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ABSTRACT

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The reaction of 8-aminoquinoline with chromium(III), manganese(II), iron(II) and (III), cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II) and platinum(II) salts has been studied. In many instances definite compounds were prepared. Magnetic moments, molar conductances, infrared, visible and ultraviolet spectra were measured for some of these compounds. Stability constants were obtained for the copper(II) complex using Leden's method. 8-Aminoquinoline was found to be very susceptible to oxidation in the presence of certain metal ions.

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Some Transition Metal Complexes of 8-Aminoquinoline[1]

by James C. Fanning and Larry T. Taylor[2]

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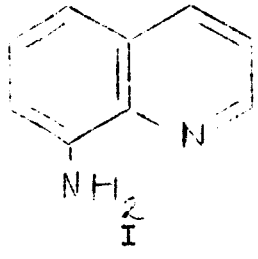
1. Presented in part at the 148th National Meeting of the American Chemical Society, Chicago, Ill., September, 1964.
2. National Aeronautics and Space Administration Predoctoral Fellow.

A study of the behavior of 8-aminoquinoline (I) as a ligand is a logical extension of the interest which has been found in the metal derivatives of ligands containing the N-C-C-N chelating linkage, where the non-metal atoms are in an aliphatic or aromatic system.



I

8-Aminoquinoline might be expected to have properties intermediate to those of ethylenediamine, where the N-C-C-N system is fully aliphatic, and to those of 1,10-phenanthroline or 2,2'-bipyridine, where the four atom system is fully aromatic.

Burrows and Ritchie[3] and Nast, Bier, and Grimm[4] have investigated some

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3. G. J. Burrows and E. Ritchie, J. Proc. Roy. Soc. N.S. Wales, 72, 113 (1939).
4. R. Nast, H. Bier, and J. Grimm, Z. Anorg. Allg. Chem., 309, 289 (1961); Chem. Ber., 94, 1185 (1961).

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of the complexes of 8-aminoquinoline. However, no exhaustive study of the complexes has been carried out. Jensen and Nielsen[5] recently studied the

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5. K. A. Jensen and P. H. Nielsen, Acta Chem. Scand., 18, 1 (1964).

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chelates derived from 8-aminoquinoline such as N,N'-bis-(8-quinoyl)-ethylenediamine and they pointed out that "the chelating properties of 8-aminoquinoline and its derivatives have been rather neglected".

EXPERIMENTAL

Materials.--Analytical grade chemicals were used without further purification. Absolute ethanol and technical grade acetone and methanol were used.

8-Aminoquinoline was obtained from Eastman Organic Chemicals.

Analyses.--The carbon, hydrogen, and nitrogen analyses were carried out by A. Bernhardt Microanalytical Laboratories and Galbraith Laboratories. The metal analyses were carried out after decomposing the complexes in mixtures of HNO_3, H_2SO_4, and $HClO_4$. Copper and cobalt were determined electrolytically. Nickel, zinc, and cadmium were determined by complexometric titration with EDTA. Iron, chlorine, and bromine were determined gravimetrically.

Preparation of the Complexes.--All of the complexes were prepared following generally the same procedure. In each case, the metal salt and 8-aminoquinoline were mixed in the correct stoichiometric ratio at room temperature. The copper complexes as well as $Ni(am)_2(NO_3)_2 \cdot 2H_2O$ and $Ni(am)_2Cl_2 \cdot 5/2H_2O$ were prepared by adding the amine dissolved in methanol to a 0.1 M aqueous solution of the metal salt. To prepare $Cu(am)_2(C_2H_3O_2) \cdot 3H_2O$, it was necessary to saturate the aqueous solution with sodium acetate. After stirring for fifteen minutes, the precipitates were filtered, washed with methanol or ethanol, and dried in air. All of the complexes were slightly soluble in water with the exception of $Cu(am)_2(ClO_4)_2$. The complexes had negligible solubility in methanol, benzene, acetone, and carbon tetrachloride. The complexes appear to decompose in N,N-dimethylformamide. Each compound decomposes in air when heated. Some of the compounds change color when heated and then decompose at a higher temperature. Data for the complexes are recorded in Table I.

Blue and Red Copper(II) Chloride and Bromide Complexes.-- When blue $Cu(am)_2Cl_2 \cdot 2H_2O$ or blue $Cu(am)_2Br_2 \cdot 2H_2O$ is dissolved in water, a blue solution is obtained. After twenty-four hours the solution is maroon in color and after three to four days the solution is dark brown. The conductivity and the pH of the solution remain constant during the color change. A dark red-brown solid was isolated after the intensely colored solution was evaporated to near dryness under reduced pressure. This compound had the same elemental analysis, magnetic susceptibility, X-ray diffraction powder

TABLE I
COMPLEXES OF 8-AMINOQUINOLINE

Compound*	Color	Decomp. Temp. °C	Yield %	ANALYSES							
				Metal		C		H		Halogen	
				Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$Cu(C_9H_8N_2)Cl_2$	green	167-180	72	22.80	23.20	38.80	38.73	2.89	2.96	25.49	26.17
$Cu(C_9H_8N_2)Br_2$	green	170-180	76	17.41	17.90	29.41	29.53	2.19	1.99	43.54	43.28
$Cu(C_9H_8N_2)_2Cl_2 \cdot 2H_2O$	blue	163(green) 185-195	91	13.85	13.64	47.11	46.64	4.39	4.38	15.49	15.76
	red	195-205			13.61		45.60		4.17		16.00
$Cu(C_9H_8N_2)_2Br_2 \cdot 2H_2O$	blue	163(green) 185-195	91	11.60	12.00	39.46	39.35	3.68	3.68	29.22	28.95
	red	195-205			11.35		39.23		3.46		29.25
$Fe(C_9H_8N_2)Cl_2 \cdot 2CH_3OH$	yellow	77-80	29	16.67	17.4	39.40	39.20	4.78	4.72	21.19	21.72
$Zn(C_9H_8N_2)Cl_2$	white	270-276	96	---	---	38.57	38.11	2.86	2.92	25.36	25.26
										N	
										Calcd	Found
$Cu(C_9H_8N_2)_2(ClO_4)_2$	pink	Explodes Ca 170	96	11.53	11.48	39.24	38.72	2.91	2.98	---	---
$Cu(C_9H_8N_2)_2(NO_3)_2 \cdot H_2O$	blue	173-188	95	12.87	12.82	43.77	43.16	3.65	3.81	---	---
$Cu(C_9H_8N_2)_2(C_2H_3O_2)_2 \cdot 3H_2O$	blue	105-110	62	12.13	12.28	51.14	51.39	5.35	5.02	---	---
$Cu(C_9H_8N_2)SO_4 \cdot H_2O$	blue	210(green) 225-230	86	19.73	19.81	33.54	33.35	3.11	3.44	8.69	8.58
$Ni(C_9H_8N_2)_2Cl_2 \cdot 3CH_3OH$	gray	150(green) 263-278	49	11.45	11.86	48.93	48.74	5.44	4.97	10.87	10.80
$Ni(C_9H_8N_2)_2Cl_2 \cdot 5/2H_2O$	violet	180(green) 290-300	67	12.74	12.69	46.65	46.65	4.54	4.53	12.09	11.91
$Ni(C_9H_8N_2)_2(NO_3)_2$	violet	257-262	74	12.53	12.36	45.86	46.30	3.40	3.56	17.83	18.17
$Ni(C_9H_8N_2)_2(NO_3)_2 \cdot 2H_2O$	violet	120(blue) 250-260	72	11.72	11.51	42.94	42.85	3.98	3.86	16.57	15.70
$Co(C_9H_8N_2)_2Cl_2 \cdot 3CH_3OH$	orange	110-121	48	11.45	12.22	48.93	48.63	5.44	4.85	10.87	10.70
$Zn(C_9H_8N_2)_2(NO_3)_2$	white	218-225	92	13.63	13.71	45.29	44.39	3.33	3.28	17.61	17.52
$Cd(C_9H_8N_2)Cl_2 \cdot H_2O$	white	>300	98	32.58	33.03	31.30	31.63	2.90	2.72	8.12	8.11
$Cd(C_9H_8N_2)_2(NO_3)_2$	white	215-223	86	21.37	21.72	41.22	40.43	3.05	2.98	16.03	15.92

