

# Synthesis and characterization of some new mononuclear complexes of Co(II), Ni(II), Cu(II) and Zn(II) with N<sub>2</sub>S<sub>2</sub> donor Schiff base ligands

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**Abstract :** Two new tetradentate ligands (L1 and L2) N,N'-bis {(o-aminophenylthio)bromo propyl} 1-phenyl butane 1,3-dilidene (L1), N, N'-bis (3- bromo propyl (phenylthio) imino)1,1,1-trifluoro -3-(2-theonyl) acetone (L2) were prepared from the reaction of equimolar amount of (o-aminophenylthio) propylbromide and benzoylacetone or 2-theonyltrifluoro acetone in (2:1) molar ratio. Reaction of the above ligands with cobalt(II), nickel(II), copper (II) and zinc(II) chloride salts gave the complexes of the general formulas: [M(L)]Cl<sub>2</sub> and [Zn(L)Cl<sub>2</sub>], M= Co(II), Ni(II), Cu(II) and Zn(II), L= L1-L2. The synthesized ligands and their complexes were characterized by their elemental analysis FTIR, UV-Vis, metal content, conductivity measurement and magnetic measurement. On the basis of these studies at four coordinate tetrahedral geometry around the metal ion has been proposed and the ligands behave as tetradentate from nitrogen atoms of the azomthine and two sulfur atoms while for zinc (II) complexes from the two sulfur atoms and two chloride ions.

## INTRODUCTION

Studies of transition metal complexes of Schiff bases include wide subject comprising organometallic compounds and several aspect of biocoordination chemistry. These complexes allow systematic studies based on modified ancillary ligands<sup>(1-2)</sup>, and play important role in the development of coordination chemistry related to catalysis and enzymatic reactions, magnetism and bioinorganic modeling studies<sup>(3,4)</sup>. Koizami et.al<sup>(5)</sup> were studied the synthesis of nickel (II) complexes bearing, a K<sup>3</sup>SNS-pincer ligand, 2, 5-bis (benzylaminothio- carbonyl) pyrrolyl and K<sup>3</sup>SCS-pincer ligand, 2,6-bis(benzylaminothio- carbonyl) phenyl, their structures and their electrochemical properties were characterized. The crystal structures of [Ni(SNS)Br] and [Ni(SCS)Br] were determined by X-ray crystallography. The electrochemical and crystallographic data obtained from the complexes revealed that the K<sup>3</sup>SCS ligand has a stronger electron donating ability than the K<sup>3</sup>SNS ligands. Copper (II) complexes of a series of linear pentadentate ligands containing two benzimidazole, two thioether sulfurs and amine nitrogen vis N,N'-bis(4'(2"-benzimidazolyl)3'-thiabutyl)amine (L<sup>1</sup>),N,N'-bis(4'(2"-benzimidazolyl)methyl-3'-thiabutyl)N-methylamine (L<sup>2</sup>) 2,6-bis-(4'(2"-benzimidazolyl) (methyl)-3'-thiabutyl) pyridine (L<sup>3</sup>) have been isolated and characterized by electronic absorption and EPR spectroscopy, cyclic and differential pulse voltammetry of these complexes. The [Cu(L<sup>1</sup>)] (BF<sub>4</sub>)<sub>2</sub> (1) and [Cu(L<sup>2</sup>)](BF<sub>4</sub>)<sub>2</sub>(2) have been structurally characterized by X-ray crystallography. The coordination geometries around copper(II) in (1) and (2) are described as trigonal bipyramidal distorted square based pyramidal geometry.<sup>(6)</sup> Four zinc (II) and four cobalt(II) compounds derived from (N-benzothiazol-2yl)-dithiocarbamicmethylester,1,benzothiazol-2-ylid-3-mthyl-thiourea, 1-benzothiazol-2yl-3,3-dimethyl-isothiourea and N-(benzothiazol-2yl)-5,5'-dimethyldithiocarbomine are reported<sup>(7)</sup>. The complexes were characterized in the solid state by UV-Vis –NIR diffuse reflectance ,IR. Mass spectrometry and by single crystal X-ray diffraction analysis.

