

Binuclear Complexes of Co(II), Ni(II), Cu(II) & Zn(II) With Mixed Ligand triethylenetetraamine dithiocarbamate & glycine

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Abstract:

New transition metal dithiocarbamates or dithiocarbamates and glycine complexes of the type $[M_2(L)A_2Cl_2]$, $[M_2(L)_2]$, and $[M_2(L)_2(A)_2]$ where M= Co(II), Ni(II), Cu(II) and Zn(II), A=amino acid, L=triethylene tetra amine dithiocarbamate, where prepared from triethylenetetraamine, CS_2 and Sodium hydroxide. The prepared ligands and complexes were characterized by IR, UV. Visible spectra, conductivity measurements and magnetic measurements.

The electronic spectra and magnetic measurements indicates that some of the complexes have square planer, tetrahedral and the other contain octahedral geometry .

معقدات ثنائية للكوبلت (II) والنيكل (I) والنحاس (II) والخاصين
(II) مع خليط من ترايإثيلنتترامين دايتايوكاربامات بين مع
الكلاسين

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ملخص البحث :

حضرت معقدات جديدة للعناصر الانتقالية مع الدايتايوكارباميت والدايتايوكارباميت
مع الكلاسين من نوع $[M_2(L)_2]$, $[M_2(L)A_2Cl_2]$ و $[M_2(L)_2(A)_2]$ حيث إن $M =$
Co(II) Ni(II) ، Cu(II) و Zn(II) و A = حامض اميني (كلاسين) و تراي إثلين نتترامين
دايتايوكارباميت . حضر الليكند من تراي إثلين نتترامين و CS_2 مع هيدروكسيد الصوديوم .

شخصت الليكندات والمعقدات المحضرة باستخدام طيف الاشعة تحت الحمراء وطيف الاشعة فوق البنفسجية والمرئية وقياس التوصيلية الكهربائية والقياسات المغناطيسية .
أوضحت قياسات الطيف الالكتروني والمغناطيسية إن بعض المعقدات تمتلك بنية مربع مستوي ورباعي السطوح والبعض الآخر من المعقدات يمتلك شكل ثماني السطوح .

Introduction

Dithiocarbamates are known to display both mono and bidentate ligands to transition metal centers. Transition metal complexes of dithiocarbamates present a wide range of application in agriculture, medicine, industry, analytical and organic chemistry⁽¹⁻³⁾. They were also used as molecular precursors in chemical vapour deposition processes ⁽⁴⁾ .

Square planar complexes of Ni(II) and Cu(II) with potassium 3-dithiocarboxy-3-aza-5-amino pentanoate have been prepared by direct synthesis. The obtained neutral complexes were characterized by elemental analysis, magnetic susceptibility measurements, infrared and electronic spectra. These results indicates that the complexes are contain square planer geometry ⁽⁵⁾ .

Nickel(II) amino acid dithiocarbamates complexes of the composition $[\text{Ni}(\text{AAdtc})(\text{PPh}_3)(\text{NCS})]$, $[\text{Ni}(\text{AAdtc})(\text{PPh}_3)(\text{CN})]$ and $[\text{Ni}(\text{AAdtc})(\text{PPh}_3)]\text{ClO}_4$, {(AAdtc=dithiocarbamate) derivative from amino acids i.e. glycine (glydtc), L-iso-leucine (i-leudtc) and L-proline (prodtc) were synthesized. The complexes were characterized by IR and electronic spectroscopy, thermal analysis, cyclic voltammetry and conductivity measurements⁽⁶⁾ .

Trinuclear complexes of the type $[\text{Sn}(\text{tch})_2\{\text{M}_2(\text{dtc})_4\}]$ where tch=thiocarbohydrazide,where prepared M=Mn(II), Fe(II), Co(II), Ni(II) and Cu(II), dtc=diethyldithiocarbamate. They were characterized on the basis of microanalytical, thermal, spectral (IR, UV-Vis, EPR, ¹HNMR) studies⁽⁷⁾ .

Many protein contain cystein and methanione residue and hence dithiocarbamate derivatives of α -amino acids may be valid models for the study of the coordination of proteins to the metal ions. The complexes formed between metal ions and dithiocarbamate derivatives of amino acids have been reported⁽⁸⁻¹⁰⁾ .