*$C_9H_8N_2$ = 8-aminoquinoline, free base.

pattern, and infrared spectrum as the original compound (Tables I and II). The red solid, however, was much less soluble in water than the blue compound. The color change of the solution was accelerated by bubbling air through the solution or by adding H_2O_2. The presence of nitrate ions in solution decreased the rate of the color change very markedly.

Magnetic Measurements.-- The magnetic susceptibilities were obtained at room temperature by the Gouy method, using mercury(II) tetrathiocyanatocobaltate(II) as the calibrant. Table II lists the molar susceptibilities and the magnetic moments of several of the complexes. The molar diamagnetic corrections used in calculating μ are: for 8-aminoquinoline, -183×10^{-6}; for Cl^- anion, -40×10^{-6}; for Br^- anion, -61×10^{-6}; and for water, -13×10^{-6} c. g. s. units.

Conductivity Measurements.-- Molar conductances were measured using an Industrial Instruments Inc. Model RC-1632 Conductivity Bridge and a cell with a cell constant of 0.1412 cm^{-1}. The measurements were made at 25° C by employing 10^{-3} M aqueous solutions and a bridge frequency of 1000 c. p. s. The deionized water used for these measurements had a specific conductance of less than 10^{-6} ohm^{-1}.

Spectra.--Infrared spectra were obtained with Perkin-Elmer Model 137 and Model 221 Recording Spectrophotometers equipped with sodium chloride optics. The pressed KBr pellet technique and Nujol mull method were used. High resolution measurements were made, using the Model 221, in the region of 7 to 8 microns. Water vapor was used for calibration.

Ultraviolet-visible spectra of the aqueous solutions were measured from 350 to 700 mμ, using a Perkin-Elmer 4000A Spectrophotometer. Reflectance spectra were obtained with a Beckman DU Spectrophotometer. These spectra were measured from 320 to 1000 mμ, using a magnesium carbonate block as the reference material.

Stability Constant Measurements.-- In order to obtain the stability constants of the copper(II) 8-aminoquinoline complex, the electromotive force of cells of the following type was measured:

Cu-Hg	$Cu(NO_3)_2$	C'_m	$Cu(NO_3)_2$	0.0035M	Cu-Hg
	KNO_3	0.5M	KNO_3	0.5M	
	HNO_3	0.0014M	HNO_3	0.0022M	
	am	C_L	μ	0.50	
	μ	0.50			

TABLE II

Magnetic Data, X_m and μ, of Some 8-Aminoquinoline(am) Complexes.

Compounds		$X_m \times 10^6$	μ (B.M.)
$Cu(am)_2Cl_2 \cdot 2H_2O$	(Blue)	1415	1.97
	(Red)	1440	1.99
$Cu(am)_2Br_2 \cdot 2H_2O$	(Blue)	1255	1.89
	(Red)	1195	1.85
$Ni(am)_2Cl_2 \cdot 3CH_3OH$		3937	3.18
$Co(am)_2Cl_2 \cdot 3CH_3OH$		10964	5.19
$FeamCl_2 \cdot 2CH_3OH$		11736	5.34

The potential measurements were carried out by adding successive amounts of a titrant in milliliter increments and noting the change in voltage. The titrant had the following composition;

am	C_L mM
KNO_3	0.5 M
HNO_3	0.0034 M
μ	0.50

Titrations were made at four different metal-ion concentrations, C'_m = 0.863, 0.432, 0.259 and 0.130 mM. Readings were continued until an excess of ligand had been added or until a blue precipitate was seen in the reaction vessel.

The stability constants, β_n, were calculated for the following reaction:

$$Cu^{+2} + n\ am \rightleftharpoons Cu(am)_n^{+2}$$

$$\beta_n = \frac{[Cu(am)_n^{+2}]}{[Cu^{+2}][am]^n}$$

The e.m.f. of the concentration cell can be written as:

$$E = \frac{RT}{nF} \ln \frac{C}{M}$$

where C is the concentration of copper(II) nitrate in the reference cell and $[M]$ is the concentration of uncomplexed copper(II) in the reaction cell. If the e.m.f. for the special case of $C_L = 0$, $[M] = C_m = C'_m$ is denoted by E', we obtain

$$E' - E = E_m = \frac{RT}{nF} \ln \frac{Cm}{[M]}$$

At every point during the titrations, C_m and C_L were known from the concentration of the solutions used. Since the titrant did not contain any copper ions, C_m continuously decreased as C_L increased. The difference between the e.m.f., E, at a definite point in the titration and the initial e.m.f., E', was therefore caused by dilution as well as by complex formation. To find the difference, E_m, defined as due only to complex formation a correction was necessary as follows:

$$E_m = E' - E - \frac{RT}{nF} \ln \left[\frac{(a + v)}{a}\right]$$

where "a" is the number of milliliters initially contained in the electrode vessel(concentration C'_m) and "v" is the number of milliliters of ligand solution added. From the quantity $\frac{Cm}{[M]}$, the cumulative stability constants B_n can be calculated[6] by the method of Leden as described by Ahrland and coworkers[7] and Grenthe[8].

6. The calculations and graphs employed for the computation of β_n are deposited as Document ___ with the American Documentation Institute, Auxiliary Publication Project, Photo Duplication Service, Library of Congress, Washington 25, D.C. A copy may be secured by citing the Document Number and remitting _____ for photoprints or ____ for 35-mm. microfilm in advance payable to: Chief, Photoduplication Service, Library of Congress.

