

**New Complexes of ( 3, 4, 6, 13, 14, 16 – hexaazatricyclo [16,2,2,28,11] tetracosane- 2,5,7,12,15,17-hexaone) with Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II)**

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**ABSTRACT**

In this research, a new ligand 3,4,6,13,14,16-hexaazatricyclo [16,2,2,28,11] tetracosane- 2,5,7,12,15,17-hexaone), (DHC) was prepared from the reaction of cyclohexane-1,4-dicarboxylic acid with semicarbazide using microwave irradiation in solid state. Then, it was reacted with some transition metal(II) ions to form complexes of the type  $[M(DHC)Cl_2]$ ,  $[M(DHC)]Cl_2$ , where M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II). Adducts of the type  $[M(DHC)(PPh_3)Cl]Cl$  and  $[M(DHC)(PPh_3)]Cl_2$ , were prepared by the reaction of the above complexes with triphenylphosphine in a 1:1 molar ratio. The prepared complexes and adducts were characterized by (C,H,N) analysis, metal content analysis, molar conductance, magnetic moment measurements, electronic and IR spectroscopy, as well as the ligand was characterized by  $^1H$ ,  $^{13}C$  -NMR spectroscopy. The electronic spectra and magnetic measurements indicate that the complexes have octahedral environment around the metal ions.

**Keywords:** Microwave - assisted synthesis, macrocyclic molecules.

- [16,2,2,2,11] )  
Mn(II), Fe(II), Co(II), Ni(II), ( -17, 15,12,7,5 ,2,  
Cu(II) and Zn(II)

[16,2,2,28,11] - 16, 14, 13, 6, 4, 3 )  
-4,1- (DHC) ( -17,15,12 ,7, 5,2-

$[M(DHC)Cl_2]$ ,  $[M(DHC)]Cl_2$



out on  $10^{-3}$  M solution of all complexes in DMSO using (Conductivity Meter Model PCM3-JENWAY). Electronic spectra were recorded on (Shimadzu-UV-VIS recording, UV-1650PC-Spectrophotometer), using  $10^{-3}$  M of the complexes in DMSO. The magnetic susceptibility measurements were measured at 25 °C by Farady's method using Bruker BM6 instrument.  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  were carried out by (BRUKER 300 MHz (Switzerland)) and Shimadzu QP 5050 A (JAPAN) at Al-Albeit University – Jordan. The ligand prepared in solid state using microwave oven type morph Richards EM 820 CPT. Finally, melting points of all compounds were measured using electrothermal 9300 engineering apparatus and were uncorrected.

### Preparation of the ligand (DHC)

The ligand DHC has been synthesized according to the following procedure (Neerja *et al.*, 2010).

A solid cyclohexane-1,4- dicarboxylic acid (0.34 g, 0.002 mole) was mixed with solid (0.15 g, 0.002 mole) semicarbazide and (0.005 g, 0.0001 mole) of cerium ammonium nitrate (CAN) as a catalyst. The solid mixture was irradiated using a microwave 800 W for 10 minutes. The mixture was cooled to room temperature then, ethyl acetate (20 ml) was added and the mixture stirred for about 1hr to dissolve the CAN which was separated from the mixture by filtration, then the yellow precipitate was washed with n- hexane, ethanol and dried under vacuum for several hours. The physical data were listed in (Table 3).

### Preparation of $[\text{M}(\text{DHC})\text{Cl}_2]$ and $[\text{M}(\text{DHC})]\text{Cl}_2$ :

**M= Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II).**

The solution of the ligand DHC (0.42 g, 0.001 mole) in (10 ml) DMSO and ethanolic solution of the hydrated metal chloride salts (0.001 mole) were mixed together with stirring. The mixture was refluxed for 2 hrs. On cooling a colored precipitate was obtained, the product was filtered off, washed with cold ethanol and dried under vacuum. The physical data were listed in (Table 3).

### Preparation of the adducts $[\text{Mn}(\text{DHC})(\text{PPh}_3)\text{Cl}]\text{Cl}$ :

The metal complexes  $[\text{Mn}(\text{DHC})\text{Cl}_2]$  (0.54 g, 0.001 mole) were dissolved in (10 ml) DMF and added to a solution of triphenylphosphine (0.26 g, 0.001 mole) in (10 ml) ethanol. The mixture was refluxed for 1h then the pale brown precipitate formed was filtered off, washed with diethylether and dried. The same procedure was carried out to prepare the triphenylphosphine adducts of Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) whith using an appropriate weight. The physical data were listed in (Table 3).

