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(NJC)

(2007/4/24

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(2007/1/17

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:

Cu^{2+}

(o-Phenylenediamine)

:

Cu^{2+}

.pH

K

Abstract:

The work reports an investigation of the interaction of Cu^{2+} ion with the ligand o-Phenylenediamine (1,2-diaminobenzene). Two spectrophotometric methods namely the continuous variations and the molar ratio were used. The continuous variations was applied to determine whether, one complex or more is formed from the reaction of the metal ion Cu^{2+} with the ligand in a given pH value.

The results which are obtained from the pervious method was affirmed by the molar ratio method. Moreover, the effect of the experimental variables such as pH, concentration, time and temperature upon the extent of complex formation were studied. Also the stability constant (K) for Cu^{2+} complexes was calculated.

0-	Phenylenedihydrochloride (8-3)	Chelating	-1 Lignads)
	$[Cu(H_2O)_6]^{2+}$	Ethylenediamine + (en	
			(en)
(Continous Variation)	(10-9)	Diaminopropane	
		Dietnylenetniamine (dien)	
		(1)	
Preparation of	-2		
Copper)	Solutions 1-2 (Sulphate	$(HOOCCH_2)_2N(CH_2)_nN(CH_2COOH)_2$	
		(2) (n)	
		n = 3	
(Proamalyzi anol; analar grade)	(3-2) n = 4		
(0.1) 26.760			
	1000	o-Phenylenediamine	
(5) (0.1)		Cu^{2+}	
1000			
:	2-2		
	o-Phenylene diamine	o-	
		Phenylenehydrochloride	

				(0.1)	10.814
	1.00		1000		
		(3) (1)		(1)	
	pH			(0.1)	
		(11)			
Cu ²⁺				:	3-2
					Potassium Hydroxide Solution
					(Proanalyzi Merck, analar grade)
				(1)	0.0560
	(12)	(800 – 2350)			(0.001)
					pH
				:	-4
					Hydrochloric acid Solution
					(0.001)
					pH
	(1)				-3
			³ 10		Instruments
				:	1-3
					DR.LANGE U.V/Vis
					Spectrophotometer, LS 500,
					(Germany)
	³ 0.5	³ 9.5		:	2-3
					(WTW)-Portable pH-Meter 8120
		(21)			Weilheim i.OB (Germany)
				:	±0.0001 3-3
	(1)		³ 10		Start Qius
				:	HERAEUS TYP 4-3
					RNT 360 HANAU, (Germany)
	(3)		424	:	-4
444					Continuous
					(10-9) variation

(12) Molar Ratio Method

(5,6,7) (5) () (2,5) (444) (7,8) () (6) $\left(\frac{L}{M}\right)$ () (424) (4) (2) (1, 14) (7) : -5 Cu^{2+} () pH L/M) (= 3:1 [Cu $L_2(H_2O)_2]^{2+}$ (d⁹) [Cu (16-14) - $L_3]^{2+}$ (16)() (en) (K₃) (K₃) (25,24) (K₂, K₁) (L/M) (d⁹) [Cu(H₂O)₆]²⁺ (5) (800-350) (17-13) [Cu(en)₂(H₂O)₂]²⁺ (444) (424)

(Molar Ratio Method)

$$(5) \quad (4) \quad (2)$$

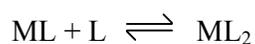
(2)

(19-18)

$$(3) \quad (2) \quad (424)$$

$$: \quad (444) \quad (3)$$

(3)



$$K_1 = \frac{[ML]}{[M][L]}$$

$$[ML] = C_m \times \frac{(A_m - A_c)}{A_{cx}}$$

$$(A_{cx}) \cdot (A_m - A_c) \cdot L \cdot M$$

C_m

$$[ML] = 0.01 \times \frac{0.510}{0.513} = 9.94 \times 10^{-3}$$

$$[M] = 0.01 - 9.94 \times 10^{-3} = 6.00 \times 10^{-5}$$

$$[L] = 0.01 - 9.94 \times 10^{-3} = 6.00 \times 10^{-5}$$

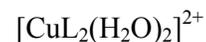
$$K_1 = \frac{9.94 \times 10^{-3}}{(6.00 \times 10^{-5})^2} = 2.76 \times 10^7$$

$$\log K_1 = 6.44$$

$$\log K_2 = 6.44 \quad : \quad K_2$$

(21-19)

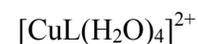
(d⁹)



(424)

(8)

(Splitting)



⁽²⁾(M.O.T.) (C.F.T.)

(23-22)

Endothermic

444 424 (10 9) [CuL₂(H₂O)₂]²⁺, [CuL(H₂O)₄]²⁺
pH=5
pH=4.5

(1)

$$18 = T \quad 5.00 =$$

$$424 = \lambda$$

$$0.01 = [L] = [Cu^{+2}]$$

$A_m - A_c$	A_c	A_m	$\frac{M}{M+L}$	L cm ³	Cu ⁺² cm ³	
0.000	0.000	0.000	1.00	0.00	10.00	1
0.173	0.008	0.181	0.95	0.50	9.50	2
0.255	0.015	0.270	0.90	1.00	9.00	3
0.396	0.023	0.419	0.85	1.50	8.50	4
0.522	0.030	0.552	0.80	2.00	8.00	5
0.662	0.038	0.700	0.75	2.50	7.50	6
0.763	0.045	0.808	0.70	3.00	7.00	7
0.901	0.053	0.954	0.65	3.50	6.50	8
1.022	0.060	1.082	0.60	4.00	6.00	9
1.075	0.068	1.143	0.55	4.50	5.50	10
1.093	0.075	1.168	0.50	5.00	5.00	11
1.121	0.083	1.204	0.45	5.50	4.50	12
1.292	0.090	1.382	0.40	6.00	4.00	13
1.407	0.098	1.505	0.35	6.50	3.50	14
1.190	0.105	1.295	0.30	7.00	3.00	15
1.020	0.113	1.133	0.25	7.50	2.50	16
0.760	0.120	0.880	0.20	8.00	2.00	17
0.621	0.128	0.749	0.15	8.50	1.50	18
0.370	0.135	0.505	0.10	9.00	1.00	19
0.190	0.143	0.333	0.05	9.50	0.50	20
0.000	0.150	0.150	0.00	10.00	0.00	21