The reaction of zinc(II) acetate with variety of 2-substituted benzothiazolines afford tetrahedral mononuclear complexes with N<sub>2</sub>S<sub>2</sub> donor set[Zn(R-Ph-C(H)=N-C<sub>6</sub>H<sub>4</sub>-S)<sub>2</sub>]<sup>(8)</sup>.The obtained zinc(II) complexes can be divided into three groups based on the characteristics of the absorption spectra group 1 (R= 2,4,6-triMe(1),2,6diCl(2)) showing the intense band at 250-300 nm and weak band at 400-450 nm. Group (2) (R=4-Cl(3),H(4),4Et(5),4-OMe(6) showing two intense band at 250-300 nm and a weak band at 400-450 nm, and group (3)(R=4-Me(7),4OEt(8) showing an intense band 280-300 nm and two very intense bands at 350-450 nm . A new Schiff ligand having a potentially coordinating thioether group(2-quinoline-N-C2'-methylthiophenyl)methyleneimine (qmtpm) has been prepared. The synthesis , structure, UV-Vis and EPR studies of one copper (II) and two cobalt (II) complexes from this ligand is reported. The X-ray structures of the Cu(II) and Co(II) chloride complexes (1) and (2) reveal the metal atoms in highly distorted square pyramidal environment<sup>(9)</sup>. The new mononuclear complexes of nitrogen-sulfur donor sets, formulated as [Fe(L)Cl<sub>2</sub>](1),[(Co<sub>2</sub>L)Cl<sub>2</sub>](2) and [Ni(L)Cl<sub>2</sub>](3), where L=1,3-bis(2-pyridylmethylthio) propane were synthesized and isolated in their pure form. All the complexes were

characterized by physicochemical and spectroscopic methods. The solid state structures of complexes(1)&(3) have been established by single crystal X-ray crystallography<sup>(10)</sup>. In continuation of our research on Schiff bases complexes<sup>(11-13)</sup> the aim of this work is to prepare and investigate some complexes of Mn(II),Co(II), Ni(II),Cu(II) and Zn(II) with recently synthesized tetradentate Schiff base ligands of N,N'-bis(aminophenylthio) bromo propane)1-phenyl butane-1,3-dilidene (L<sup>1</sup>) and N,N'-bis (3- bromo propyl (phenylthio) imino)1,1,1-trifluoro -3-(2-theonyl) acetone (L<sup>2</sup>) with nitrogen and sulfur as donor sites. The general formula of these complexes [M(L)Cl<sub>2</sub>] and [Zn(L)]Cl<sub>2</sub>.

## EXPERIMENTAL

### Material and Methods

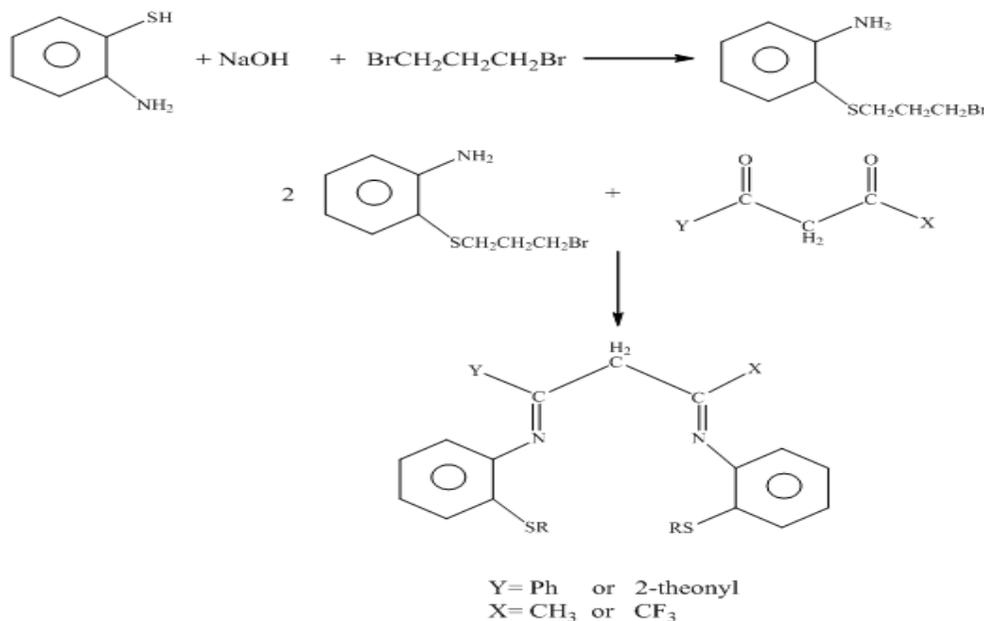
All starting materials used were analer grade, were purchased from Fluka and BDH and were used as received. Analysis of the ligands and their complexes were carried out using C.H.N.S elemental analyzer model 2400 Perkin Elmer. The metal content was estimated spectrophotometrically using Shimadzu AA670 spectrophotometer. Infrared spectra were recorded on FT-IR Brucker Tensor 27Co spectrophotometer in the 200-4000 cm<sup>-1</sup> range using CsI disc. Electronic spectra were obtained with Shimadza UV-Vis recording UV1600 spectrophotometer at room temperature, these measurements were recorded using a concentration of 10<sup>-3</sup>M of the complexes in DMSO. The magnetic measurements were carried out at 25°C on the solid state by Farady's method using Bruker BM6 instrument. Conductivities were measured using conductivity meter model PCM3 Jenway. These measurements were obtained using DMSO over the 10<sup>-3</sup>M solution of the complexes at 25°C.