## RESULTS AND DISCUSSION

Microwave irradiation of a mixture of the semicarbazide, dicarboxylic acid and CAN catalyst afforded the ligand (DHC) in 90% yield, which is stable in air, non-hydroscopic at room temperature its C.H.N analyses, and other physical properties are listed in (Table 3).


The ligand was characterized by  $^1\text{H NMR}$  and the chemical shifts data are listed in (Table 1) the band at  $\delta$  (2.3-1.8 ppm) attributed to 20 H cyclohexane ring assisted by the integration. The signal at  $\delta$  (5.9 ppm) attributed to 2H for the NH-NH-CO protons, the band at ( $\delta$  7.7 ppm) attributed to 2H for the -NH-NH-CO-Cyclo protons, and  $\delta$ (9.5 ppm) attributed to 2H for the —''— —''— proton. Table (2) shows  $^{13}\text{C-NMR}$  chemical shift's ppm

at (41.5-27.3) for (C-cyclo), (NH-NH-CO-NH) (178.3-176.1 ppm) and (155.8 ppm) for (NH-CO-cyclo).

The IR spectrum data of DHC Table (5) exhibited absorption frequencies assigned to  $\nu(\text{N-H})$  bond stretching as a strong band at ( $3225\text{ cm}^{-1}$ ),  $\delta(\text{N-H})$  appears at ( $1236\text{ cm}^{-1}$ ),  $\nu(\text{N-N})$  bond stretching vibration appears at ( $1018\text{ cm}^{-1}$ ), and the frequency assignable to  $\nu(\text{C=O})$  band at ( $1709\text{ cm}^{-1}$ ) as medium intensity (Nakamoto, 1997). The IR spectrum characteristic to bonds  $\nu(\text{N-N})$ ,  $\nu(\text{CO-NH-CO})$  and  $\nu(\text{C=O})$  stretching frequencies confirm the condensation reaction between the dicarboxylic acid and semicarbazide, to form a 20-membered hexa amide macrocycle DHC, as shown in Fig (1A).

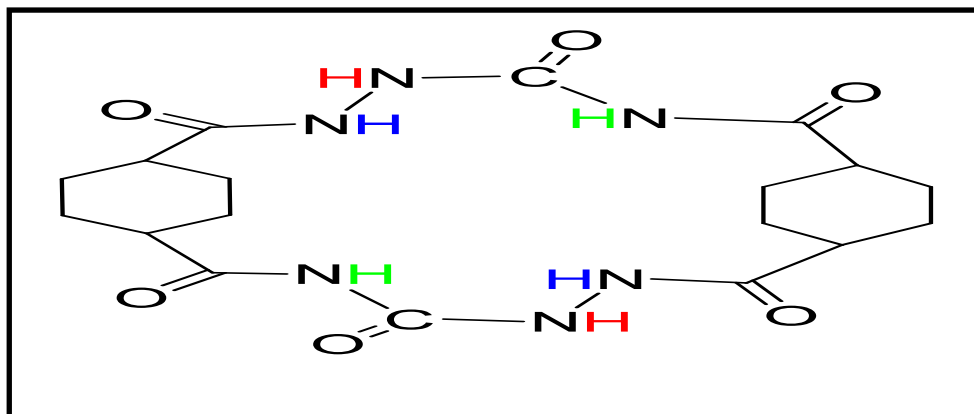
On complexation, the stretching frequencies of  $\nu(\text{N-H})$ ,  $\delta(\text{CO-NH-CO})$  and  $\nu(\text{N-N})$  shifted to a lower frequency, which indicate the coordination of two (NH) from the semicarbazide group Fig. (2), another support to this coordination comes from the appearance of new bands attributed to  $\nu(\text{M-N})$  bond stretching at ( $418\text{-}460\text{ cm}^{-1}$ ). However, the position of  $\nu(\text{C=O})$  bond stretching vibration has been shifted to lower frequencies in complexes number (1, 3, 4) and the adducts number (7, 9, 10), while in complexes number (2, 5, 6, 8, 11, 12), the  $\nu(\text{C=O})$  bond stretching are not shifted (Sulekh, 2005; Zafar, 2004). A new band attributed to the stretching of  $\nu(\text{M-O})$  bond stretching at ( $415\text{-}427\text{ cm}^{-1}$ ) may prove this coordination.