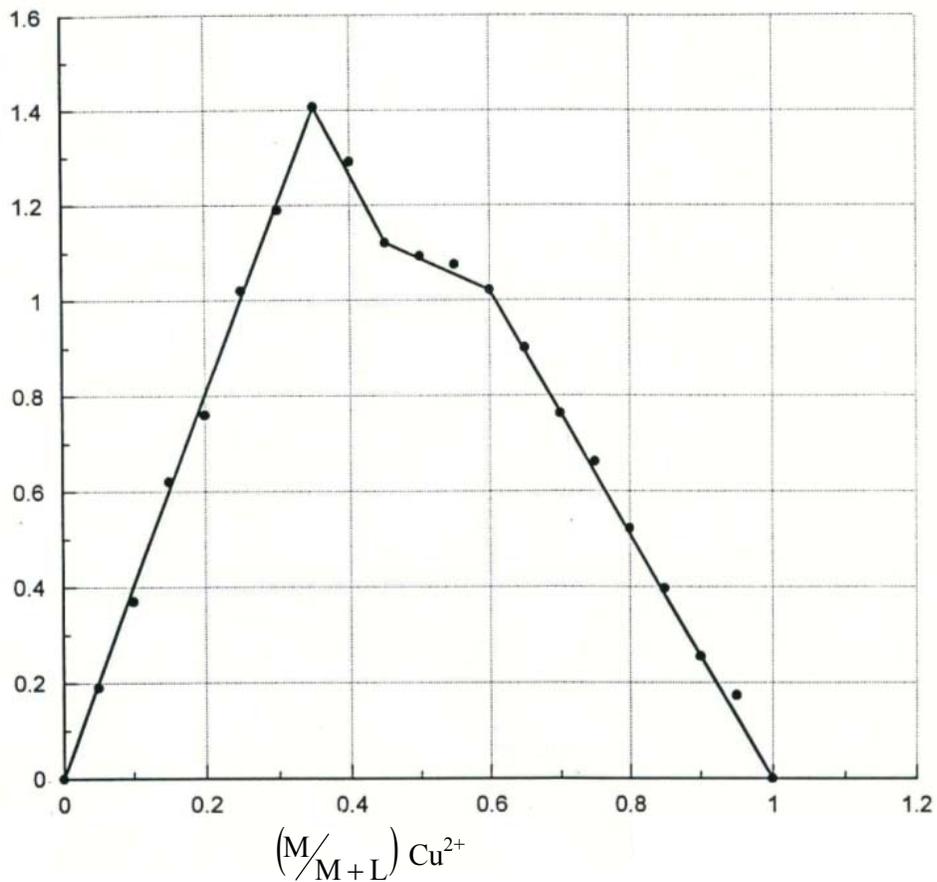
424

A_m

A_c

$A_m - A_c$

طريقة المتغيرات المستمرة



424

(1)

(2)