### 1- Synthesis of (o-aminophenylthio)propanebromide

Treatment of an ethanolic solution of o-aminothiophenol (1.25g,0.01mol) in (5 cm<sup>3</sup>) with a solution of (0.40g,0.01mol) of NaOH in (10cm<sup>3</sup>) ethanol the resulted mixture was added gradually to a solution of (2.02g,0.01mol) of 1,3-bromopropane in (5cm<sup>3</sup>) ethanol. The reaction mixture was refluxed for 2h. then left to stand at room temperature for 24h., the solid thus formed was filtered off, washed several times with ethanol and diethylether then dried under vacuum for several hours.

### 2- Synthesis of N,N'-bis {(o-aminophenylthio) bromo propyl} 1-phenyl butane 1,3-dilidene(L<sup>1</sup>)

To a solution of (o-aminophenylthio)propanebromide (2.60g, 0.01mol) in (20 cm<sup>3</sup>) methanol a solution of benzoylacetate (1.62g, 0.01gm) in (10cm<sup>3</sup>) absolute ethanol was added. The reaction mixture was refluxed for 2h. The solution was then concentrated to half of it is volume and kept overnight . The orange crystal which formal, then filtered and washed with ethanol and dried under vacuum over P<sub>2</sub>O<sub>5</sub>.

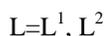


Scheme 1: Preparation of ligands L<sup>1</sup> and L<sup>2</sup>

### 3-Synthesis of N,N'-bis(3-bromo propyl (phenylthio) imino) 1,1,1-trifluoro -3-(2-theonyl) acetone (L<sup>2</sup>)

To a solution of (o-aminophenylthio)propanebromide (2.60g, 0.01mol) in (10 cm<sup>3</sup>) methanol a solution of 2-theonyltrifluoroacetone (2.22g,0.01mol) in (10cm<sup>3</sup>) ethanol was added, and preparation was continued as (L<sup>1</sup>).

**Preparation of [M(L)]Cl<sub>2</sub>, M=Co(II),Ni(II),Cu(II) and Zn(II);**



These complexes were prepared according to the following method. The metal salts (0.01 mol) in ethanol (10cm<sup>3</sup>) was added to the ligand L<sup>1</sup> (6.18 g,0.01 mol) or L<sup>2</sup>(6.46g, 0.01 mol) in methanol (10cm<sup>3</sup>). The mixture was stirred under reflux for 2h. to ensure the completion of the reaction. The solidsmm, thus obtained was filtered off , washed with ethanol, methanol, then diethylether and dried under vacuum for several

## RESULTS AND DISCUSSION

The Schiff base ligands L<sup>1</sup> & L<sup>2</sup> have been prepared according to Scheme 1, and characterized by elemental analysis, IR,UV-Vis spectra and conductivity measurement. The IR data are in accordance with the proposed structure. Disappearance of the C=O and NH<sub>2</sub> stretching, vibration related to the ketone and the amine functional groups respectively, along with the growth of strong band in the region1613-1616 cm<sup>-1</sup> due to C=N band, indicate the formation of the Schiff base ligands. The reaction of the prepared Schiff base ligands with Co(II), Ni(II),Cu(II) and Zn(II) in (1:1) ratio gives the [ML]Cl<sub>2</sub> and [Zn(L)Cl<sub>2</sub>] complexes. The elemental analysis are consistent with the proposed molecular formula (Table1). The molar conductivity of 10<sup>-3</sup>M solution of all complexes indicate that they are (1:2) electrolyte in nature<sup>(14)</sup> except for Zn(II) complexes are non electrolyte. The IR spectra of the ligands showed a characteristic band due to  $\nu$ (C=N) appeared at 1613-1616 cm<sup>-1</sup> the  $\nu$ (C-S) at 851-863 cm<sup>-1</sup>,  $\nu$ (C-H) at 2933-2990 cm<sup>-1</sup> respectively. In the complexes (Table 2) the  $\nu$ (C=N) stretching frequency shifted to higher frequency by (10-17) cm<sup>-1</sup> in the complexes of ligand (L<sup>1</sup>), suggesting that this group takes part in coordination. While in the complexes of ligand (L<sup>2</sup>) Mn(II) and Co(II) show that the stretching frequency of  $\nu$ (C=N) shifted upward by 13 and 34 cm<sup>-1</sup>, whereas in Ni(II) and Cu(II) shifted to a lower frequency by 10 and 24 cm<sup>-1</sup>, in Zn (II) complexes the  $\nu$ (C=N) frequency is not affected in coordination<sup>(15)</sup>.