7. S. Ahrland, J. Chatt, N. R. Davies, and A. A. Williams, J. Chem. Soc., 1958, 264, 276.

8. I. Grenthe, J. Am. Chem. Soc., 83, 360 (1961).

The concentration cells were connected by means of a saturated agar-potassium chloride salt bridge and the resultant voltage measured with a Leeds and Northrup Student Potentiometer. A copper amalgam pool was used as the copper electrode, and it was connected to the potentiometer by means of an insulated copper wire. The copper amalgam contained two percent copper and was prepared by the electrolysis of a concentrated copper(II) nitrate solution, using triply distilled mercury as the cathode. The amalgam was tested for uniformity by preparing two cells having the same concentration of copper(II) nitrate. The e.m.f. developed by this system did not exceed 0.5 mv. As a test for reversibility the potential difference between two cells, having different but known concentrations of copper(II) nitrate, never varied from the theoretical value by more than 1 mv. Also, if the potentiometer key was held down for a few seconds and then released the voltage very quickly returned to its original value. The latter observation was made even when one of the cells contained 8-aminoquinoline and copper(II) ions.

Since the amalgam was easily oxidized, the solutions were saturated with oxygen-free nitrogen. Nitrogen was bubbled through the solutions in the cells until the measurements were to be made. The flow of gas was stopped while the measurement of the e.m.f. was carried out.

RESULTS

8- Aminoquinoline gave well-defined products with Fe(II), Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) salts and these compounds are listed in Table I. The amine appeared to give no reaction with Mn(II) salts. For, when the aqueous metal salt solution and the yellow alcohol solution of the amine were mixed, only the very slightly water soluble yellow amine precipitated. There was no color change observed upon mixing the two solutions. Cr(III) and Fe(III) salts gave only dark maroon tars when reacted with 8-aminoquinoline. No well-defined product could be obtained when a methanol solution of the ligand was added to an aqueous solution of K_2PtCl_4. The insolubility of K_2PtCl_4 in other solvents prevented any further attempts to prepare a Pt(II) complex containing 8-aminoquinoline. Some 8-aminoquinoline complexes, $Fe(am)SO_4 \cdot 6H_2O$, $Ni(am)(NO_3)_2 \cdot 10H_2O$, $Ni(am)Cl_2 \cdot 16H_2O$, and $Cu(am)_2SO_4 \cdot 7H_2O$, have been reported[3] and attempts to repeat the preparation were unsuccessful.

No <u>tris</u> complexes of 8-aminoquinoline were able to be prepared with copper(II), nickel(II), cobalt(II), and iron(II) salts. It was found that the addition of 8-aminoquinoline in excess to an aqueous solution of these salts resulted in dark red colored filtrates and precipitates that invariably darkened after filtration. The colors of the precipitates before darkening were identical with the <u>mono</u> or <u>bis</u> compounds isolated using a stoichiometric ratio of reactants. In fact, to insure obtaining compounds that did not change color, a slight excess of the metal ion was added for the preparation of the iron and cobalt complexes. Attempts to repeat the preparation of the reported[4] $Co(am)_3(ClO_4)_2$ were unsuccessful.

The unusual color change from blue to red of the copper(II) chloride and copper(II) bromide complexes in aqueous solution is probably due to the oxidation of the ligand. Initially, it was thought that this behavior might represent some type of isomerism as has been found with copper(II) 8-quinolinol complexes[9] and certain biguanide complexes[10]. However,

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9. J. C. Fanning and H. B. Jonassen, J. Inorg. Nucl. Chem., <u>25</u>, 29 (1963).
10. P. Ray and H. Saha, Chem. Rev., <u>61</u>, 313 (1961).

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since the color change was influenced by air and H_2O_2, oxidation is now thought to be responsible for the color change. When 8-aminoquinoline,

itself, was dissolved in methanol and a few drops of 30% H_2O_2 added, the solution turned from light yellow to a deep red color. Identical results were observed if the amine solution were allowed to stand in air. A chromatographic separation on neutral alumina of this deep red solution showed that the solution contained predominantly the yellow amine with a small trace of an undefinable black compound. Thus, a trace of an oxidation product with the copper complex may cause the large change in color.

Several of the other metal complexes behaved in a manner similar to copper(II) but no products were isolated. When the iron(II) and cobalt(II) complexes are dissolved in water, the solution turns usually red-brown in color after a short period of time. Qualitative visual observations on the various metal-amine complex solutions showed that the approximate rate of change was Fe(II) $>$ Co(II) $>$ Cu(II) $>$ amine. The 8-aminoquinoline complexes of Ni(II), Zn(II) and Cd(II) showed no evidence of this change.

All of the aqueous molar conductances shown in Table III are in the expected range for 2:1 or, in the case of $CuamSO_4 \cdot H_2O$, 2:2 electrolytes. The value for the iron(II) complex is unexplainably high. This complex is very unstable in aqueous solution as described above. The $Fe(am)Cl_2$ solution was red-brown when the conductance measurement was made.

TABLE III

Molar Conductances of the Complexes of 8-Aminoquinoline(am) (0.001 M Aqueous Solution)

Compound	Λ_M, ohm^{-1} cm^2 $mole^{-1}$
$Cu(am)_2Cl_2 \cdot 2H_2O$ (blue)	270
$Cu(am)Cl_2$	248
$Cu(am)_2Br_2 \cdot 2H_2O$ (blue)	235
$Cu(am)Br_2$	272
$Cu(am)_2(NO_3)_2 \cdot H_2O$	230
$Cu(am)SO_4 \cdot H_2O$	219
$Ni(am)_2Cl_2 \cdot 3CH_3OH$	254
$Ni(am)_2Cl_2 \cdot 5/2\ H_2O$	250
$Ni(am)_2(NO_3)_2$	230
$Ni(am)_2(NO_3)_2 \cdot 2H_2O$	230
$Co(am)_2Cl_2 \cdot 3CH_3OH$	258
$Fe(am)Cl_2 \cdot 2CH_3OH$	444
$Zn(am)_2(NO_3)_2$	228
$Zn(am)Cl_2$	252
$Cd(am)_2(NO_3)_2$	235
$Cd(am)Cl_2 \cdot H_2O$	231

Stability constants were obtained for the copper(II) complex. Bjerrum's method[11] for stability constant determination was unsatisfactory

11. J. Bjerrum, "Metal Amine Formation in Aqueous Solution", Haase, Copenhagen, 1941; G. A. Carlson, J. P. McReynolds, and F. H. Verhoek, J. Am. Chem. Soc., 67, 1334 (1945).

due to the insolubility of the complex and the weak basicity of the ligand. The stability constants shown in Table IV are in agreement with those predicted by Yasuda[12] who attempted to use Bjerrum's method and experienced

12. M. Yasuda, Z. Physik. Chem. (Frankfurt), 29, 377 (1961).

similar experimental difficulties. Attempts were made to measure the

stability constants of the cadmium and zinc complexes, but they were unsuccessful. The very low solubility of the metal 8-aminoquinoline complexes prevented the measurements since the zinc and cadmium amalgam electrodes were insensitive at low metal ion concentrations.