$$^{\circ}18=T \quad 5.00 =$$

$$424 = \lambda$$

$$0.01 = [L] = [Cu^{+2}]$$

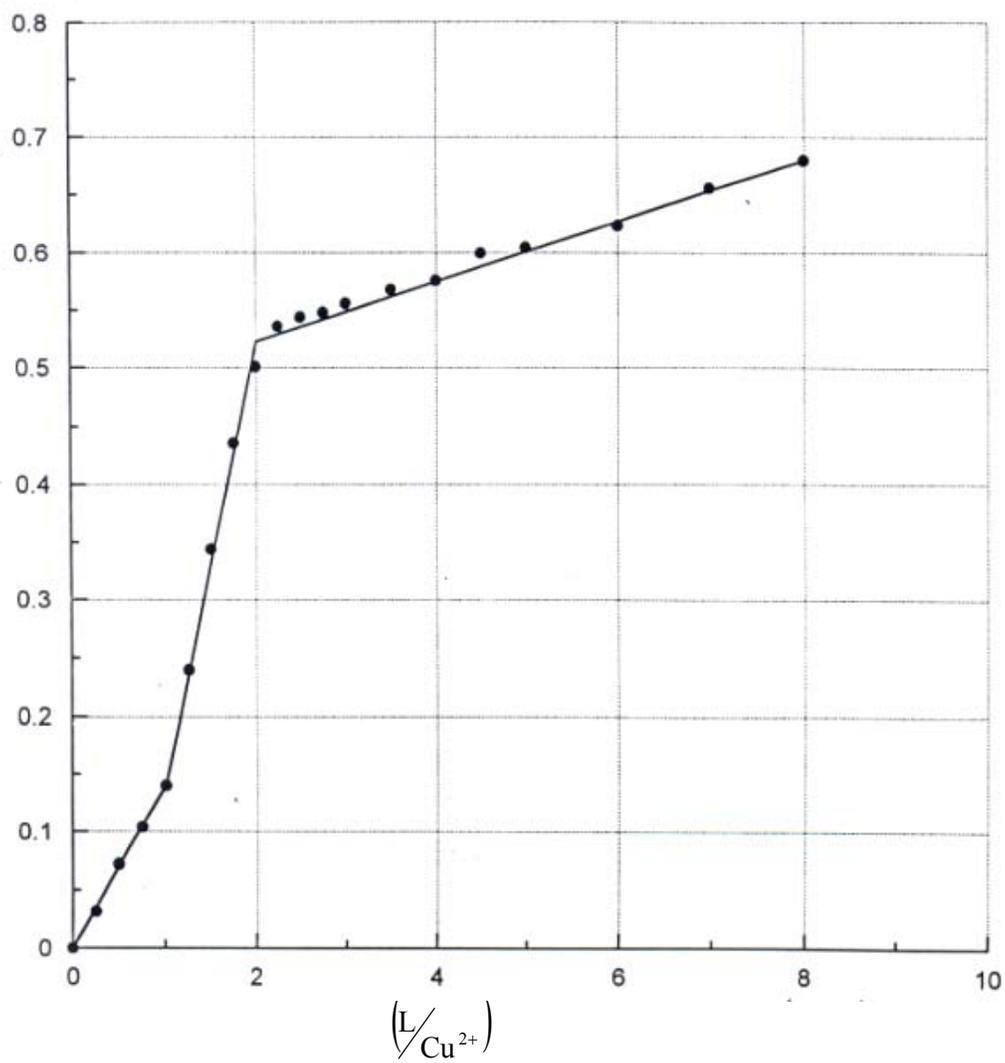
$A_m - A_c$	A_c	A_m	$\frac{M}{L}$	L cm^3	Cu^{+2} cm^3	
0.000	0.000	0.000	0.00	0.00	1.00	1
0.032	0.004	0.036	0.25	0.25	1.00	2
0.072	0.008	0.080	0.50	0.50	1.00	3
0.104	0.011	0.115	0.75	0.75	1.00	4
0.140	0.015	0.155	1.00	1.00	1.00	5
0.240	0.019	0.259	1.25	1.25	1.00	6
0.344	0.023	0.367	1.50	1.50	1.00	7
0.436	0.026	0.462	1.75	1.75	1.00	8
0.501	0.030	0.531	2.00	2.00	1.00	9
0.536	0.034	0.570	2.25	2.25	1.00	10
0.544	0.038	0.582	2.50	2.50	1.00	11
0.548	0.041	0.589	2.75	2.75	1.00	12
0.556	0.045	0.601	3.00	3.00	1.00	13
0.568	0.053	0.621	3.50	3.50	1.00	14
0.576	0.060	0.636	4.00	4.00	1.00	15
0.600	0.068	0.668	4.50	4.50	1.00	16
0.605	0.075	0.680	5.00	5.00	1.00	17
0.624	0.090	0.714	6.00	6.00	1.00	18
0.656	0.105	0.761	7.00	7.00	1.00	19
0.680	0.120	0.800	8.00	8.00	1.00	20
0.000	0.135	0.135	00	9.00	0.00	21

424

A_m

A_c

$A_m - A_c$



424

L/M

(2)

(3)

$${}^{18}T = 5.00 =$$

$$444 = \lambda$$

$$0.01 = [L] = [Cu^{+2}]$$

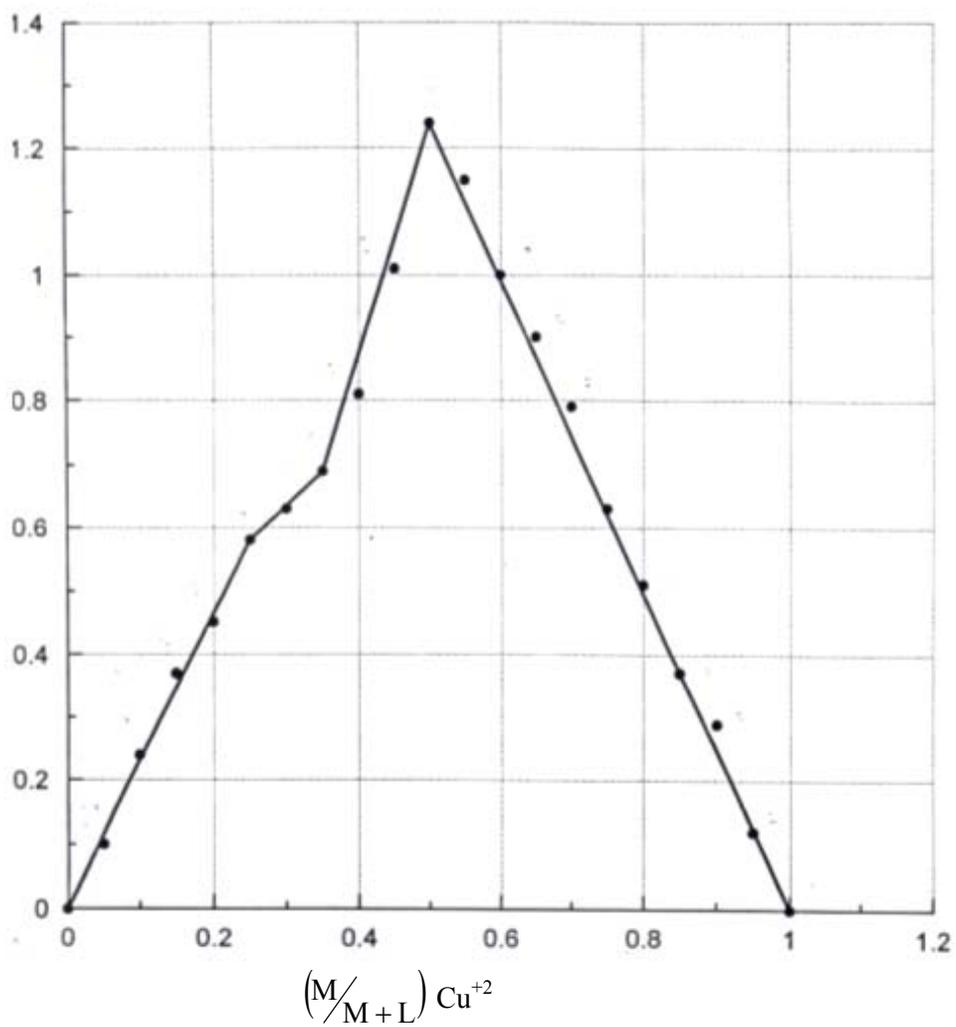
$A_m - A_c$	A_c	A_m	$\frac{M}{M+L}$	L cm^3	Cu^{+2} cm^3	
0.000	0.000	0.000	1.00	0.00	10.00	1
0.120	0.005	0.125	0.95	0.50	9.50	2
0.290	0.009	0.299	0.90	1.00	9.00	3
0.371	0.014	0.385	0.85	1.50	8.50	4
0.510	0.019	0.529	0.80	2.00	8.00	5
0.630	0.023	0.653	0.75	2.50	7.50	6
0.790	0.028	0.818	0.70	3.00	7.00	7
0.900	0.033	0.933	0.65	3.50	6.50	8
1.000	0.037	1.037	0.60	4.00	6.00	9
1.150	0.042	1.192	0.55	4.50	5.50	10
1.240	0.047	1.287	0.50	5.00	5.00	11
1.010	0.051	1.061	0.45	5.50	4.50	12
0.810	0.057	0.867	0.40	6.00	4.00	13
0.690	0.060	0.750	0.35	6.50	3.50	14
0.630	0.065	0.695	0.30	7.00	3.00	15
0.580	0.070	0.650	0.25	7.50	2.50	16
0.451	0.074	0.525	0.20	8.00	2.00	17
0.370	0.080	0.450	0.15	8.50	1.50	18
0.240	0.084	0.324	0.10	9.00	1.00	19
0.100	0.090	0.190	0.05	9.50	0.50	20
0.000	0.093	0.093	0.00	10.00	0.00	21