In the present work, we report the synthesis and characterization of some mixed ligand complexes of dithiocarbamate and amino acids.

Experimental :

All reagents were of analytical grade and used without further purification .

Synthesis of dithiocarbamate ligand (L) :

An aqueous solution of sodium hydroxide (0.8 g, 0.02 mol) was added with stirring to (1.5ml, 0.01mol) of triethylenetetraamine. The resulting mixture was cooled in ice, then (1.2 ml, 0.02 mol) carbon disulfide was added drop wise with continuous stirring.

The formed paste was extracted by (100cm³) ether filtered off, washed with ether and dried in vacuum .

Synthesis of [M₂(L)(A)₂Cl₂] :

A solution of CoCl₂.6H₂O(4.72 g, 0.02) in ethanol (10cm³) was added drop wise to an aqueous solution of (3.42 g, 0.01 mol) of the correspond dithiocarbamate ligand, to this mixture a solution of glycine (1.5 g, 0.02 mol) in ethanol (10cm³) was added. The resulting mixture was heated under reflux for 3h and then the solvent was evaporated the precipitate was filtered off, washed with ethanol and then diethylether and dried under vacuum .

Preparation of $[M_2(L)_2]$ complexes :

To a well stirred solution of ligand (L1) (6.84 g, 0.02 mol) in ethanol (15 cm³) was added (10 cm³) solution of metal dichloride (2 mmol) in the same solvent. This resulted in an immediate precipitation of the complexes. However, in few cases refluxing was also carried out in order to ensure complete precipitation. It was filtered off, washed with ethanol, then ether and dried under vacuum for several hours.

Preparation of $[M(L)_2(A)_2]$:

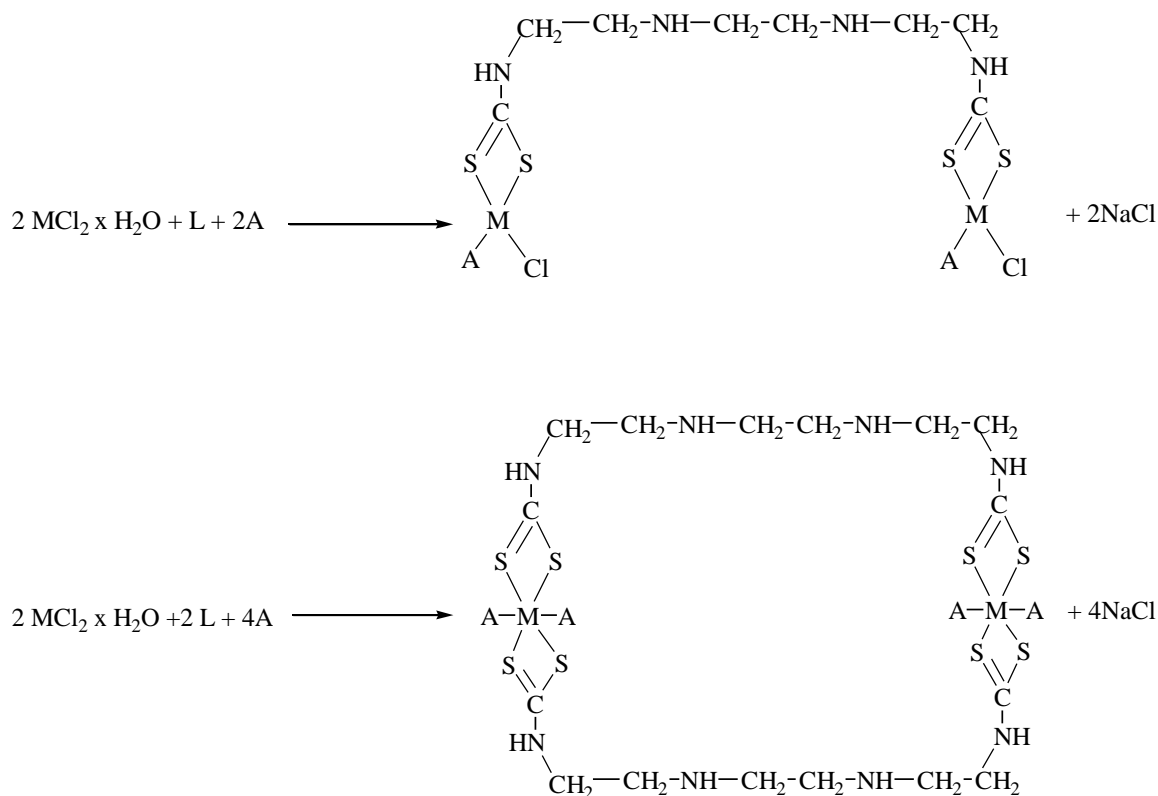
A mixture $[M_2(L)_2]$ (1 mmol) in dimethyl formamide (10 cm³) and glycine (2 mmol) in ethanol (10 cm³) was stirred for 3h , which afforded a thick precipitate, it was filtered, washed with ethanol and dried in vacuum.