TABLE IV

Stability Constants Data*

Metal	Ligand	Method	pk of HL^{+}	pk of H_2L^{+2}	log K_1	log K_2	log β_2	Reference
Cu	am	M-Hg	3.93	1.07	5.10	3.89	8.99	a
Cu	am	gl	-	-	>5	-	ca. 10	b
Ni	am	gl	-	-	4.1	3.6	7.7	b
Cu	bipy	gl	-	-	8.47	5.58	14.05	c
Cu	phen	gl	4.96	-	6.30	6.15	12.45	d
Cu	en	gl	9.87	7.23	10.55	9.05	19.60	d

* Abbreviations: am, 8-aminoquinoline; bipy, 2, 2'-bipyridine; phen, 1, 10-phenanthroline; en, enthylenediamine; M-Hg, metal-mercury amalgam electrode; gl, glass electrode

References: (a) This work. (b) M. Yasuda, Z. Physik. Chem. (Frankfurt), 29, 379 (1961). (c) S. Cabani, et al. J. Chem. Soc., 1962, 88. (d) Stability Constants. Part I; Organic Ligands. 1957. London; The Chemical Society.

Infrared spectra were obtained for all of the compounds prepared as well as 8-aminoquinoline and 3-aminoquinoline dihydrochloride. The intense band in the region of 1325 cm^{-1} has been assigned to the aromatic carbon-aliphatic nitrogen stretching frequency[13]. This band was studied

13. L. J. Bellamy, "The Infrared Spectra of Complex Molecules", John Wiley, Inc., New York, 1962, p. 257.

at high resolution and the frequencies for the various chloride complexes are shown in Table V. This band is shifted to a lower frequency by coordination as would be expected. No correlation could be drawn between

the C-N stretching frequency of the amine and the atomic weight or ionic radius of the metal to which it is coordinated. In the case of the 8-quinolinol complexes, there was a correlation between the aromatic carbon-aliphatic oxygen stretching frequenty and the atomic weight of the metal[14].

14. R. G. Charles, H. Freiser, R. Friedel, L. E. Hilliard, and W. D. Johnston, Spectrochim. Acta, 8, 1 (1956).

TABLE V

C-N Stretching Frequencies for 8-Aminoquinoline(am), 8-Aminoquinoline Dihydrochloride(am·2HCl) and Some Complexes of 8-Aminoquinoline.

Compound	cm^{-1}
am	1336
am·2HCl	1296
$CuamCl_2$	1315
$Cu(am)_2Cl_2 \cdot 2H_2O$ (blue)	1320
$Cu(am)_2Cl_2 \cdot 2H_2O$* (blue)	1321
$Ni(am_2Cl_2 \cdot 3CH_3OH$	1324
$Ni(am)_2Cl_2 \cdot 2H_2O$	1322
$Co(am)_2Cl_2 \cdot 3CH_3OH$	1322
$FeamCl_2 \cdot 2CH_3OH$	1316
$ZnamCl_2$	1322
$CdamCl_2 \cdot H_2O$	1323

*Hexachlorobutadiene mull was used to obtain infrared spectra. The KBr pellet technique was used for the others.

The ultraviolet-visible spectra of the aqueous solutions of the complexes were obtained, but the spectra proved to be unsatisfactory for two reasons. First, the aqueous solutions of the complexes were more susceptible to oxidation than the solid; and second, the 350-450 mμ region of the spectra is masked due to very intense bands. This strong absorption is most likely due to charge transfer; for, Jørgensen has pointed out that aromatic amines when coordinated should display charge-transfer bands in this region.[15]

15. C. K. Jørgensen, Acta Chem. Scand., 9, 1362 (1955).

The absorption maxima found in the reflectance spectra of the complexes are presented in Table VI. While the relative heights of the bands cannot be deduced from the data, the position of the bands can be measured exactly in the reflectance spectra. From a study of 25 paramagnetic nickel(II) complexes, Bostrup and Jørgensen have shown that the spectra of a given complex in solution and in the solid state are very similar[16].

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16. O. Bostrup and C. K. Jørgensen, Acta Chim. Scand., 11, 1223 (1957).

The reflectance spectrum of the nickel(II) chloride complex was chosen to be studied in more detail because of the large abundance of spectral data that is available on nickel(II) complexes[16]. Unfortunately the tris complex of nickel(II) was not able to be prepared and so assignments had to be made using the bis complex. Since the chloride ions, no doubt, complete the octahedral arrangement about the nickel ion in the solid, the symmetry of the complex can be no higher than D_{4h}. Also, the rule of "average environment" cannot be directly applied to the absorption bands because Cl and N are quite far apart in the spectrochemical series. As a consequence of its low symmetry, $Ni(am)_2Cl_2 \cdot 3CH_3OH$ is probably quite tetragonally distorted which leads to a splitting of the $^3T_{2g}(F)$ level. A similar case of tetragonal splitting has been found in the visible spectrum of trans-$Ni(py)_4Cl_2$[16]. Assuming D_{4h} symmetry for the Ni(II) complex, the following assignments can be made:

$$^3A_{2g} \longrightarrow {}^3T_{2g}(F) \qquad 11{,}950\ cm^{-1} \qquad 13{,}400\ cm^{-1}$$

$$\longrightarrow {}^3T_{1g}(F) \qquad 17{,}700\ cm^{-1}$$

The $^3A_{2g}$ - $^3T_{1g}(P)$ transition that might be expected, is masked by charge transfer bands. Since the $^3T_{2g}(F)$ state is tetragonally split, an assignment of a Dq value is made very difficult.

TABLE VI

Absorption Maxima in the Reflectance Spectra of the Complexes of 8-Aminoquinoline(am)

Compound	Wave Number (cm^{-1})
$CuamCl_2$	27,400
	14,300[a]
$Cu(am)_2Cl_2 \cdot 2H_2O$	30,000
	17,200[a]
$Ni(am)_2Cl_2 \cdot 3CH_3OH$	ca. 31,000
	17,700
	13,400
	11,950
$Co(am)_2Cl_2 \cdot 3CH_3OH$	28,600
	15,400[a]
$FeamCl_2 \cdot 2CH_3OH$	23,500
	13,300[a]

[a]Broad.

DISCUSSION

The metal complexes of 8-aminoquinoline appear to be resistant to change in solution provided the metal ion has but one common oxidation state. Fallab has studied the metal ion catalysis of the autoxidation of o-phenylenediamine and its derivatives and found that metal ions like Co(II) and Cu(II) accelerate the oxidation; Zn(II) is inactive as a catalyst and Ni(II) hinders the oxidation[17]. Krumholtz has found a

17. S. Fallab, J. Inorg. Nucl. Chem., 8, 631 (1958).

similar catalytic effect with Fe(II) and 2,2'-bipiperidine[18]. 8-Amino-

18. P. Krumholtz, J. Am. Chem. Soc., 75, 2163 (1953).

quinoline is possibly undergoing a similar oxidation, but as yet the exact nature of the reaction and the oxidation products are not known. A recent spectrophotometric determination of iron is based on the oxidation of 8-aminoquinoline with Fe(III)[19]. Since the oxidation of the

19. V. K. Gustin and T. R. Sweet, Anal. Chem., 35, 1395 (1963).

ligand occurs with great ease, especially in the presence of certain metal ions, one must exercise extreme caution to keep from classifying an oxidation product as a pure coordination compound.