444

A_m

A_c

$A_m - A_c$



444

(3)

(4)

$$^{\circ}19=T \quad 5.00 =$$

$$444 = \lambda$$

$$0.01 = [L] = [Cu^{+2}]$$

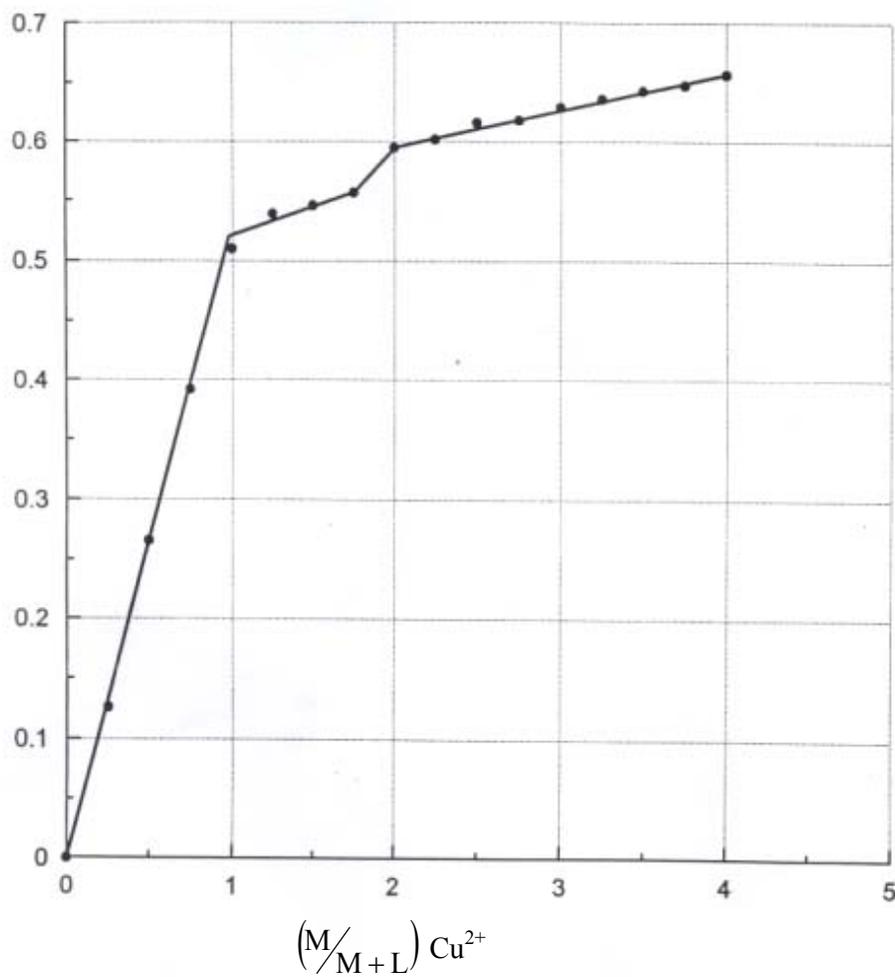
$A_m - A_c$	A_c	A_m	$\frac{M}{L}$	L cm^3	Cu^{+2} cm^3	
0.000	0.000	0.000	0.00	0.00	1.00	1
0.126	0.005	0.131	0.25	0.25	1.00	2
0.266	0.009	0.275	0.50	0.50	1.00	3
0.392	0.014	0.406	0.75	0.75	1.00	4
0.510	0.019	0.529	1.00	1.00	1.00	5
0.539	0.023	0.562	1.25	1.25	1.00	6
0.546	0.028	0.574	1.50	1.50	1.00	7
0.557	0.033	0.590	1.75	1.75	1.00	8
0.595	0.037	0.632	2.00	2.00	1.00	9
0.602	0.042	0.644	2.25	2.25	1.00	10
0.616	0.047	0.663	2.50	2.50	1.00	11
0.618	0.051	0.669	2.75	2.75	1.00	12
0.629	0.056	0.685	3.00	3.00	1.00	13
0.636	0.060	0.696	3.25	3.25	1.00	14
0.643	0.065	0.708	3.50	3.50	1.00	15
0.648	0.070	0.718	3.75	3.75	1.00	16
0.650	0.074	0.724	4.00	4.00	1.00	17
0.000	0.093	0.093	00	5.00	0.00	18