The  $\nu$ (C-S) band was shifted in all complexes to lower frequency by (31-47) cm<sup>-1</sup> which indicated that it was shared in coordination with metal ions. Further support for the above coordination provided by the appearance of new bands at 430-495 cm<sup>-1</sup> and 360-395 cm<sup>-1</sup>, which tentatively attributed to  $\nu$ (M-N) and  $\nu$ (M-S) respectively<sup>(16)</sup>. In order to obtain some information about the coordination properties of the metal ions, the electronic spectra has been recorded for 10<sup>-3</sup>M solution in DMSO and the results were listed in Table 2. The band observed at 27700-27932 and 29761-33670 cm<sup>-1</sup> due to the ligand which may assigned to  $\pi$ - $\pi^*$  or n- $\pi^*$  transition respectively. The spectrum of Mn(II) complexes (1,5) shows absorption bands at 24270-28490 cm<sup>-1</sup> indicating that Mn(II) complexes contain tetrahedral geometry. In tetrahedral field the transition are all spin forbidden, but no longer parity forbidden<sup>(17)</sup>. The magnetic moment of Mn(II) complexes (1,5) are 5.10,5.56 B.M (Table 1). These values of magnetic moments reveal the presence of five unpaired electrons there by showing the complexes are of high spin type. The electronic spectrum of cobalt (II) complexes (2,7) show a bands at (14285,15384) cm<sup>-1</sup>. These bands are assigned to <sup>4</sup>A<sub>2g</sub> →<sup>4</sup>T<sub>1g</sub>(p) and the other band at 26954 cm<sup>-1</sup> is assigned to charge transfer, these bands suggest that Co(II) have tetrahedral geometry<sup>(18)</sup>. The magnetic moments of cobalt (II) complexes (2,7) are 4.62 and 4.73) B.M suggest the presence of three unpaired electrons. These values are higher than spin only formula that is due to orbital contribution .

The electronic spectra for Ni(II) complexes (3,8) the observed band at 12500 and 14660 cm<sup>-1</sup> are due to <sup>3</sup>T<sub>1</sub>(F)→<sup>3</sup>T<sub>1</sub>(p)( $\nu_3$ ) transition in tetrahedral symmetry. The magnetic moment measurement indicates that Ni(II) complexes (3,8) are (3.30 and 3.41) B.M which suggest a tetrahedral environment around nickel ion<sup>(19)</sup>. The Cu(II) complexes (4 and 9) showed a band at 16393 and 16694 cm<sup>-1</sup> which are assigned to <sup>2</sup>T<sub>2</sub> →<sup>2</sup>E and another band at 28571 cm<sup>-1</sup> which assigned to charge transfer transition in tetrahedral environment. The magnetic moment of mononuclear complexes (4 and 9) has been found to be (1.63 and 1.81)B.M which indicate the presence of one unpaired electron. The magnetic susceptibility measurements showed that the Zn(II) complexes ( 5 and 10) were diamagnetic and the electronic spectra of these complexes do not show any d-d band so the suggested as tetrahedral geometry.

Based on elemental data, magnetic moments, molar conductivity and spectral studies (IR and UV-Vis) structural formula of the new complexes were proposed as in Fig 1. The ligands act as tetradentate from the two azomethine nitrogen and two

thioether sulfur for all complexes expect for Zn(II) complexes, the ligand act as bidentate and coordinate from the sulfur atoms and the two chloride ions.

