00)
.05	−1.003	1.37
.10	−1.006	1.72
.15	−1.008	2.01
.20	−1.011	2.54
.25	−1.012	2.75
.30	−1.014	3.21
.50	−1.018	4.40
.60	−1.020	5.11

tion (stability) constant of the MF⁺ species in each system was estimated from the limiting slope of the $F_0(X)$ plot. The limiting slopes hold well in the range 0–0.3 M fluoride and it is not necessary to rely on data taken at higher concentrations where the ionic environment is appreciably changed from that of pure sodium perchlorate solutions. The precision of the measurements leads to an uncertainty of about ±0.5 in each constant. All three metals show complexes of about

Table IV
COMPARISON OF REPORTED β_1 VALUES

Author	Copper	Zinc	Cadmium
Ahrland–Rosengren[a]	9 ± 1	5.9 ± 0.6	...
Connick–Paul[b]	5.0 ± 1	5.4 ± 1	...
Leden[c]	...	...	2.9
This paper	6.8 ± 0.5	7.0 ± 0.5	6.4 ± 0.5

[a] Potentiometric: quinhydrone, 1 M NaClO₄. [b] Potentiometric: Fe(III)/Fe(II), 0.5 M NaClO₄. [c] Potentiometric: Cd–Hg, 1 M NaClO₄