444

A_m

A_c

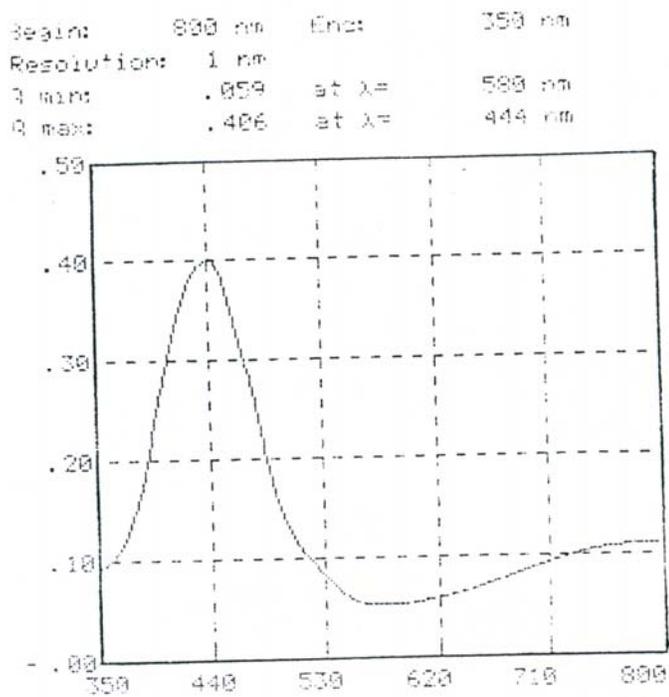
$A_m - A_c$



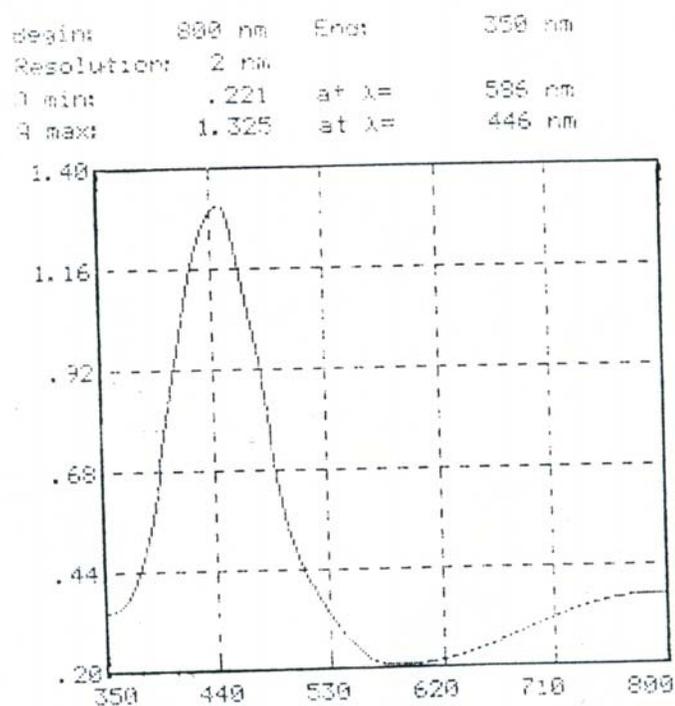
444

$$\frac{L}{M}$$

(4)

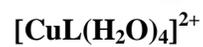


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(444)



(5)

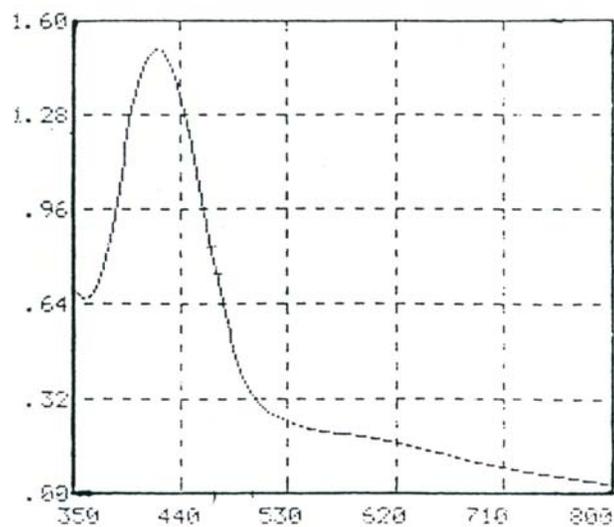
(.4)

(5)

(2)

