

## **Synthesis, structural studies of some nucleic acids metal complexes**

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### **Abstract**

Some mixed ligand complexes of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with Adenine-uracil base pair have been prepared and characterized by their elemental analysis, infrared, UV-visible, magnetic measurement and powder X-ray diffraction studies.

### **Introduction**

Uracil is one of the four bases found in RNA and may be utilized preferentially for nucleic acid biosynthesis in tumor cells (Berg et al 2001). Substitution of hydrogen atom in 5-position of uracil by different halogen atoms resulted the drastic changes in the biological properties of uracil i.e, 5-fluorouracil (5FURL) and up to some extent 5-chlorouracil (5CLURL) have been reported to be active as chemotherapeutic agents (Heidelberger et al 1957), whereas 5-iodouracil (5IURL) has lethal and mutagenic effect (Byrd et al 1977).

Adenine (ADN) is one of the most common naturally occurring purine derivatives, found in variably almost in all the living tissues as components of nucleic acids, many antibiotics and various coenzyme systems. It is also found in all the living cells as the mono-, di-, and triphosphate of nucleosides, viz adenosine monophosphate (AMP), adenosine diphosphate (ADP) and adenosine triphosphate (ATP), which play vital roles in many metabolic processes. Many of these drugs have an increased anticancer activity when administered as metal complexes (Krischner et al 1966), Livingstone et al 1970).

Many workers have reported the complexes of uracil and halouracil and their metal complexes. Terron et al (Terron et al 2004) synthesized complexes of uracilato and 5-halouracilato with the divalent ions, viz., Ni(II), Cu(II), Zn(II) and reported the X-ray structure of [Ni(5-chlorouracilato-N)<sub>2</sub>(en)<sub>2</sub>].2H<sub>2</sub>O, [Cu(5-chlorouracilato-N)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>].2H<sub>2</sub>O, and [Zn(5-chlorouracilato-N)<sub>2</sub>(NH<sub>3</sub>)<sub>3</sub>].(5-chlorouracilato-N).(H<sub>2</sub>O). Liu et al (Liu et al 2004) studied the photodissociation of gaseous metal ion-nucleobase complexes; Mg<sup>+</sup>-uracil and Mg<sup>+</sup>-thymine by photodissociation and density functional theory calculation. Atbir et al (Atbir et al 2002) reported the complex formation of Cu(II) and Cd(II) with uracil, thymine

and other substituted analogues and determined the protonation constant of the ligand and the stability constant of the above complexes by potentiometric techniques. Kufelnick et al (Kufelnick et al 2002) reported potentiometric pH studies on complexes of Cu(II), Ca(II), and Mg(II) with uracil, thymine, 6-chloromethyluracil, 5-hydroxymethyluracil, 6-methyluracil and diethyl-6-uracilphosphate derivatives. Masoud and coworkers (Masoud et al 2002) reported the synthesis, structural and thermal properties of a few complexes with some pyrimidines. Chandra et al (Chandra et al 2002) reported the theoretical study on protonated and deprotonated 5-fluorouracil, 5-chlorouracil, other 5-substituted uracil derivatives and their complexes with water. They also discussed the effect of the intermolecular hydrogen bonding in 5-aminouracil.

The present paper reports the synthesis, structural characterization of ternary complexes of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with adenine and uracil mixed ligands. It was thought to be of interest to study the formation of metal complexes of purine-pyrimidine base pair due to the biological important activity.

### Experimental

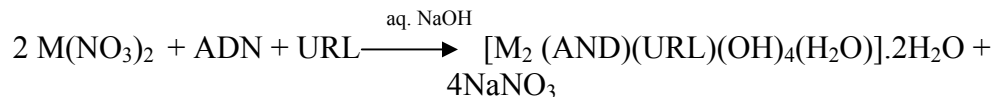
All the reagents used were analytical grade. Metal nitrates are from Merck ADN and URL used were from BDH and Loba chemie respectively.