**Table 1: Chemical shift for  $^1\text{H-NMR}$**

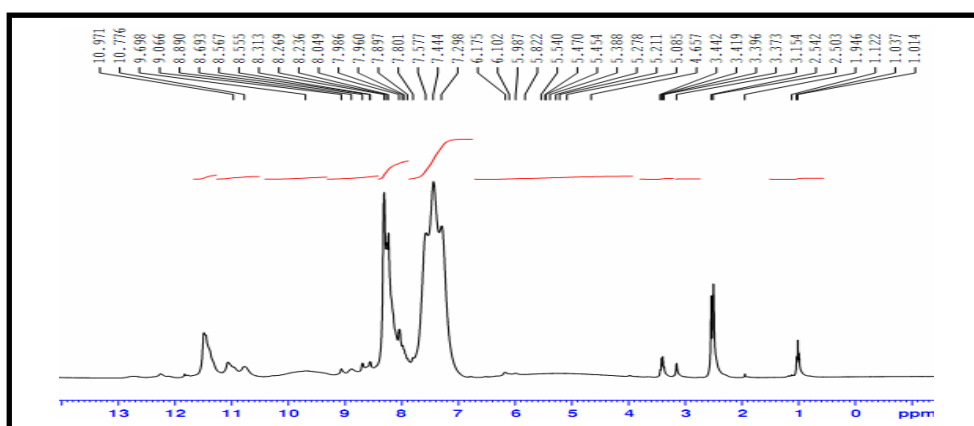
Compound	-NH-C=O=O 2H	-NH-NH-CO-Cyclo 2H	CO-NH-NH-NH 2H	H- Cyclo 4H	 16H
L	9.5	7.7	5.9	2.38	1.8

**Table 2: Chemical shift for  $^{13}\text{C-NMR}$**

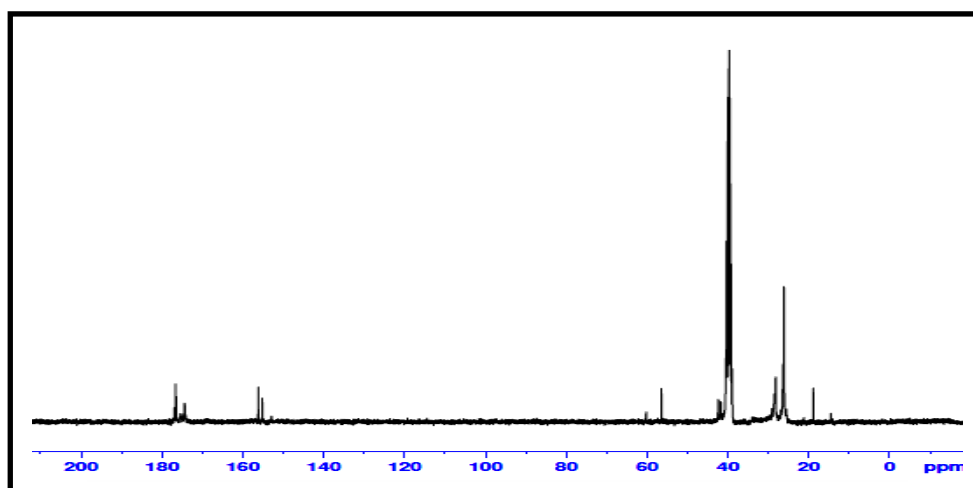
Compound	C-cyclo	NH-NH-CO-NH	NH-CO-cyclo
L	41.5 -27.3 ppm	155.8 ppm	178.3-176.1 ppm



(A): structure of the ligand DHC



(B):  $^1\text{H}$  NMR for DHC ligand



(C):  $^{13}\text{C}$  NMR for DHC ligand

Fig. 1: A,B,C

### Electronic Spectra and Magnetic Measurements

The U.V spectrum of the DHC ligand has bands in the spectra at ( 36760 and 45871  $\text{cm}^{-1}$ ), assigned to  $\pi \longrightarrow \pi^*$  and  $n \longrightarrow \pi^*$  transition, respectively.

The electronic spectra data and the magnetic moments for all complexes are given in Table (4). The two manganese complexes have a magnetic moment (5.81–5.8 B.M) corresponding to five unpaired electrons, while the U.V – visible spectrum show bands at (34965 – 47169  $\text{cm}^{-1}$ ) which may be due to charge transfer (Lever, 1970).

The magnetic moment values for the Fe(II) complexes (4.81 – 4.70 B.M) as well as the electronic band at 9823–10917  $\text{cm}^{-1}$  one attributed to the  ${}^5\text{T}_{2g} \longrightarrow {}^5\text{E}_g$  transition, indicating octahedral structure.