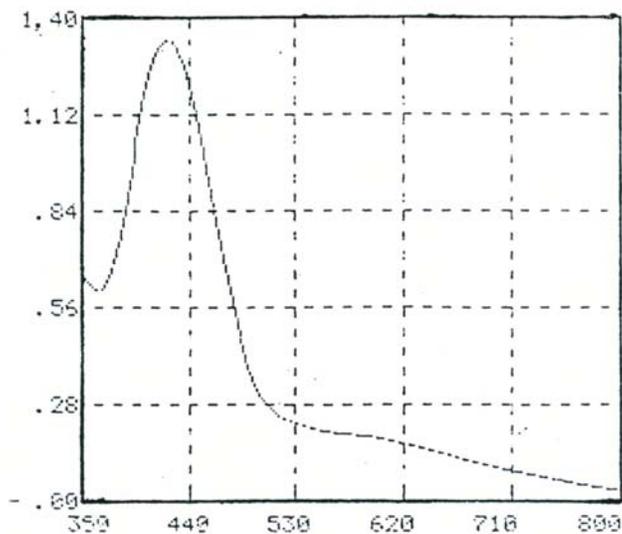
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Begin: 800 nm End: 350 nm
 Resolution: 2 nm
 A min: .055 at λ = 800 nm
 A max: 1.528 at λ = 424 nm



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Begin: 800 nm End: 350 nm
 Resolution: 2 nm
 A min: .054 at λ = 800 nm
 A max: 1.359 at λ = 424 nm

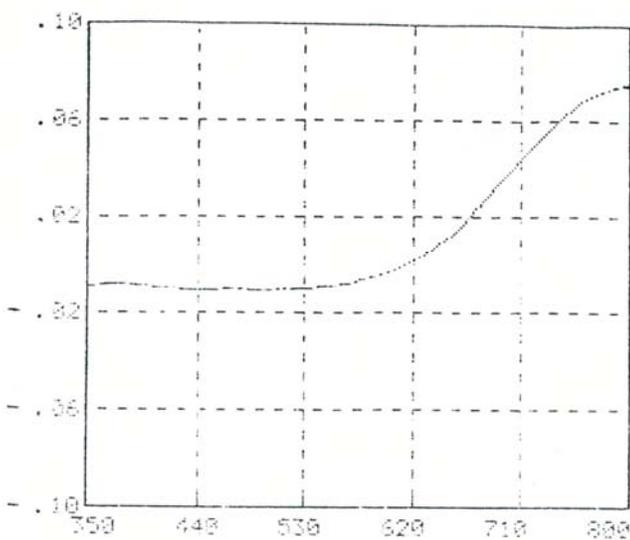


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(424) $[\text{CuL}(\text{H}_2\text{O})_4]^{2+}$ (6)

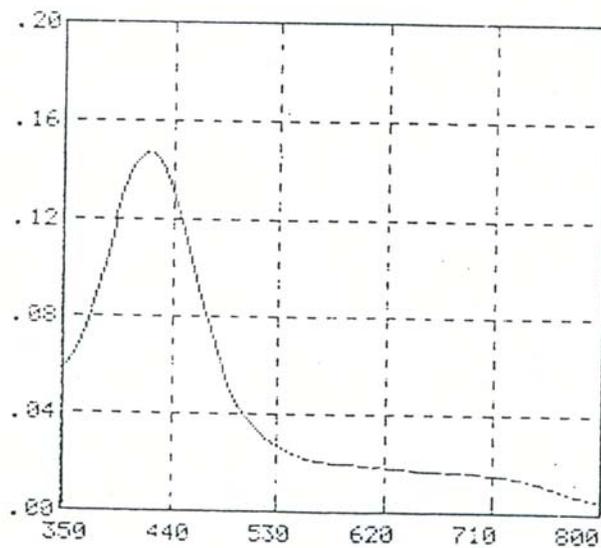
(4) (8) - (7) -

Begin: 800 nm End: 350 nm
 Resolution: 2 nm
 A min: -.009 at λ = 496 nm
 A max: .077 at λ = 800 nm



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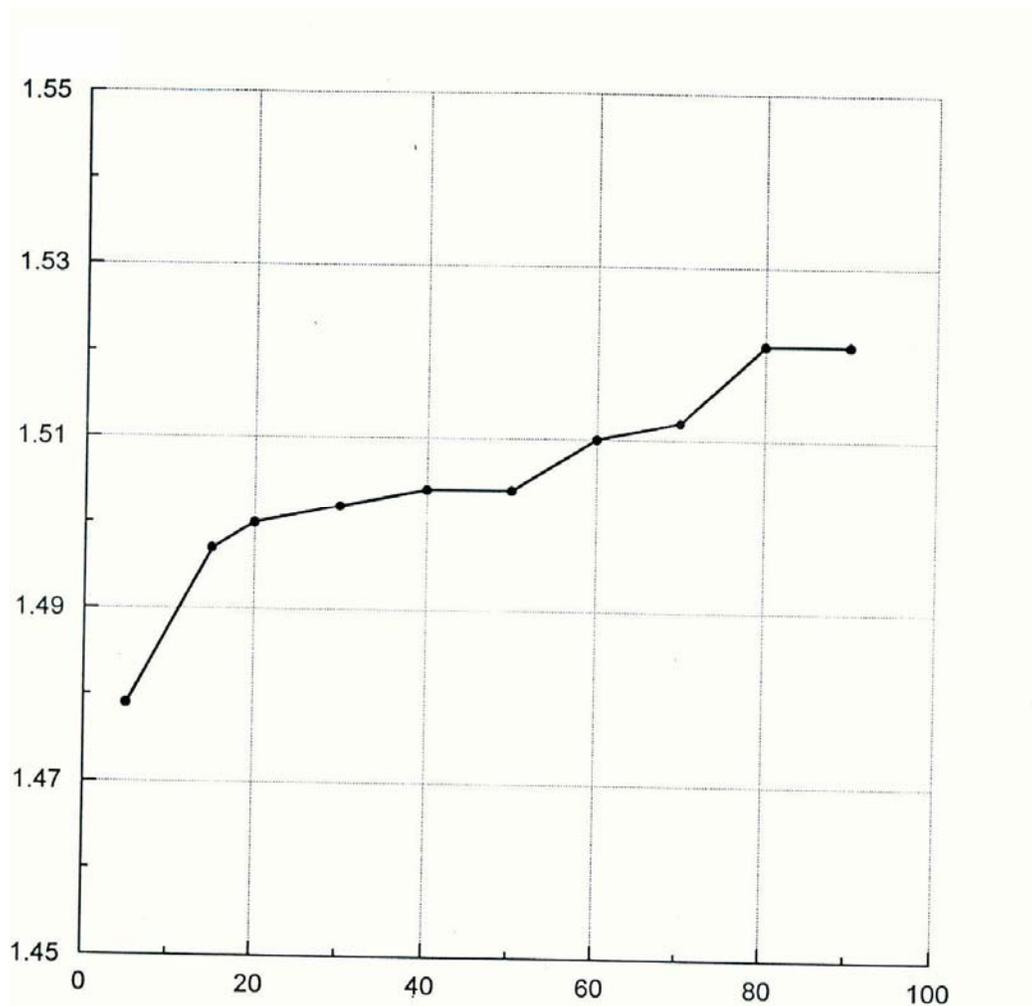
Begin: 800 nm End: 350 nm
 Resolution: 2 nm
 A min: .007 at λ = 796 nm
 A max: .150 at λ = 420 nm



