# 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 charactericed 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) والخارصين (II) مع خليط من تراياثلينتترامين دايثايوكاربامات بين مع الكلاسين

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## ملخص البحث :

حضرت معقدات جديدة للعناصر الانتقالية مع الداي ثايوكارباميت والداي ثايوكارباميت مع الكلايسين من نوع $[M_2(L)A_2Cl_2]$،$[M_2(L)_2]$ و $[M_2(L)_2(A)_2]$ حيث إن M= Ni(II) Co(II) ، Cu(II) وZn(II) و A= حامض اميني (كلايسين) و تراي اثلين تترا امين داي كارباميت . حضر الليكند من تراي اثلين تترامين 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 الأخر 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 [Ni(AAdtc)($PPh_3$)(NCS)] , [Ni(AAdtc)($PPh_3$)(CN)] and [Ni(AAdtc)($PPh_3$)]$ClO_4$, {(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 voltammetery and conductivity measurements(6) .

Trinuclear complexes of the type [Sn(tch)$_2${$M_2$(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, $^1$HNMR) 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 (100cm$^3$) ether filtered off, washed with ether and dried in vacuum .

**Synthesis of $[M_2(L)(A)_2Cl_2]$ :**

A solution of $CoCl_2.6H_2O$(4.72 g, 0.02) in ethanol (10cm$^3$) 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 (10cm$^3$) 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 $cm^3$) was added (10 $cm^3$) 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 inorder to ensure complete precipitation. It was filtered off, washed with ethanol, then ether and dried under vacuum for several hours.

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

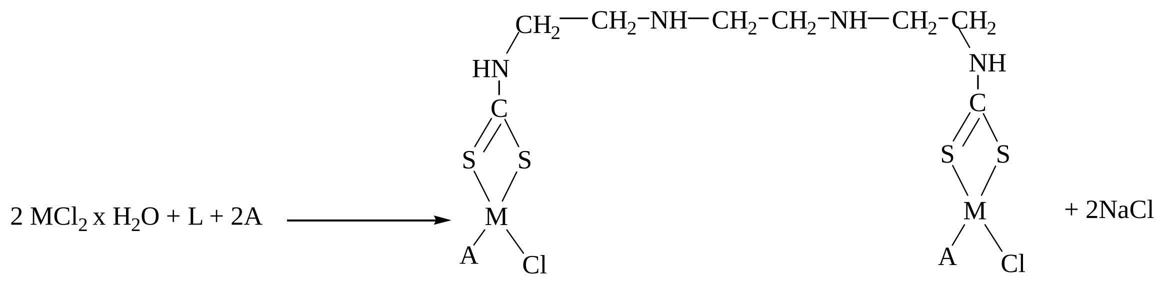
A mixture $[M_2(L)_2]$(1 mmol) in dimethyl formamade (10 $cm^3$) and glycine (2 mmol) in ethanol (10 $cm^3$) was stirred for 3h , which afforded athick precipitate, it was filtered, washed with ethanol and dried in vacuum.

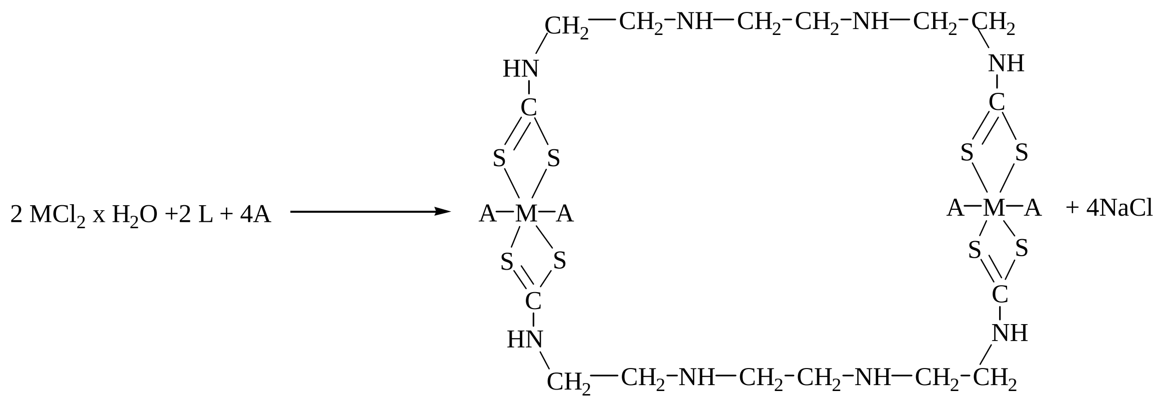
## Physical Measurement :

The metal contents have been determined by atomic a 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$10^{-3}$M solution of the ligand and their complexes in dimethylsulfoxide (DMSO) at 25°C using 1cm cell. Conductivity measurements have been carried out with with an electrolytical conductivity measuring PCM3 (Jenway) conductivity using $10^{-3}$M 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 succeded .