The metal ions were determined by dissolving the complexes in very dilute acids and titrating against EDTA (Vogel 1989). Carbon, hydrogen and nitrogen were analyzed by a Vario EL III CHNOS Elemental analyzer. Infrared spectra were recorded as KBr pellets using Nexus model Thermo-Nicolet FT – IR Spectrophotometer covering the range 4000-200  $\text{cm}^{-1}$ . Solid state (Nujol mull) electronic spectra were measured with a Perkin-Elmer Lambda 35 spectrophotometer in the 200 – 1100 nm were carried out in Chemistry Dept. IIT Roorkee. At room temperature magnetic susceptibility measurements using Cahn magnetic balance model PAR 155 and X-ray powder diffraction data of the complexes were obtained on a Bruker AXS, model D8 Advance X-ray diffractometer using Cu  $K\alpha$  radiation were done at IIC, IIT Roorkee. Indexing of X-ray powder lines was done by Ito's method (Azoroff 1969).

ADN and URL in a molar ratio of 1:1 were refluxed in ethanol for 6 hrs till all the ligands dissolved. The resultant solution was mixed with each metal solution separately and the resultant mixtures (2:1:1) were refluxed for several hours. The pH of the solution was adjusted to about 7.0 by adding sodium hydroxide (0.01 M) with continuous stirring, which resulted in the formation of precipitates. They were filtered and washed several times with absolute ethanol, finally with ether and dried at about 50°C.

### Results and Discussion

The composition of the complexes, molecular weight and analytical data are given in Table 1. The new complexes were obtained according to the general reaction in aqueous ethanolic solution.



All the complexes, display [Metal (ADN)(URL)] 2:1:1 stoichiometry, are basic in nature, colored except those of zinc and cadmium. They are insoluble in common organic solvents as well as in water. Due to the insolubility of the mixed complexes in different solvents, studies in solution could not be performed (e.g. molar conductivities, NMR etc.). One can conclude from the insolubility of the mixed – ligand complexes in the organic solvents that they are polymeric in nature.

### Infrared Spectral Studies

The infrared spectra of URL (Ghose 1989) AND (Specia et al 1979), are reported in the literature. The important IR frequencies of the above ligands and their corresponding tentative frequencies exhibited by the mixed complexes are given in Table 2.

Various possible sites for the coordination of ADN (Specia et al 1979 and Mikulski 1985) and URL (Sarkar et al 1983, Goodgame 1977) with metal ions are reported in the literature. But the hydrogen bond of the AND – URL pair will influence the coordination of the cations. Hence, in discussing the IR spectra of the complexes, the hydrogen bonding has also been taken into consideration. In the region 3500-3000  $\text{cm}^{-1}$  several bands appeared, which may be attributed to N-H, O-H and C-H stretching mode. The OH of water absorbed in 3500-3250  $\text{cm}^{-1}$  region. The appearance of bands in this region of spectra of the complexes indicates the presence of water molecules in the complex lattice (Specia et al 1979). The presence of  $\nu$  (M-O) water bands in the lower frequency region of these compounds confirm the binding of some water molecules to the complexes (Nacamoto 1970), suggesting a bridge between molecules and the metals.

The  $\nu$  (NH<sub>2</sub>) and  $\delta$  (NH<sub>2</sub>) bands (Table 2) of ADN shift towards the lower frequency side upon complex formation. Such a frequency shift may be occurring due to the hydrogen bonding of the NH<sub>2</sub> group with the oxygen bonded to the C<sub>(4)</sub> position of the URL which is also evident from the lowering of the carbonyl frequency of the 4-keto group of the complexes with respect to the free URL i.e., HN<sub>(6)</sub>-H ...O=C<sub>(4)</sub> bonding. The  $\nu$  (N<sub>(1)</sub>-H) frequencies of ADN are lower to appreciable extent (Table 2),  $\delta$ (N<sub>(3)</sub>-H)

frequency which appeared at  $1416\text{ cm}^{-1}$  of URL is also lowered or at lower frequency in the complexes, which may be due to the formation of hydrogen bond between  $N_{(1)}$  of ADN and  $N_{(3)}\text{-H}$  of URL as  $N_{(1)}\dots\text{H-N}_{(3)}$ . It is also evident from the infrared spectra studies that the frequencies of  $\nu(N_{(3)}\text{-H})$  and  $\nu(N_{(7)}\text{-H})$  bands are lowered considerably in comparison to the  $\nu(N_{(9)}\text{-H})$  band of the complexes with respect to those of ADN frequencies. On the basis of these observation it may be proposed that the two binding sites of AND are  $N_{(3)}$ ,  $N_{(7)}$  and not  $N_{(9)}$ .