Physical Measurement :

The metal contents have been determined by atomic absorption spectroscopy using a perkin Elmer spectrophotometer model . The infrared spectra has been recorded on FT-IR Brucker type Tensor 2710 in the range 200-4000 cm⁻¹ using CsI disc-Electronic spectra has been recorded on Shimadzu UV-1650, UV-Visible spectrophotometer for 10⁻³M solution of the ligand and their complexes in dimethylsulfoxide (DMSO) at 25°C using 1cm cell. Conductivity measurements have been carried out with an electrolytical conductivity measuring PCM3 (Jenway) conductivity using 10⁻³M dimethyl sulfoxide solution at 25°C. Magnetic susceptibility of the complexes have been determined by Brucker BM6 .

Results and discussion :

The complexes $[M_2(L)A_2Cl_2]$, $[M_2(L)_2]$ and $[M_2(L)_2(A)_4]$ were prepared as follows and gave satisfactory metal content (Table 1) L =disodium triethylene dithiocarbamate, A =glycine, M =Co,Ni,Cu,Zn .



The complexes are stable at room temperature. The conductivity measurements (10^{-3}M) in DMSO indicated that they are non-electrolytic nature ⁽¹¹⁾ and are insoluble in common organic solvents so all attempts to recrystallize these complexes were succeeded .

IR Spectra :

The most important IR bands of the complexes are given in Table (2). Tentative assignments are made according to the literature⁽¹²⁾ . The C–N and C–S stretching frequencies that can be used to differentiate between mono and bidentate modes of binding of dithiocarbamate ligands⁽¹³⁾ . The $1500\text{--}1470\text{ cm}^{-1}$ region allows to identify the nature of the

resulting complexes, in the complexes showing an $\nu(\text{CSS})$ chelate to metal coordination, the $\nu(\text{C-N})$ stretching frequencies are shifted to higher frequency by about 50cm^{-1} on coordination with metal ion⁽¹⁴⁾.

In the complexes reported in this paper, the presence of only one band in the region $(815-988)\text{ cm}^{-1}$ the $\nu(\text{CSS})$, suggests asymmetrical behaviour of the bidentate dithiocarbamate moiety.

The most diagnostic features of the infrared spectra are listed in (Table 2). The infrared spectra of the dithiocarbamate ligand showed a sharp bands at $890, 992, 1470, 3390\text{ cm}^{-1}$ which assigned to $\nu(\text{C-S})$, $\nu(\text{C=S})$, $\nu(\text{C-N})$ and $\nu(\text{NH}_2)$ respectively⁽¹⁵⁾ while for amino acid (Glycine) the following bands were observed at $3400, 1700, 3390\text{ cm}^{-1}$ which assigned to $\nu(\text{OH})$, $\nu(\text{C=O})$ and $\nu(\text{NH}_2)$ of amino acid. In complexes (1-4) the glycine amino acid was attached to the metal ions from $\nu(\text{OH})$, that was observed from decrease in the absorption of this band (Table 2), in complexes (5-8) the dithiocarbamate ligand coordinated to the metal ion bidentate fashion, in complexes (9-12) the amino acid was coordinated to the metal ions in the complexes through $\nu(\text{CO})$ which was obvious from the decrease of the stretching frequency of this band (Table 2). Further support of coordination of these derivatives was provided by the appearance of new bands at $460-380$ and $530-550\text{ cm}^{-1}$ which are assignal to $\nu(\text{M-S})$ and $\nu(\text{M-O})$ respectively⁽¹⁶⁾.