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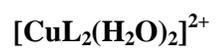
(424) $[\text{CuL}(\text{H}_2\text{O})_4]^{2+}$ (7)

(4) (14) - (1) -

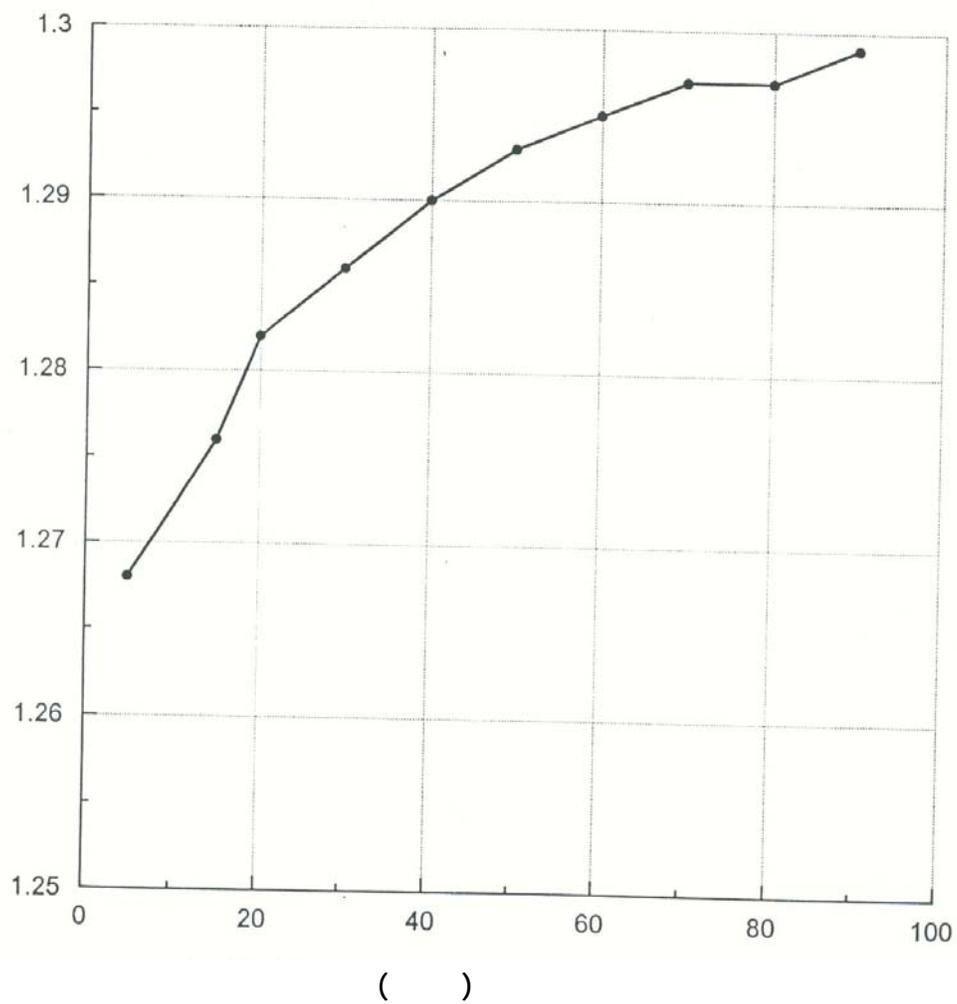


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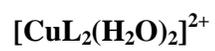
424