The two cobalt complexes number 3 and 9 have a magnetic moment values (4.59 and 4.79 B.M) corresponding to three unpaired electrons [Table 2].The U.V– visible spectra show three bands at 11363 –11700  $\text{cm}^{-1}$ , 14792  $\text{cm}^{-1}$  and 16447 $\text{cm}^{-1}$  due to the transitions  ${}^4\text{T}_{1g}(\text{F}) \longrightarrow {}^4\text{T}_{2g}(\text{F}) \nu_1$ ,  ${}^4\text{T}_{1g}(\text{F}) \longrightarrow {}^4\text{A}_{2g}(\text{F}) \nu_2$  and  ${}^4\text{T}_{1g}(\text{F}) \longrightarrow {}^4\text{T}_{1g}(\text{P}) \nu_3$ , respectively. These data may attribute to octahedral structure which are similar to found else where ( Sulekh, 2004).

The UV – visible spectra of the Ni (II) complexes number(4,10) shows three bands at (10121 ,10860  $\text{cm}^{-1}$ ), (11261 ,16501  $\text{cm}^{-1}$ ) and (25212, 26000  $\text{cm}^{-1}$ ) corresponding to three spins allowed transition  ${}^3\text{A}_{2g}(\text{F}) \longrightarrow {}^3\text{T}_{2g}(\text{F}) (\nu_1)$ ,  ${}^3\text{A}_{2g}(\text{F}) \longrightarrow {}^3\text{T}_{1g}(\text{F}) (\nu_2)$ , and  ${}^2\text{A}_{2g}(\text{F}) \longrightarrow {}^3\text{T}_{1g}(\text{P}) (\nu_3)$ , respectively. The magnetic moment values (3.29 and 3.03B.M) agree with high spin configuration, indicating an octahedral environment around the Ni(II) ions (Sulekh, 2004).

The magnetic moment of the Cu(II) complexes number (5,11) lie in the range ( 1.83 – 2.04 B. M ), corresponding to one unpaired electron and electronic spectra have a band in the range (10548 - 10917  $\text{cm}^{-1}$ ) assigned to the  ${}^2\text{E}_{2g}(\text{F}) \longrightarrow {}^2\text{T}_{2g}$  transition in distorted octahedral environment (Lever , 1968).

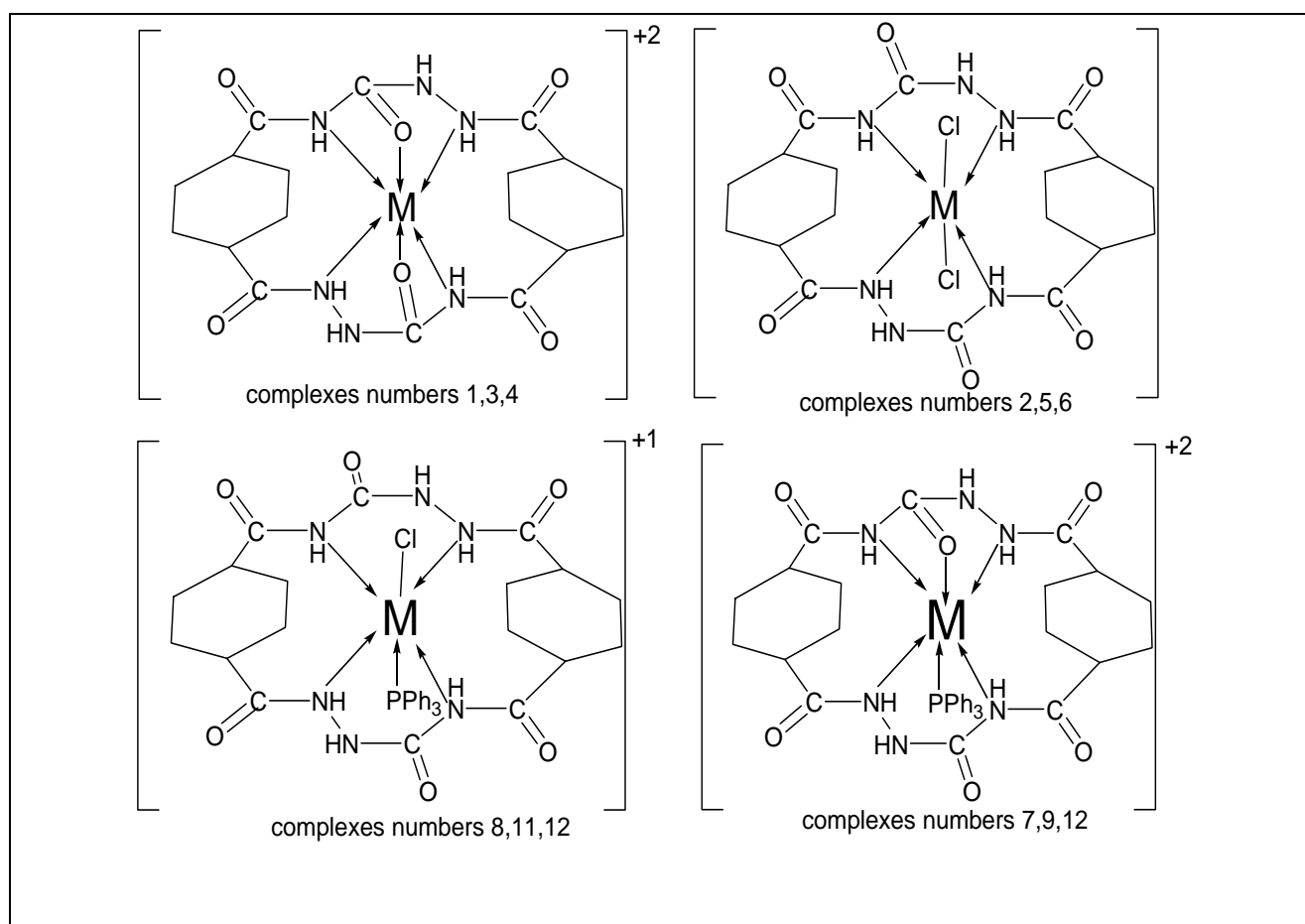
The  $\mu_{\text{eff}}$  values of the two Zn(II) complexes were diamagnetic as expected.