The electronic spectra of the complexes were recorded as 10^{-3}M solution in DMSO and the results were presented in (Table 2). The broad bands observed in the range $(31847-37313)\text{ cm}^{-1}$ are due to $\pi-\pi^*$ or $n-\pi^*$ within the dithiocarbamate group.

The magnetic moment values of Co(II) complexes no.(1,5) are (2.58 and 2.50 B.M) these values correspond to low spin square planer geometry for the complexes. The electronic spectra of the complexes show a band at $14792, 16447$ and 24906 cm^{-1} which may be assigned to

$^2A_{1g} \rightarrow ^2E_g$ transition in square planer geometry and a band at 37313 and 31847 cm^{-1} which may be assigned as charge transfer .

The magnetic moment of Co(II) complex(9) is 4.80 B.M which suggest an octahedral geometry of the complex. The electronic spectra of the complex (9) show the presence of three bands in the region 10204, 14836 and 16447 cm^{-1} which are assigned to $^4T_{1g}(F) \rightarrow ^4T_{2g}(F) \nu_1$, $^4T_{1g}(F) \rightarrow ^4A_{1g}(F) \nu_2$, $^4T_{1g}(F) \rightarrow ^4T_{2g}(p) \nu_3$ transition respectively. The band show that the position of spectra band have changed from square planer to octahedral environment⁽¹⁷⁾ .

The magnetic moment of Ni(II) complex (2,6) (0.3 and 0.8 B.M) which suggest a square planer geometry for these complexes.

The electronic spectra of the above complexes show one band at 14792 and 15105 cm^{-1} , this band assigned to $^1A_{1g} \rightarrow ^1B_{2g}$ transition . These results suggest a square planer geometry around nickel ion⁽¹⁸⁾ .

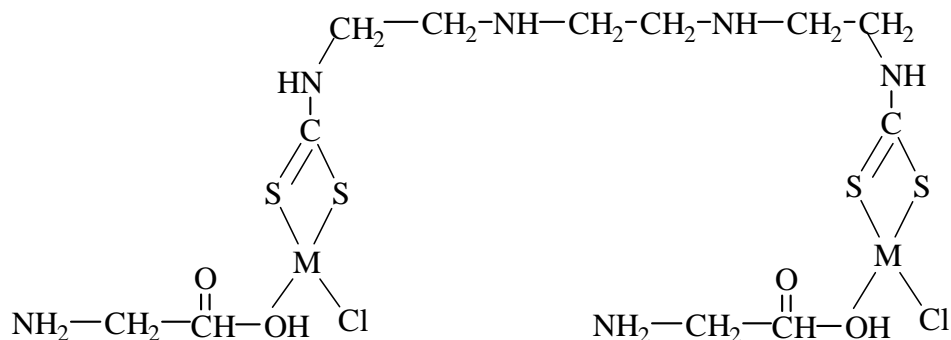
The magnetic moment of Ni(II) complex (10) is 2-80 B.M indicates the presence of two electrons and have octahedral geometry. The electronic spectra of Ni(II) complex (10) show the presence of three band in the region 10383, 15898 and 21929 cm^{-1} which were assigned to $^3A_{2g} \rightarrow ^3T_{2g} (F_T) (\nu_1)$, $^3A_{2g} \rightarrow ^3T_{1g} (F) (\nu_2)$ and $^3A_{2g} \rightarrow ^3T_{1g} (p)$ respectively this show that the geometry of the complex is octahedral⁽¹⁹⁾.

The magnetic moment of Cu(II) complexes (3,7) has been found 2.20 and 1.06 B.M which indicates the presence of one unpaired electron.

The electronic spectra of Cu(II) complexes show a bands at 16666 and 15151 cm^{-1} which are assigned to $^2T_2 \rightarrow ^2E$ transition in tetrahedral environment⁽²⁰⁾. For Cu(II) complex (11) have a band at 16600 and 23148 cm^{-1} which may be assigned to $^2B_{1g} \rightarrow ^2A_{1g}$, $^2B_{1g} \rightarrow ^2B_{2g}$ transition respectively. This show that Cu(II) complex have distorted octahedral geometry.