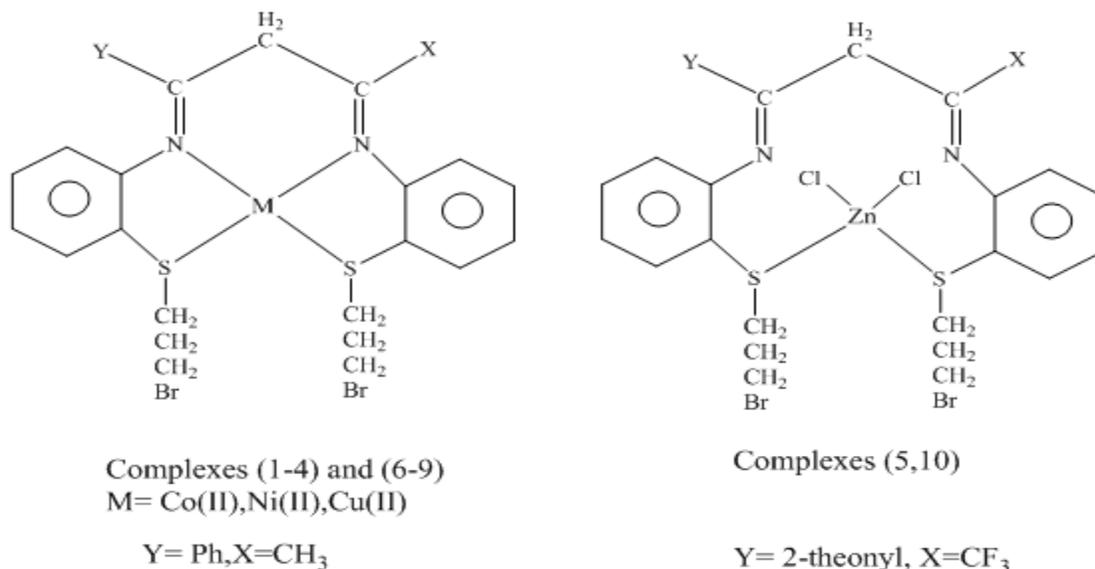


Fig 1: Suggest structures for the prepared complexes

Table 1: Physical properties of the prepared ligands and their complexes

| Seq.           | compound   | Color          | m.p<br>(°c)      | Yield<br>% | Analysis ,found (calc.)% |            |            |              |            | $\mu_{eff}$ | $(\Lambda)$<br>$cm^2 \cdot ohm^{-1} \cdot mol^{-1}$ |
|----------------|--|----------------|------------------|------------|--------------------------|------------|------------|--------------|------------|-------------|---|
|                |  |                |                  |            | C                        | H          | N          | S            | M          |             |   |
| L <sup>1</sup> | C <sub>28</sub> H <sub>20</sub> S <sub>2</sub> N <sub>2</sub> Br <sub>2</sub>                | Orange         | 160 <sup>d</sup> | 80         | 54.30(54.36)             | 4.80(4.85) | 4.50(4.53) | 10.31(10.35) | ----       | ----        | ---   |
| 1              | [Mn(L <sup>1</sup> )]Cl <sub>2</sub>   | orange         | 190 <sup>d</sup> | 72         | 45.71(45.78)             | 4.30(4.33) | 3.29(3.32) | 8.69(8.72)   | 7.41(7.49) | 5.56        | 80  |
| 2              | [Co(L <sup>1</sup> )]Cl <sub>2</sub>   | Dark brown     | 210 <sup>d</sup> | 75         | 45.50(45.54)             | 4.03(4.06) | 3.71(3.79) | 8.60(8.67)   | 7.91(7.98) | 4.62        | 70  |
| 3              | [Ni(L <sup>1</sup> )]Cl <sub>2</sub>   | Brownish green | 195 <sup>d</sup> | 80         | 45.50(45.55)             | 4.01(4.06) | 3.71(3.79) | 8.61(8.68)   | 7.92(7.96) | 3.30        | 62  |
| 4              | [Cu(L <sup>1</sup> )]Cl <sub>2</sub>   | Dark brown     | 186 <sup>d</sup> | 70         | 44.61(44.65)             | 3.87(3.98) | 3.69(3.72) | 8.49(8.51)   | 8.35(8.44) | 1.63        | 75  |
| 5              | [Zn(L <sup>1</sup> )]Cl <sub>2</sub>   | Dark yellow    | 200 <sup>d</sup> | 69         | 44.49(44.54)             | 3.92(3.97) | 3.68(3.71) | 8.39(8.48)   | 8.61(8.67) | ---         | 20  |
| L <sup>2</sup> | C <sub>26</sub> H <sub>15</sub> N <sub>2</sub> S <sub>3</sub> F <sub>3</sub> Br <sub>2</sub> | Green          | 130-132          | 80         | 40.21(40.27)             | 3.88(3.86) | 4.30(43.3) | 9.89(9.91)   | ----       | ---         | ---   |
| 6              | [Mn(L <sup>1</sup> )]Cl <sub>2</sub>   | Pale green     | 190-192          | 85         | 40.31(40.42)             | 3.20(3.24) | 3.59(3.62) | 8.30(8.29)   | 7.20(7.24) | 5.10        | 78  |
| 7              | [Co(L <sup>1</sup> )]Cl <sub>2</sub>   | Dark green     | 180-182          | 70         | 40.18(40.21)             | 3.14(3.22) | 3.59(3.61) | 8.20(8.24)   | 7.55(7.59) | 4.73        | 72  |
| 8              | [Ni(L <sup>1</sup> )]Cl <sub>2</sub>   | Green          | 210-212          | 62         | 40.16(40.22)             | 3.19(3.22) | 3.59(3.61) | 8.20(8.25)   | 7.54(7.59) | 3.41        | 79  |
| 9              | [Cu(L <sup>1</sup> )]Cl <sub>2</sub>   | Olive          | 250 <sup>d</sup> | 60         | 39.81(39.87)             | 3.15(3.20) | 3.52(3.58) | 8.14(8.18)   | 8.10(8.12) | 1.81        | 80  |
| 10             | [Zn(L <sup>1</sup> )]Cl <sub>2</sub>   | Pale green     | 200 <sup>d</sup> | 65         | 39.89(3.99)              | 3.16(3.19) | 3.51(3.57) | 8.16(8.20)   | 8.31(8.37) | ---         | 25  |