8-Aminoquinoline unfortunately forms no tris complexes; therefore, this makes very difficult any comparisons between it, as a ligand, and ethylenediamine, 2,2'-bipyridine and 1,10-phenanthroline. Very little information on the magnetic and spectral properties is available concerning the mono and bis complexes of these three ligands. The low values of the stability constants for 8-aminoquinoline with copper(II) relative to 2,2'-bipyridine, 1,10-phenanthroline and ethylenediamine, as seen in Table III, indicate that the complexes of 8-aminoquinoline are the most unstable of the group. This instability is primarily due to the weak basicity of the amine as evidenced by the low pK_a values. The low pK_a's for 8-aminoquinoline as compared to the other aminoquinoline isomers have been ascribed by Albert[20] to be due to intramolecular hydrogen

20. A. Albert, R. Goldacre and J. Phillips, J. Chem. Soc., 1949, 2240.

bonding. The other aminoquinolines have pK_a's around six.

The stability constants for Ni(II) are also shown in Table III as determined by Yasuda using Bjerrum's method since the Ni(II) complexes of 8-aminoquinoline are much more water soluble than those of Cu(II). The Irving-Williams stability order appears to hold since $\log \beta_2$ is greater for Cu(II) than Ni(II).

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APPENDIX

Stability Constant Calculations for the Copper(II) 8-Aminoquinoline Complex

In order to obtain the stability constants of the copper(II) 8-aminoquinoline(am) complex, the electromotive force of cells of the following type was measured:

Cu-Hg	$Cu(NO_3)_2$	C'_m	‖	$Cu(NO_3)_2$	0.0035 M	Cu-Hg
	KNO_3	0.5 M	‖	KNO_3	0.5 M	
	HNO_3	0.0014 M	‖	HNO_3	0.0022 M	
	am	C_L	‖	μ	0.50	
	μ	0.50	‖			

The potential measurements were carried out by adding successive amounts of a titrant in milliliter increments and noting the change in voltage. The titrant had the following composition:

am	C_L mM
KNO_3	0.5 M
HNO_3	0.0034 M
μ	0.50

Titrations were made at four different metal-ion concentrations, C'_m = 0.863, 0.432, 0.259 and 0.130 mM. Readings were continued until an excess of ligand had been added or until a blue precipitate was seen in the reaction vessel.

The stepwise stability constants, K_1 and K_2, were calculated for the following reactions:

$$Cu^{+2} + am \rightleftharpoons Cu(am)^{+2}$$

$$Cu(am)^{+2} + am \rightleftharpoons Cu(am)_2^{+2}$$

Applying the law of mass action to the preceeding reactions:

$$K_1 = \frac{[Cu(am)^{+2}]}{[Cu^{+2}][am]} \qquad K_2 = \frac{[Cu(am)_2^{+2}]}{[Cu(am)^{+2}][am]}$$

and $\beta_1 = K_1$, $\beta_2 = K_1 \cdot K_2$.

The e.m.f. of the concentration cell can be written as

$$E = \frac{RT}{nF} \ln \frac{C}{[M]}$$

where C is the concentration of copper(II) nitrate in the reference cell,

$[M]$ is the concentration of uncomplexed copper(II) in the reaction cell, T is 303°K, F is 96,493 coulombs, R is 8.314 joules/mole·degree and n is 2. If the e.m.f. for the special case of $C_L = 0$, $[M] = C_m = C'_m$ is denoted by E', we obtain

$$E' - E = E_m = \frac{RT}{nF} \ln \frac{C_m}{[M]} = \frac{RT}{nF} \ln X$$

where

$$X = \frac{C_m}{[M]}$$

and

$$X = 1 + \beta_1 [L] + \beta_2 [L]^2$$

$[L]$ is a measure of the free 8-aminoquinoline concentration. At every point during the titration, C_m and C_L were known from the concentration of the solution used. Since the titrant did not contain any copper ions, C_m continuously decreased as C_L increased. The difference between the e.m.f., E', was therefore caused by dilution as well as by complex formation. To find the difference, E_m, defined as due only to complex formation, a correction was necessary as follows

$$E_m = E' - E - \frac{RT}{nF} \ln \left[\frac{(a+v)}{a}\right]$$

where "a" is the number of milliliters initially contained in the electrode vessel (40 ml.) and "v" is the number of milliliters of ligand solution added.

Since X is a function only of $[L]$ and since E is a function only of X, there is for every E_m a unique value of $[L]$, independent of the total metal concentration, C_m. To find corresponding values of E_m and $[L]$, E_m is determined experimentally as a function of C_L at several values of C_m (Fig. 1 and Table I). The family of curves obtained are cut at a number of values of E_m, and then from the coordinates of the intersections, C_L can be plotted against C_m for every constant E_m value selected (Fig. 2 and Table 2). In order to obtain this plot, a correction is necessary since the total copper concentration is continually decreasing as titrant is added. By combining $C_m = C'_m \cdot \frac{a}{(a+v)}$ and $C_L = C'_L \cdot \frac{v}{(a + v)}$ the linear relation between C_m and C_L is:

$$C_m = C'_m - \frac{C'_m}{C'_L} (C_L)$$

where C'_L is the concentration of 8-aminoquinoline in the titrant and C'_m

is the concentration of copper(II) when C_L equals zero. This correction is easily applied by plotting the points corresponding to ($C_L = 0$, $C_m = C'_m$) and ($C_L = 1.00$ mM, $C_m = C'_m - \frac{C'_m}{C'_L}$) and connecting the points (Fig. 2). For complexes with $\beta_1 > 1500$ 1/mole, the highest complex in solution, $Cu(am)_2^{+2}$, is completely dominating and $C_m = [Cu(am)_2^{+2}]$. The function X, which can be directly calculated from E_m can then be simplified to:

$$X = \beta_2 [L]_a^2$$

The corresponding values of $X([L]_a)$ and $[L]_a$ are chosen within a C_L range where $[L]_a$ can be determined as the intercept on the C_L axis (Fig.2). This C_L range must be greater than $2 \cdot C_m$ and then the slope of the $C_L - C_m$ lines within this range is constant and equal to 2. From the E_m parameter equal to 42.5 mv, the values of X = 26.10 and $[L]_a = 0.163$ mM are used to calculate β_2:

$$\beta_2 = (26.10)\ (1.63 \times 10^{-4}\ \text{Moles/l})^{-2}$$

$$\beta_2 = 9.81 \times 10^{8}\ (\text{l/mole})^2$$

In order to find β_1, it can be conveniently done graphically by plotting $1/\bar{n}$ as a function of log X (Fig. 3 and Table 3). $\bar{n}$ is the formation function and is equal to the slope of the corresponding E_m parameter. The areas under the curve are measured from a fixed upper limit, $\log X([L]_a)$, to various lower limits, $\log X([L]_j)$. These lower limits must be in the range $1 < \bar{n} > 0$ where the predominating complex is assumed to be $Cu(am)^{+2}$. The area under the curve is $\log \frac{[L]_a}{[L]_j}$. The best values of $[L]_a$ and $X([L]_a)$ to serve as the fixed upper limit $[L]_a = 0.163$ mM and X = 26.10.