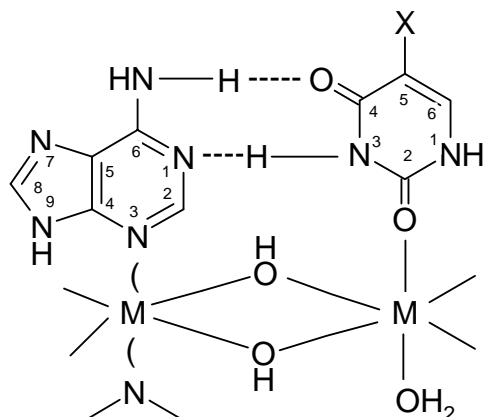
Similarly the  $\nu(C_{(2)}=\text{O})$  band of URL shifts towards the lower frequency region after complexation, indicating that  $C_{(2)}=\text{O}$  group is involved in metal coordination and directly enhances the proton donor ability at the  $N_{(3)}$  atom of URL. On the basis of the above arguments it may be tentatively suggested that out of the metal binding sites of ADN i.e. ( $N_{(3)}$ ,  $N_{(7)}$ ,  $N_{(9)}$ ,  $C_{(6)}\text{-NH}_2$ ) and of URL ( $C_{(4)}=\text{O}$ ,  $C_{(2)}=\text{O}$ ,  $N_{(3)}\text{-H}$  and  $N_{(1)}\text{-H}$ ) the sites employed for bonding with A are  $N_{(3)}$  and  $N_{(7)}$  whereas in URL, it is  $C_{(2)}=\text{O}$ . The presence of  $\nu(\text{M-O})$  (Goodgame and John 1977) and  $\nu(\text{M-N})$  bands in the lower frequency region suggest the coordination number six for Co(II), Ni(II), Cu(II), Zn(II) and Cd(II). The bridging OH stretching vibration appear at about  $3300 - 3400\text{ cm}^{-1}$  and the bridging OH bending mode appears at about  $950\text{ cm}^{-1}$  for the metal ions suggesting an OH bridging polymeric structure of the complexes.

### Electronic Spectra and magnetic moments

The magnetic moments value is 3.67 B.M. for Co(II)(ADN)(URL), suggesting that they have octahedral structure with a high spin nature of cobalt complex. The electronic spectra exhibit bands at 835 nm, 540 nm, supporting octahedral geometry for  $\text{Co}_2(\text{ADN})(\text{URL})$  complex (Ferraro and Walker 1965). In above complexes, the  ${}^4T_{2g}(\text{F}) \leftarrow {}^4T_{1g}(\text{F})$  ( $\square_1$ ) transition could not be observed, as it is likely to appear beyond 1000 nm.

The electronic spectral bands at 630 nm, 390 nm for  $\text{Ni}_2(\text{ADN})(\text{URL})$  favor octahedral geometry for the mixed ligand complexes (Lever 1968, Cotton and Wilkinson 1988). Which have the magnetic moment values of 3.25 B.M. The  $\square_1$  transition however could not be obtained, as they are likely to appear beyond 1000 nm.

The magnetic moment values of Cu(II) compounds with (ADN)(URL) is 2.23 B.M. showing the presence of one unpaired electron. The occurrence of d-d transition bands at 604 nm for  $\text{Cu}_2(\text{ADN})(\text{URL})$  indicating the hexa-coordination of the metal ion.



X = H

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

### X – ray Powder Diffraction studies

The X-ray powder diffraction Fig. 1, data (Table 3) of the complexes have been indexed according to the Ito's method (Azoroff 1969).