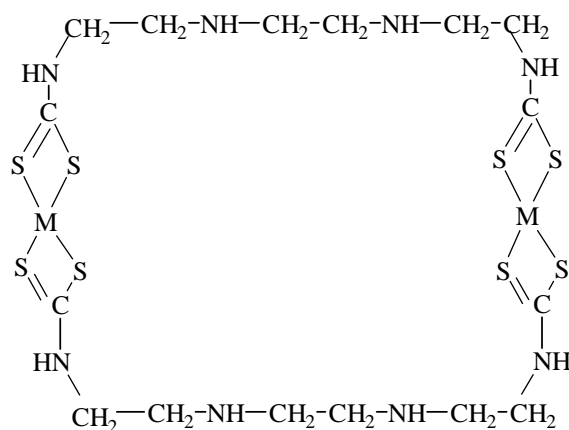
The μ_{eff} values of Zn(II) complexes (4,8,12) shows that they are diamagnetic as expected and the electron spectra of 4 & 8 show they are tetrahedral and 12 is octahedral geometry.

From the foregoing discussion and depending upon the different measurements we can suggest the following structures for the complexes:



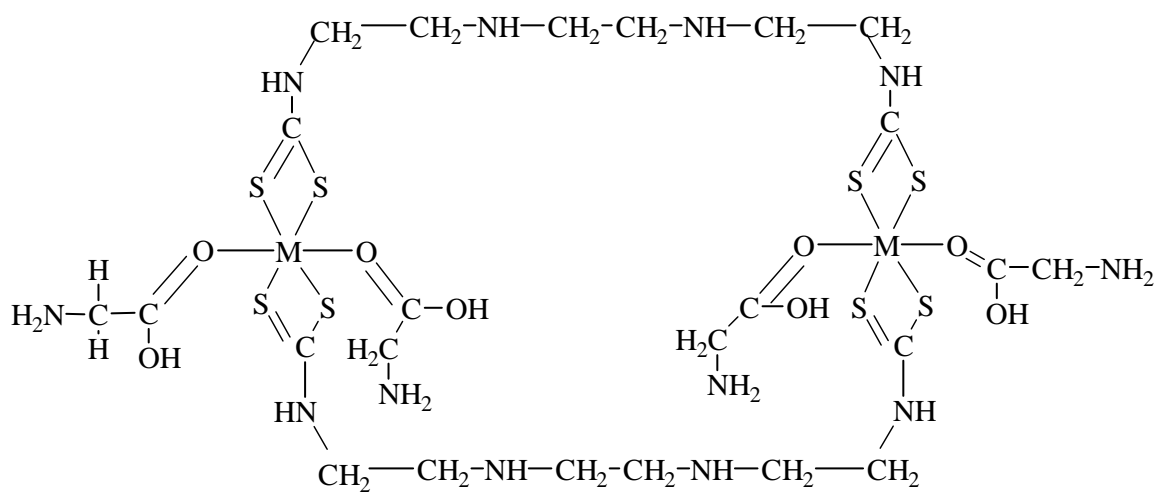
M= Co(II), Ni(II), Cu(II), Zn(II)

Fig (1): Suggested structure for the complexes
 $[\text{M}_2(\text{C}_6\text{H}_{18}\text{N}_4\text{C}_2\text{S}_4)(\text{NH}_2\text{CH}_2\text{COOH})_2(\text{Cl})_2]$



M= Co(II), Ni(II), Cu(II), Zn(II)

Fig (2): Suggested structure for the complexes
 $[\text{M}_2(\text{C}_6\text{H}_{18}\text{N}_4\text{C}_2\text{S}_4)_2]$



M= Co(II), Ni(II), Cu(II), Zn(II)

Fig (3): Suggested structure for the complexes
 $[M_2(C_6H_{18}N_4C_2S_4)_2(NH_2CH_2COOH)_4]$

Table (1) : physical properties of compounds and complexes :