Choosing $E_m = 10$ mv, a sample calculation would be as follows:

$$\bar{n} = 0.423$$

$$1/\bar{n} = 2.36$$

$$X = 2.15$$

$$\log X = 0.333$$

$$\log 26.10 = 1.417$$

$\log \frac{0.163\ \text{mM}}{[L]_j} = 1.2065$ = the area under the curve from log 26.10 = 1.417 to log X = 0.333

$$[L]_j = 1.00 \times 10^{-5}\ \text{moles/l}$$

By definition

$$\frac{(X - 1)}{[L]_j} = X_1 = \beta_1 + \beta_2 [L]$$

$$X_1 = \frac{(2.15 - 1.00)}{1.00 \times 10^{-5}} = 1.15 \times 10^5 \text{ 1/mole}$$

If X_1 is plotted against $[L]_j$ and extrapolated to cut the X_1 axis, we obtain β_1 as the intercept (Fig. 4 and Table 3).

The method of least squares was used to find the intercept. E_m values of 8, 10, 12, 15 and 17 mv were employed.

$$\beta_1 = K_1 = 12.72 \times 10^4 \text{ 1/mole} = \text{intercept}$$

$$\beta_2 = K_1 \cdot K_2$$

$$9.81 \times 10^8 \text{ (1/mole)}^2 = 12.72 \times 10^4 \text{ 1/mole} \cdot K_2$$

$$K_2 = 7.73 \times 10^3 \text{ 1/mole}$$

TABLE 1

E_m as a function of C_L

C_m'(mM) ⟶		0.863	0.432	0.259	C_m'(mM) ⟶		0.130
		$C_L' = 3.33$ mM					$C_L' = 1.36$ mM
ml.	C_L(mM)	E_m(mv)	E_m(mv)	E_m(mv)	ml.	C_L(mM)	E_m(mv)
0	0.0	0.0	0.0	0.0	0	0.0	0.0
1	0.0813	1.6	2.4	3.8	1	0.0329	1.4
2	0.159	2.6	4.6	8.1	2	0.0642	3.5
3	0.233	5.3	7.5	13.5	3	0.0940	6.0
4	0.303	6.8	9.5	19.7	4	0.122	8.2
5	0.370	8.8	12.6	25.9	5	0.150	11.3
6	0.435	10.8	14.9	31.6	6	0.176	13.1
7	0.496	12.3	17.6	37.0	7	0.201	15.7
8	0.556	14.7	21.2	--	8	0.225	18.3
9	0.612	16.3	23.5	41.7	9	0.247	20.8
10	0.669	18.7	25.5	45.1	10	0.269	27.1
11	0.719	20.8	28.3	50.3	11	0.291	30.6
12	0.769	23.0	29.6		13	0.330	36.8
13	0.818	25.5	30.5		15	0.367	42.2
14	0.864	28.0	30.8		17	0.402	45.8
15	0.909	30.3	31.2		19	0.434	49.4
16	0.952	33.0	34.9		21	0.464	52.7
17	0.994	--	33.6		23	0.492	54.8
18	1.03	35.6			25	0.518	53.9
					27	0.543	58.0
					29	0.566	60.8
					31	0.588	62.5