## 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 1500-1470 $cm^{-1}$ region allows to identify the nature of the resulting complexes, in the complexes showing an υ(CSS) chelate to metal coordination, the υ(C–N) stretching frequencies are shifted to higher frequency by about 50$cm^{-1}$ on coordination with metal ion[14] .

In the complexes reported in this paper, the presence of only one band in the region (815-988) $cm^{-1}$ the υ(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 $cm^{-1}$ which assigned to υ(C–S), υ(C=S), υ(C–N) and υ($NH_2$) respectively[15] while for amino acid (Glycine) the following bands were observed at 3400, 1700, 3390 $cm^{-1}$ which assigned to υ(OH), υ(C=O) and υ($NH_2$) of amino acid. In complexes (1-4) the glycine amino acid was attached to the metal ions from υ(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 υ(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 $cm^{-1}$ which are assignal to υ(M–S) and υ(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) $cm^{-1}$ 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

$^2A^1g \rightarrow {}^2Eg$ 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 $^4T_1g(F) \rightarrow {}^4T_2g(F)\ \upsilon_1$ , $^4T_1g(F) \rightarrow {}^4A_1g(F)\ \upsilon_2$ , $^4T_1g(F) \rightarrow {}^4T_2g(p)\ \upsilon_3$ 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) .

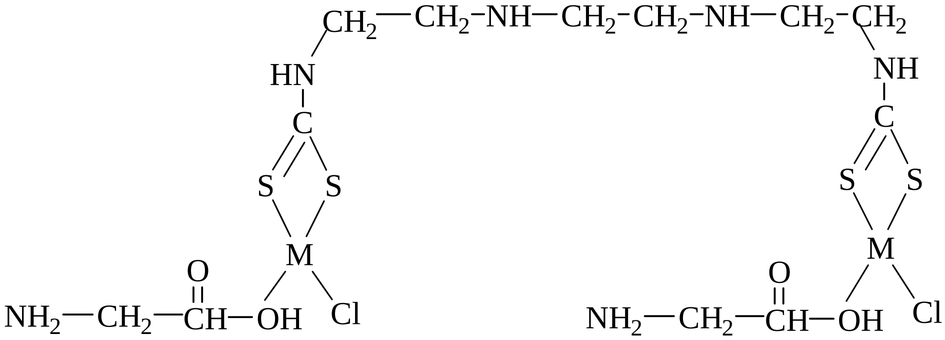
The magnetic moment of Ni(II) complex (10) is 2-80 B.M indicates the presence of two electrons and have octahedral geometry. The electronic spectra of Ni(II) complex (10) show the presence of three band in the region 10383, 15898 and 21929 $cm^{-1}$ which were assigned to $^3A_2g \rightarrow {}^3T_2g\ (F_T)\ (\upsilon_1)$ , $^3A_2g \rightarrow {}^3T_1g\ (F)\ (\upsilon_2)$ 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.

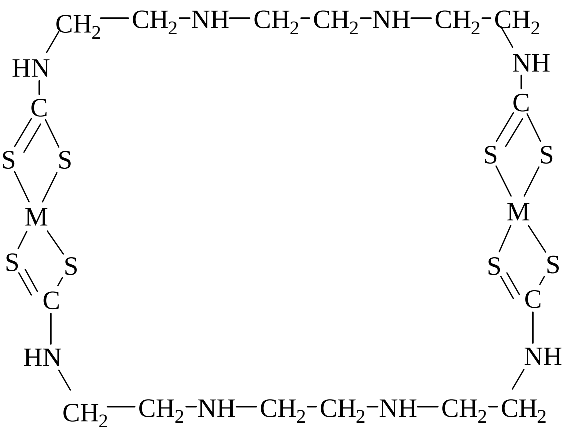
The µeff values of Zn(II) complexes (4,8,12) shows that they are diamagnetic as expected and the electron spectra of 4 & 8 show they are tetrahedral and 12 is octahedral geometry.