**Table 3: Some physical properties including molar conductance and elemental analysis data of the complexes**

No	Compound	Color	M.P, C°	yield, %	Molar conductance, $\Omega^{-1} \text{ cm}^2 \cdot \text{mol}$	CHN Elemental analysis data found (calculated %)			
						%C	%H	%N	Metal %
	Ligand(DHC)	Pale yellow	150-152	90		51.18(51.58)	6.16(6.47)	19.90(20.34)	—
1	[Mn(DHC)]Cl <sub>2</sub>	Pale brown	165-167	62	84	39.43(39.01)	4.74(4.30)	15.33(15.06)	10.02(9.89)
2	[Fe(DHC) Cl <sub>2</sub> ]	Gray	122-124	73	16	—	—	—	10.19(10.02)
3	Co(DHC)]Cl <sub>2</sub> [	Dark blue	170-172	69	85.5	39.15(39.01)	4.71(4.41)	15.22(15.12)	10.68(10.58)
4	[Ni(DHC)]Cl <sub>2</sub>	Dark blue	135-137	63	83	—	—	—	10.64(10.13)
5	[Cu(DHC) Cl <sub>2</sub> ]	Pale green	153	78	18	—	—	—	11.42(11.01)
6	[Zn(DHC)Cl <sub>2</sub> ]	Pale yellow	125	55	10.8	—	—	—	11.71(11.32)
7	[Mn(DHC)(pph <sub>3</sub> )]Cl <sub>2</sub>	Pale brown	170	59	85.1	—	—	—	5.98(5.75)
8	[Fe(DHC)(pph <sub>3</sub> ) Cl]Cl	Pale brown	155-157	65	65	53.28(53.22)	5.05(5.01)	10.36(9.36)	6.08(5.95)
9	Co(DHC)(pph <sub>3</sub> )]Cl <sub>2</sub> [	Deep blue	146-148	75	83.6	—	—	—	6.39(6.09)
10	[Ni(DHC)(pph <sub>3</sub> )]Cl <sub>2</sub>	Brilliant green	162-164	70	80	—	—	—	5.87(5.53)
11	[Cu(DHC)( pph <sub>3</sub> )Cl]Cl	White	171-173	65	68	52.78(52.05)	5.01(5.16)	10.26(9.31)	6.85(6.72)
12	[Zn(DHC)(pph <sub>3</sub> )Cl]Cl	Pale brown	160-161	70	70	—	—	—	6.46(6.21)

### COUNCLUSION

On the basis of the above results, we proposed the following structures for the Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) complexes, and adducts.