No.	Compound	Colour	m.p (°C)	μ_{eff} (B.M)	Ω_{m}^{-1} 1,cm ² .mol ⁻¹	M%	
						Found	(calculated)%
1.	[Co ₂ (C ₆ H ₁₈ N ₄ C ₂ S ₄)(NH ₂ CH ₂ COOH) ₂ (Cl) ₂]	Green	180	0.3	13	18.78	(18.65)
2.	[Ni ₂ (C ₆ H ₁₈ N ₄ C ₂ S ₄)(NH ₂ CH ₂ COOH) ₂ (Cl) ₂]	Deep green	230	2.58*	16	18.66	(18.57)
3.	[Cu ₂ (C ₆ H ₁₈ N ₄ C ₂ S ₄)(NH ₂ CH ₂ COOH) ₂ (Cl) ₂]	Green	220	2.2	19	19.75	(19.87)
4.	[Zn ₂ (C ₆ H ₁₈ N ₄ C ₂ S ₄)(NH ₂ CH ₂ COOH) ₂ (Cl) ₂]	White	160	----	16.8	20.19	(20.35)
5.	[Co ₂ (C ₆ H ₁₈ N ₄ C ₂ S ₄) ₂]	Green	180	2.5	13.3	16.45	(16.59)
6.	[Ni ₂ (C ₆ H ₁₈ N ₄ C ₂ S ₄) ₂]	Deep green	160	0.8	17	16.70	(16.54)
7.	[Cu ₂ (C ₆ H ₁₈ N ₄ C ₂ S ₄) ₂]	yellowish green	260	1.6*	15.1	17.59	(17.67)
8.	[Zn ₂ (C ₆ H ₁₈ N ₄ C ₂ S ₄) ₂]	White	170	----	7.7	17.65	(17.58)
9.	[Co ₂ (C ₆ H ₁₈ N ₄ C ₂ S ₄) ₂ (NH ₂ CH ₂ COOH) ₄]	Green	150	4.8*	7.6	11.87	(11.71)
10.	[Ni ₂ (C ₆ H ₁₈ N ₄ C ₂ S ₄) ₂ (NH ₂ CH ₂ COOH) ₄]	Deep green	180	2.8*	8.6	11.75	(11.67)
11.	[Cu ₂ (C ₆ H ₁₈ N ₄ C ₂ S ₄) ₂ (NH ₂ CH ₂ COOH) ₄]	yellowish green	220	1.8*	9.0	12.44	(12.52)
12.	[Zn ₂ (C ₆ H ₁₈ N ₄ C ₂ S ₄) ₂ (NH ₂ CH ₂ COOH) ₄]	White	160	----	16.1	12.78	(12.83)

* per metal ion .

Table (2) : Electronic and IR spectral data compounds and complexes

U.V-Vis bands cm ⁻¹					Selected IR bands cm ⁻¹											
Comp.No.	ν_1	ν_1	ν_1	C.I	Comp.No.	$\nu(\text{C-S})$	$\nu(\text{C=S})$	$\nu(\text{C=O})$	$\nu(\text{C=N})$	$\nu(\text{C-H})$	$\nu(\text{N-H})$	$\nu(\text{NH}_2)$	$\nu(\text{O-H})$	$\nu(\text{Al-Cl})$	$\nu(\text{Al-O})$	$\nu(\text{Al-S})$
(C ₆ H ₁₃ N ₄ C ₂ S ₄)	----	----	----	31847	(S(S)(NHR) ₂	890	1050	----	1470	2934	3100	3390	----	----	----	----
1	14792	16447	----	37313	2	875	1020	1665	1484	2920	3080	3345	3330	310	431	350
2	14792	----	----	----	1	860	1025	1700	1456	2924	3094	3390	3350	300	470	370
3	16666	----	----	----	3	870	1015	1640	1423	2930	3104	3330	3365	310	479	375
4	----	----	----	----	4	885	1025	1650	1477	2929	3132	3300	3380	295	446	390
5	25906	----	----	31847	6	870	998	----	1499	2925	3020	----	----	----	----	380
6	15105	----	----	----	5	865	1010	----	1490	2925	3140	----	----	----	----	410
7	15151	----	----	----	7	880	980	----	1503	2935	3080	----	----	----	----	400
8	----	----	----	----	8	865	960	----	1478	2932	3098	----	----	----	----	395
9	10204	14863	16447	----	10	885	1020	1630	1486	2926	3104	3223	3443	320	535	380
10	10383	15898	21929	----	9	870	998	1650	1490	2925	3050	3325	3417	300	540	360
11	16600	23148	----	----	11	880	1030	1645	1475	2924	3080	3225	3443	300	530	375
12	----	----	----	----	12	875	998	1637	1480	2900	3094	3300	3454	290	550	370

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