d= decomposition temperature

**Table 2: IR and electronic spectral data of the ligands and their metal complexes**

| No.            | UV-Vis absorption bands (cm <sup>-1</sup> ) | IR spectral bands (cm <sup>-1</sup> ) |                          |                          |                          |                           |
|----------------|---|---------------------------------------|--------------------------|--------------------------|--------------------------|---------------------------|
|                |   | $\nu(\text{C}=\text{N})$              | $\nu(\text{C}-\text{S})$ | $\nu(\text{M}-\text{N})$ | $\nu(\text{M}-\text{S})$ | $\nu(\text{M}-\text{Cl})$ |
| L <sup>1</sup> | 27932,33670                                 | 1613 <sub>s</sub>                     | 851 <sub>s</sub>         | ---                      | ---                      | ---                       |
| 1              | 28490                                       | 1629 <sub>s</sub>                     | 820 <sub>s</sub>         | 460 <sub>m</sub>         | 370 <sub>m</sub>         |                           |
| 2              | 15384,26954                                 | 1650 <sub>s</sub>                     | 838 <sub>s</sub>         | 440 <sub>m</sub>         | 385 <sub>m</sub>         |                           |
| 3              | 14660                                       | 1592 <sub>s</sub>                     | 829 <sub>s</sub>         | 435 <sub>m</sub>         | 360 <sub>w</sub>         |                           |
| 4              | 16694,28571                                 | 1600 <sub>s</sub>                     | 819 <sub>s</sub>         | 470 <sub>m</sub>         | 372 <sub>m</sub>         |                           |
| 5              | 27932                                       | 1616 <sub>s</sub>                     | 816 <sub>s</sub>         |                          | 395 <sub>w</sub>         | 325                       |
| L <sup>2</sup> | 27700,29761                                 | 1616 <sub>s</sub>                     | 863 <sub>s</sub>         | ---                      | ---                      | ---                       |
| 6              | 24271                                       | 1624 <sub>s</sub>                     | 826 <sub>s</sub>         | 430 <sub>m</sub>         | 380 <sub>w</sub>         |                           |
| 7              | 14285                                       | 1623 <sub>s</sub>                     | 827 <sub>s</sub>         | 480 <sub>m</sub>         | 377 <sub>m</sub>         |                           |
| 8              | 12500                                       | 1630 <sub>s</sub>                     | 830 <sub>s</sub>         | 440 <sub>m</sub>         | 390 <sub>w</sub>         |                           |
| 9              | 16393                                       | 1625 <sub>s</sub>                     | 835 <sub>s</sub>         | 495 <sub>m</sub>         | 365 <sub>m</sub>         |                           |
| 10             | 28250                                       | 1629 <sub>s</sub>                     | 820 <sub>s</sub>         |                          | 385 <sub>w</sub>         | 320 <sub>m</sub>          |

S= strong, m=medium, w= weak

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