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



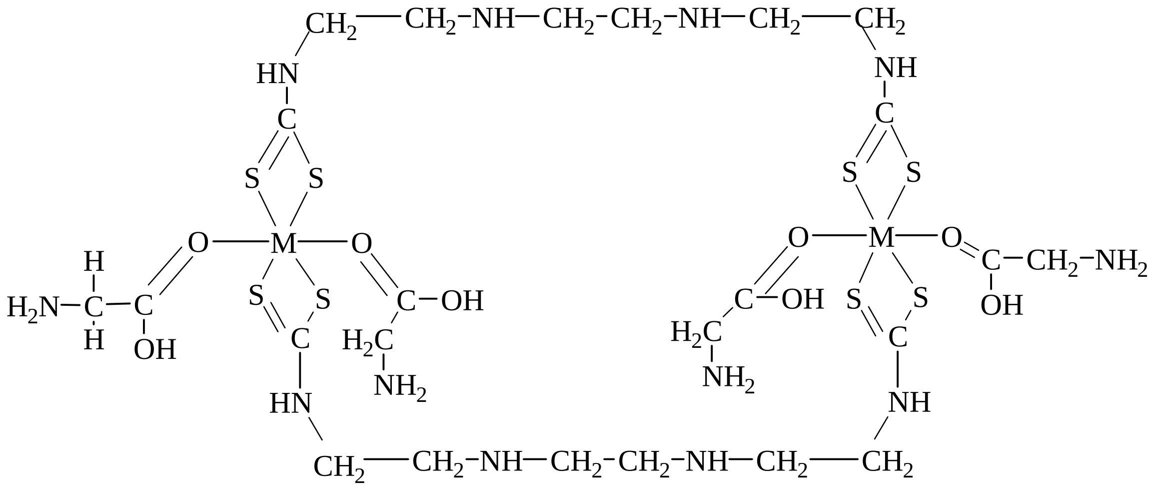
**M= Co(II), Ni(II), Cu(II), Zn(II)**

**Fig (1): Suggested structure for the complexes $[M_2(C_6H_{18}N_4C_2S_4)(NH_2CH_2COOH)_2(Cl)_2]$**



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

**Fig (2): Suggested structure for the complexes $[M_2(C_6H_{18}N_4C_2S_4)_2]$**



**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) | μeff (B.M) | $Ohm^{-1}.cm^2.mol^{-1}$ | M% Found | M% (calculated)% |
|---|---|---|---|---|---|---|---|
| **1.** | $[Co_2(C_6H_{18}N_4C_2S_4)(NH_2CH_2COOH)_2(Cl)_2]$ | Green | 180 | 0.3 | 13 | 18.78 | (18.65) |
| **2.** | $[Ni_2(C_6H_{18}N_4C_2S_4)(NH_2CH_2COOH)_2(Cl)_2]$ | Deep green | 230 | 2.58* | 16 | 18.66 | (18.57) |
| **3.** | $[Cu_2(C_6H_{18}N_4C_2S_4)(NH_2CH_2COOH)_2(Cl)_2]$ | Green | 220 | 2.2 | 19 | 19.75 | (19.87) |
| **4.** | $[Zn_2(C_6H_{18}N_4C_2S_4)(NH_2CH_2COOH)_2(Cl)_2]$ | White | 160 | ---- | 16.8 | 20.19 | (20.35) |
| **5.** | $[Co_2(C_6H_{18}N_4C_2S_4)_2]$ | Green | 180 | 2.5 | 13.3 | 16.45 | (16.59) |
| **6.** | $[Ni_2(C_6H_{18}N_4C_2S_4)_2]$ | Deep green | 160 | 0.8 | 17 | 16.70 | (16.54) |
| **7.** | $[Cu_2(C_6H_{18}N_4C_2S_4)_2]$ | yellowish green | 260 | 1.6* | 15.1 | 17.59 | (17.67) |
| **8.** | $[Zn_2(C_6H_{18}N_4C_2S_4)_2]$ | White | 170 | ---- | 7.7 | 17.65 | (17.58) |
| **9.** | $[Co_2(C_6H_{18}N_4C_2S_4)_2(NH_2CH_2COOH)_4]$ | Green | 150 | 4.8* | 7.6 | 11.87 | (11.71) |
| **10.** | $[Ni_2(C_6H_{18}N_4C_2S_4)_2(NH_2CH_2COOH)_4]$ | Deep green | 180 | 2.8* | 8.6 | 11.75 | (11.67) |
| **11.** | $[Cu_2(C_6H_{18}N_4C_2S_4)_2(NH_2CH_2COOH)_4]$ | yellowish green | 220 | 1.8* | 9.0 | 12.44 | (12.52) |
| **12.** | $[Zn_2(C_6H_{18}N_4C_2S_4)_2(NH_2CH_2COOH)_4]$ | 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.** | $\upsilon_1$ | $\upsilon_1$ | $\upsilon_1$ | C.T | **Comp. No.** | υ(C–S) | υ(C=S) | υ(C=O) | υ(C=N) | υ(C–H) | υ(N–H) | $\upsilon(NH_2)$ | υ(O–H) | υ(M–Cl) | υ(M–O) | υ(M–S) |
| $(C_6H_{18}N_4C_2S_4)$ | ---- | ---- | ---- | 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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