TABLE 2

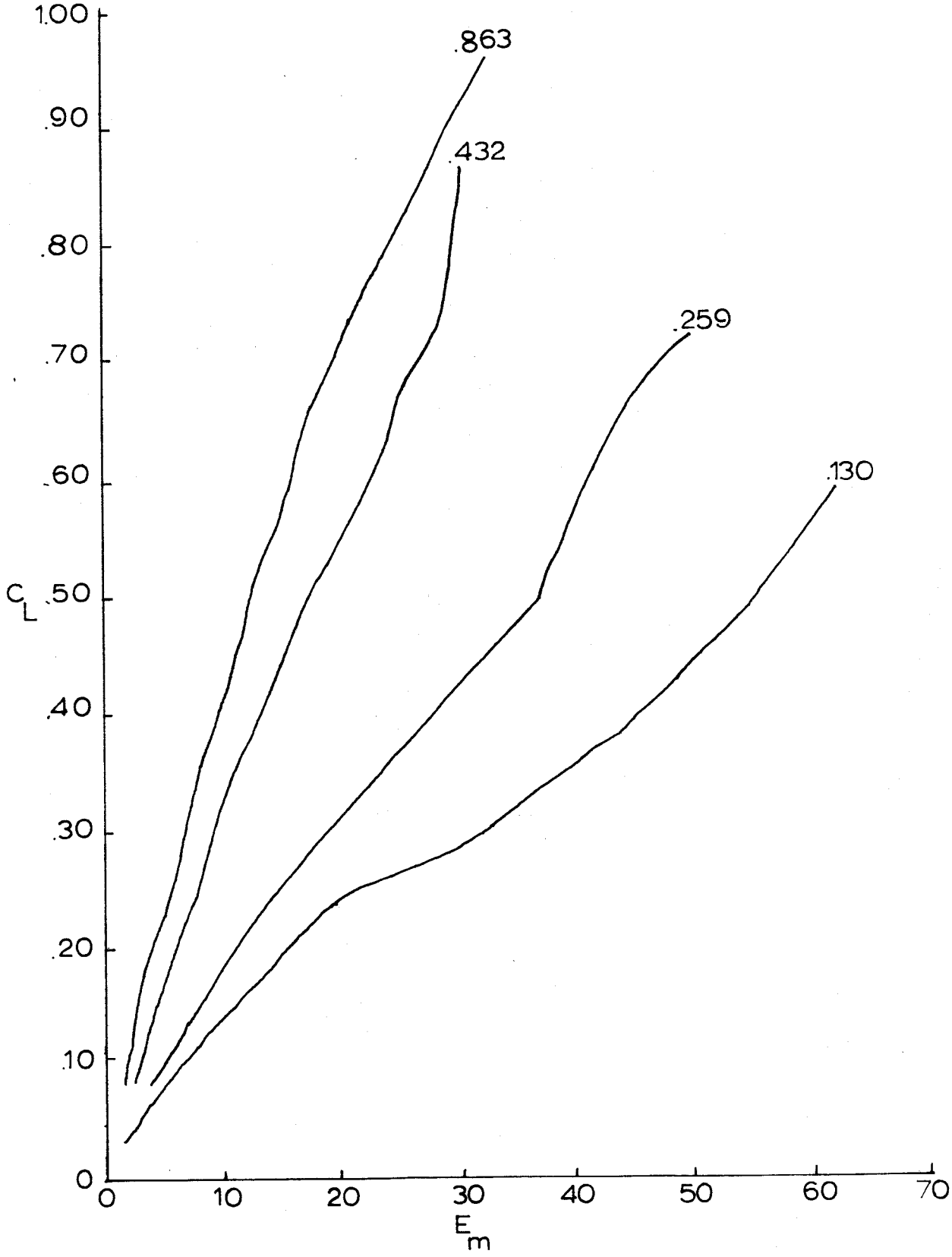
Determination of $\bar{n}$

C'_m(mM) →	0.863	0.432	0.259	0.130			
E_m(mv)	C_L(mM)	C_L(mM)	C_L(mM)	C_L(mM)	$\bar{n}$	$1/\bar{n}$	log X
5	0.228	0.150	0.103	0.080	.217	4.61	0.167
8	0.353	0.250	0.154	0.118	.360	2.78	0.264
10	0.410	0.322	0.187	0.138	.423	2.36	0.333
12	0.483	0.369	0.215	0.158	.522	1.92	0.397
15	0.565	0.435	0.255	0.189	.614	1.63	0.500
17	0.640	0.486	0.275	0.213	--	--	0.567
20	0.710	0.537	0.310	0.240	.812	1.23	0.667
25	0.803	--	0.365	0.263	.982	1.02	0.833
30	--	--	0.418	0.284	1.09	.918	1.000
35	--	--	0.472	0.315	1.29	.777	1.167
40	--	--	0.570	0.353	1.82	.548	1.333
42.5	--	--	0.625	0.373	2.20	.455	1.417
45	--	--	0.664	0.393	2.37	.423	1.500

TABLE 3

Calculation of $[L]_j$ and derivation of β_1 ($[L]_a$ = 0.163 mM)

E_m(mv)	$\log \frac{[L]_a}{[L]_j}$	$[L]_j$ (10^5) moles/l	X	X_1(10^{-4}) l/mole
5	1.7240	0.308	1.47	15.2
8	1.3720	0.692	1.34	12.1
10	1.2065	1.000	2.15	11.5
12	1.0570	1.430	2.50	10.5
15	0.8730	2.180	3.16	9.91
17	0.7535	2.88	3.69	9.35
20	0.6355	3.77	4.64	9.65
25	0.4575	5.69	6.81	10.2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C_L
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60
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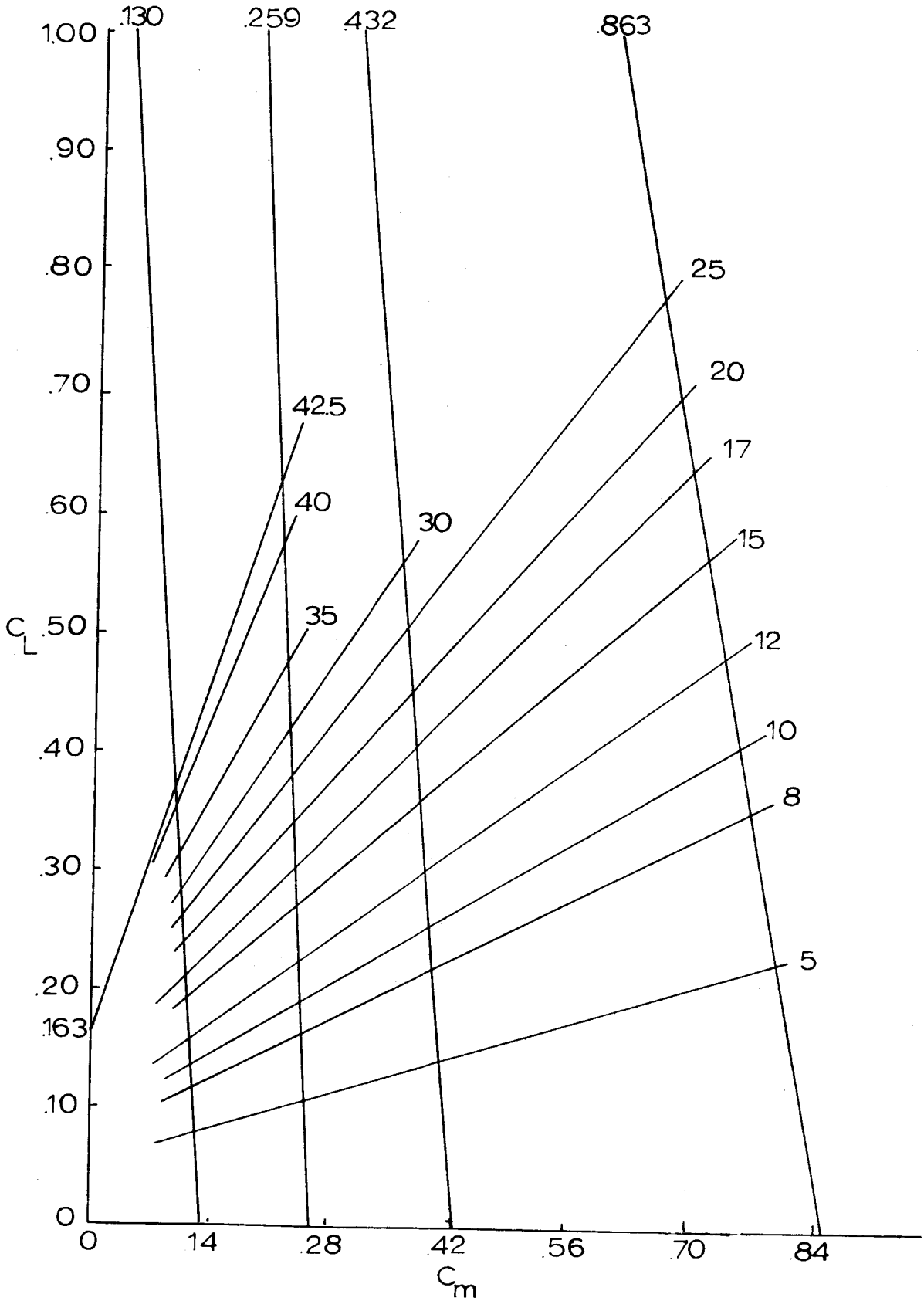
E_m

Figure 1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C_L
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C_m