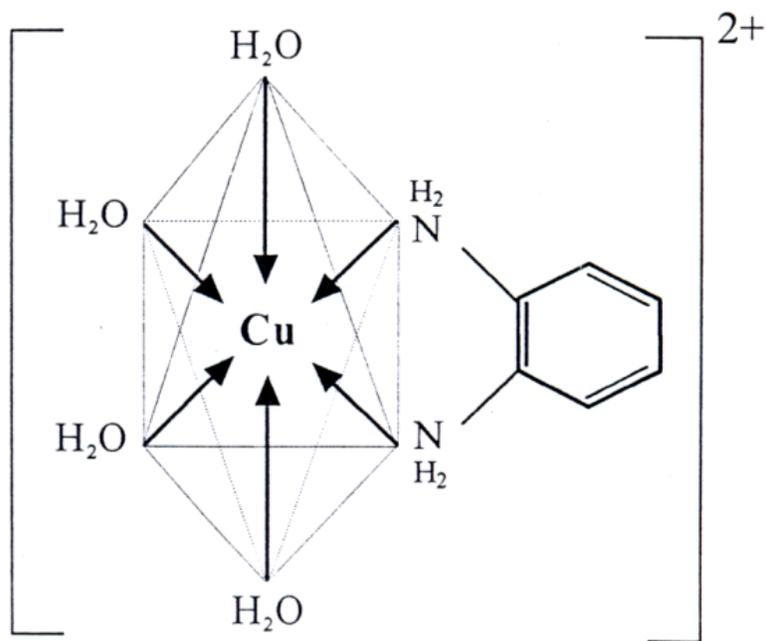
(8)



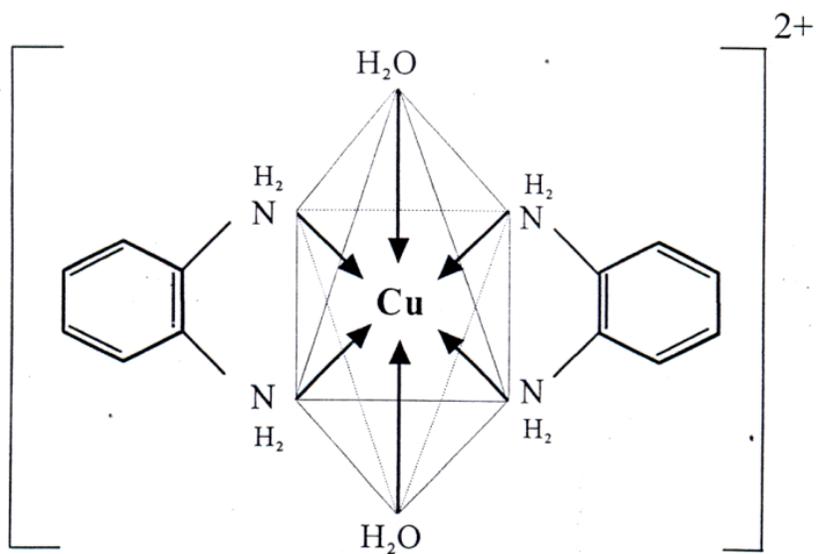
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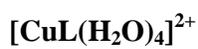
(9)



الشكل الفراغي للمعقد $[\text{CuL}(\text{H}_2\text{O})_4]^{+2}$

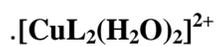


$[\text{Cu}_2\text{L}_2(\text{H}_2\text{O})_2]^{+2}$



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(10)



16. .
(1983)
17. Hathaway, B.J. and Billing, *Coord. Chem. Rev.*, 1970, 5, 1.
18. Beck, M.T., Chemistry of complex equilibria, Van Nostrand, London, 1976.
19. Sigel, H., *Angew. Chem., Int. Ed.*, 1976, 13, 394 .
20. Advanced Inorganic chemistry, Cotton, F.A. and Wilkinson, G.W., Fourth Edition, John Wiley Sons, Inc. U.S.A., (1976).
21. Concise Inorganic chemistry, Lee, J.D. and Hall, *Fourth Edition*, (1993).
22. Modern Inorganic chemistry, Lagowski, J.J. Marcel Dekker, Inc., New Youk ,2005.
23. Harvey, A.E. and Manning, J.A., *Chem. Soc.*, 1950, 72, 4488.
24. Bjerrum, J. and Nielson, E. *J., Acta. Chem. scan*, 1948, 7, 297 .
25. Gorden, G. and Birdwhistell, J., *Am. Chem soc.*, 1959, 81, 3567 .
1. Dittler-Klingeman, A.M. and Hahm, F.E., *Inorg. Chem.* 1996-1997, 35, .
2. Inorganic chemistry, Shriver & Atkins, Fourth *Edition*, *Oxford University Pres.* 2006.
3. Harvey, A.E. and Manning, J.A., *J. A. Chem. Soc.* 1950, 72, 4488 .
4. Golla, E.D. and Ayress, G.H., *Talanta* ,1973, 20, 199-210 .
5. Sufficient evidence of carcinogenicity in experimental animals, (NCI 1978).
6. Sufficient evidence of carcinogenicity in experimental animals (IARC 1982_{a,b}).
7. Handbook of carcinogenic potency and Genotoxicity Database, Gold and Zeiger, CRC Press, *Inc. Boca Raton*, 1997.
8. Supplement to the carcinogenic potency database, Gold L.S; Manley, N.B.; Slone, T.H. and Rohnbach, L. (CPDB 1999).
9. Reproductive and Cancer Hazard Assessment section, Office of environmental health assessment (DEHHA), California Environmental protection agency, August, 2003 .
10. Job, P. *Ann. Chem. (Paris)*, 1982, 9, 113.
11. Vosburgh, W.C. and Cooper, G.R., *J. Chem. Soc.* 1941, 63, 437.
12. Yoe, J.H. and Jones, A.C., *Inc. Eng. Chem., Anal. Ed.*, 1944, 16, 111 .
13. Hathaway, B.J. and Tomlinson, A.A.G., *Goord. Chem. Rev.*, 1970, 5, 143.
14. Gazo, J.; *et al.*, *Coord. Chem. Rev.*, 18, 253 .
15. Inorganic chemistry, Sharpe, A.G.; *Longman Group limited, U.K.* 1982 .