**Fig. 2: The proposed structures of the complexes and the adducts M=Mn(II), Fe(II), Co(II), Ni(II),Cu(II) and Zn(II),(DHC)**

**Table 4: Magnetic moment and electronic spectral data of the complexes**

No.	Compound	$\mu_{\text{eff}}$ , B.M (25 °C)	$\lambda_{\text{max}}$ , (cm <sup>-1</sup> )
1	[Mn(DHC)]Cl <sub>2</sub>	5.81	34965, 47169
2	[Fe (DHC)Cl <sub>2</sub> ]	4.81	9823, 32679, 36760, 47296
3	[Co (DHC)]Cl <sub>2</sub>	4.59	11700,14792, 16447, 37037, 46728
4	[Ni (DHC)]Cl <sub>2</sub>	3.29	10860,16501, 37037, 25000, 48076
5	[Cu(DHC)Cl <sub>2</sub> ]	2.04	10548, 32258, 47160
6	[Zn (DHC)Cl <sub>2</sub> ]	diamagnetic	—
7	[Mn(DHC)(pph <sub>3</sub> )]Cl <sub>2</sub>	5.88	36764, 38563
8	[Fe(DHC)(pph <sub>3</sub> )Cl]Cl	4.91	10917, 318471, 35971
9	[Co(DHC)(pph <sub>3</sub> )]Cl <sub>2</sub>	4.79	11363, 14792, 16447, 32258, 37313
10	[Ni(DHC)(pph <sub>3</sub> )]Cl <sub>2</sub>	3.03	92420, 10121, 11261, 25212, 35714
11	[Cu(DHC)(pph <sub>3</sub> )Cl]Cl	1.83	10917, 32051, 45871
12	Zn(DHC) pph <sub>3</sub> Cl]Cl[	diamagnetic	—



**Table 5: Selected I.R bands in  $\text{cm}^{-1}$  and their assignment**

No.	$\nu(\text{N-H})$	$\delta(\text{N-H})$	$\nu(\text{N-N})$	$\nu(\text{C=O})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$
ligand	3225 <sub>(m)</sub>	1236 <sub>(s)</sub>	1018 <sub>(s)</sub>	1709 <sub>(m)</sub>	—	—
1	3186 <sub>(w)</sub>	1201 <sub>(w)</sub>	1005 <sub>(m)</sub>	1684 <sub>(s)</sub>	...	424 <sub>(s)</sub>
2	3186 <sub>(m)</sub>	1200 <sub>(m)</sub>	1012 <sub>(s)</sub>	1689 <sub>(s)</sub>	—	459 <sub>(s)</sub>
3	—	1208 <sub>(m)</sub>	989 <sub>(s)</sub>	1662 <sub>(m)</sub>	415	465 <sub>(m)</sub>
4	3201 <sub>(w)</sub>	1196 <sub>(m)</sub>	999 <sub>(s)</sub>	1684 <sub>(m)</sub>	418	428 <sub>(m)</sub>
5	3209 <sub>(m)</sub>	1198 <sub>(s)</sub>	989 <sub>(s)</sub>	1697 <sub>(m)</sub>	—	450 <sub>(m)</sub>
6	3215 <sub>(w)</sub>	1210 <sub>(m)</sub>	1005 <sub>(s)</sub>	1696 <sub>(s)</sub>	—	460 <sub>(s)</sub>
7	3178 <sub>(m)</sub>	1195 <sub>(m)</sub>	997 <sub>(m)</sub>	1653 <sub>(m)</sub>	...	418 <sub>(m)</sub>
8	3192 <sub>(m)</sub>	1212 <sub>(m)</sub>	997 <sub>(m)</sub>	1674 <sub>(m)</sub>	—	418 <sub>(w)</sub>
9	3215 <sub>(w)</sub>	1209 <sub>(s)</sub>	953 <sub>(s)</sub>	1655 <sub>(s)</sub>	420	450 <sub>(s)</sub>
10	3178 <sub>(s)</sub>	1199 <sub>(m)</sub>	997 <sub>(s)</sub>	1665 <sub>(m)</sub>	427	449 <sub>(m)</sub>
11	3209 <sub>(w)</sub>	1201 <sub>(m)</sub>	980 <sub>(m)</sub>	1701 <sub>(m)</sub>	—	426 <sub>(m)</sub>
12	3215 <sub>(m)</sub>	1319 <sub>(m)</sub>	1005 <sub>(s)</sub>	1697 <sub>(s)</sub>	—	430 <sub>(m)</sub>

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