Figure 2

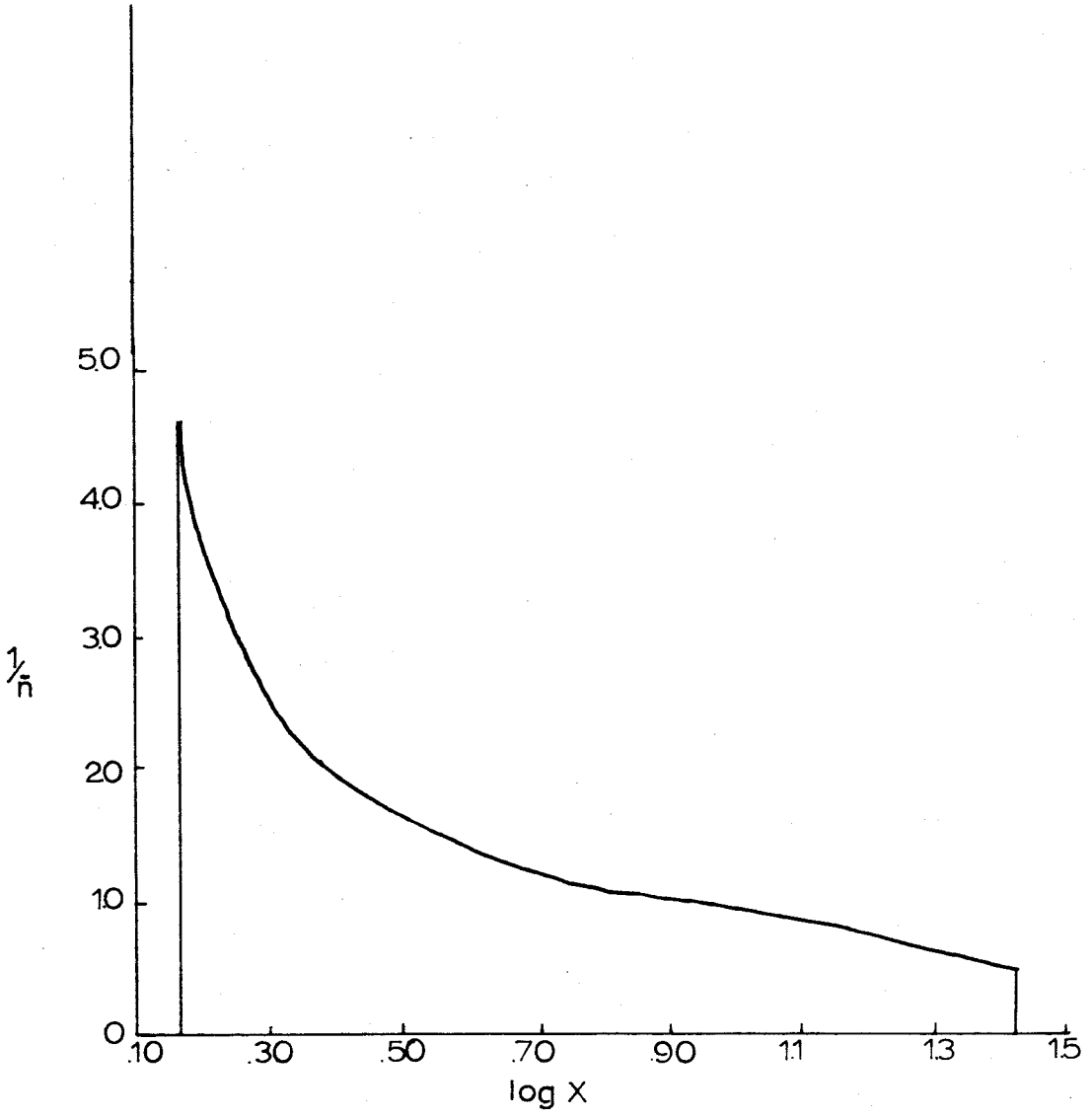

Figure 3

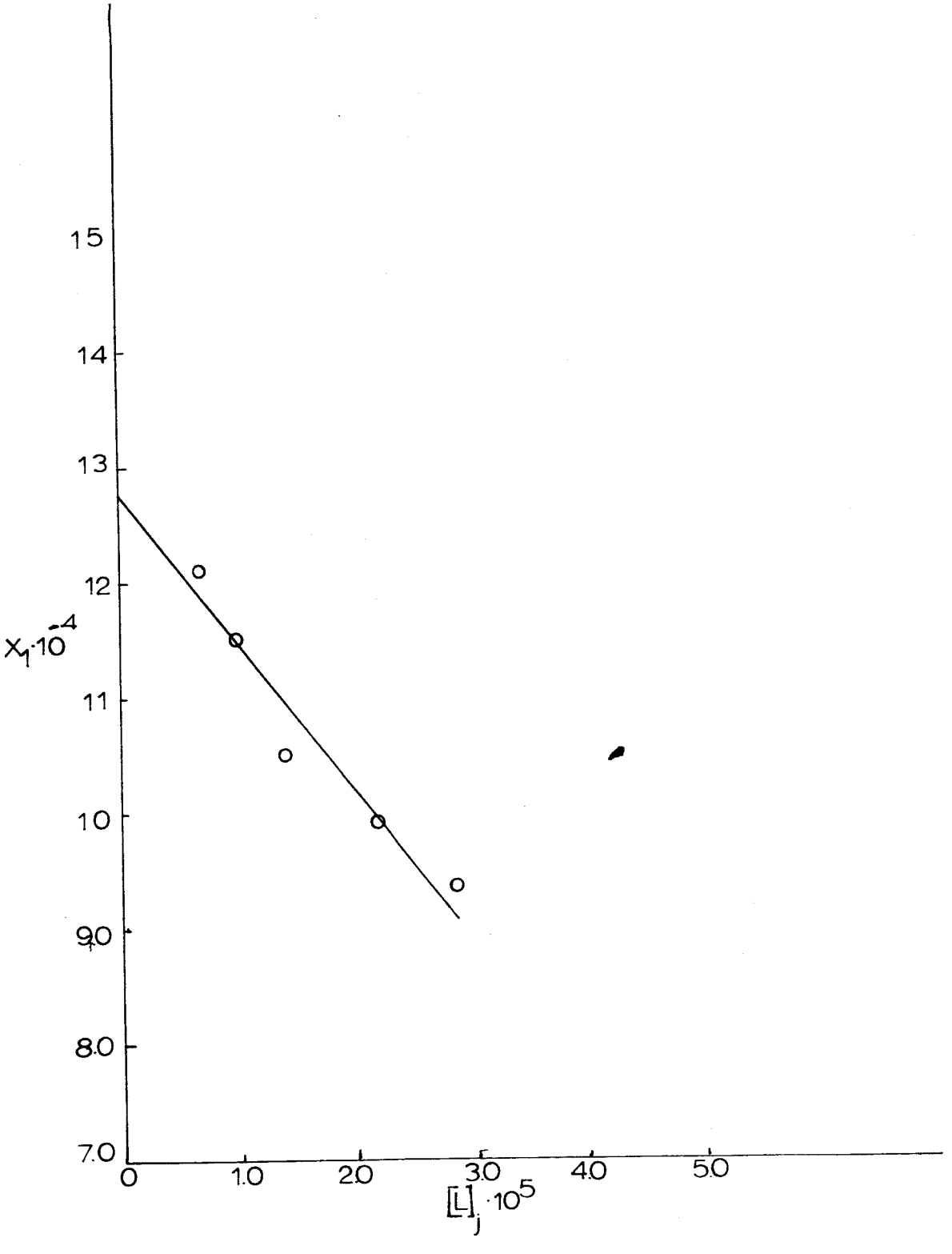

Figure 4