The indexing pattern yield lattice constants  $a=14.96$ ,  $b=10.03$ ,  $c=8.74$   $\text{\AA}^\circ$  for  $[\text{Co}_2(\text{ADN})(\text{URL})(\text{OH})_4(\text{H}_2\text{O})].2\text{H}_2\text{O}$ ;  $a=8.03$ ,  $b=6.06$ ,  $c=6.55$   $\text{\AA}^\circ$  for  $[\text{Ni}_2(\text{ADN})(\text{URL})(\text{OH})_4(\text{H}_2\text{O})].2\text{H}_2\text{O}$ ;  $a=9.14$ ,  $b=7.01$ ,  $c=5.60$   $\text{\AA}^\circ$  for  $[\text{Cu}_2(\text{ADN})(\text{URL})(\text{OH})_4(\text{H}_2\text{O})].2\text{H}_2\text{O}$ ;  $a=11.03$ ,  $b=9.14$ ,  $c=6.14$   $\text{\AA}^\circ$  for  $[\text{Zn}_2(\text{ADN})(\text{URL})(\text{OH})_4(\text{H}_2\text{O})].2\text{H}_2\text{O}$ ;  $a=6.90$ ,  $b=5.97$ ,  $c=5.60$   $\text{\AA}^\circ$  for  $[\text{Cd}_2(\text{ADN})(\text{URL})(\text{OH})_4(\text{H}_2\text{O})].2\text{H}_2\text{O}$  indicating orthorhombic symmetry for all above complexes.

On the basis of the above studies, the structure of the complexes may be supported as shown in (I), the complexes are polymeric in nature involving adenine as well as  $-\text{OH}$  group as bridging ligands. During polymerization one metal atom is bound via  $-\text{N}_{(3)}$  atom of one adenine ligand and  $-\text{N}_{(7)}$  atom of other adenine ligand.

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**Table 1. Analytical data and colors of the complexes.**

Formula	Color	M%		C%		H%		N%		Yield %
		Cal.	Found	Cal.	Found	Cal.	Found	Cal.	Found	
[Co <sub>2</sub> (ADN)(URL)(OH) <sub>4</sub> (H <sub>2</sub> O)].2H <sub>2</sub> O C <sub>9</sub> H <sub>18</sub> Co <sub>2</sub> N <sub>7</sub> O <sub>9</sub>	Violet	24.19	24.20	22.20	22.01	3.72	3.70	20.13	20.09	90
[Ni <sub>2</sub> (ADN)(URL)(OH) <sub>4</sub> (H <sub>2</sub> O)].2H <sub>2</sub> O C <sub>9</sub> H <sub>18</sub> Ni <sub>2</sub> N <sub>7</sub> O <sub>9</sub>	yellowish green	24.23	24.18	22.21	22.33	3.72	3.71	20.15	20.19	80
[Cu <sub>2</sub> (ADN)(URL)(OH) <sub>4</sub> (H <sub>2</sub> O)].2H <sub>2</sub> O C <sub>9</sub> H <sub>18</sub> Cu <sub>2</sub> N <sub>7</sub> O <sub>9</sub>	Bluish green	25.60	25.71	21.77	21.73	3.65	3.69	19.75	19.74	82
[Zn <sub>2</sub> (ADN)(URL)(OH) <sub>4</sub> (H <sub>2</sub> O)].2H <sub>2</sub> O C <sub>9</sub> H <sub>18</sub> Zn <sub>2</sub> N <sub>7</sub> O <sub>9</sub>	White	26.15	26.04	21.61	21.58	3.62	3.57	19.60	19.55	83
[Cd <sub>2</sub> (ADN)(URL)(OH) <sub>4</sub> (H <sub>2</sub> O)].2H <sub>2</sub> O C <sub>9</sub> H <sub>18</sub> Cd <sub>2</sub> N <sub>7</sub> O <sub>9</sub>	white	37.84	37.78	18.19	18.12	3.05	3.01	16.50	16.56	78



**Table 2. Infrared spectral data for adenine, 5-fluorouracil and its mixed ligand complexes (cm<sup>-1</sup>).**

Band assignment	ADN	URL	Co <sup>2+</sup>	Ni <sup>2+</sup>	Cu <sup>2+</sup>	Zn <sup>2+</sup>	Cd <sup>2+</sup>
v(NH <sub>2</sub> )	3355s,b	-	3340s	3316m	3318s	3324m	3322m
v (NH <sub>2</sub> ) 2δ(NH <sub>2</sub> )	3293s	-	-	-	-	-	-
v (C <sub>(6)</sub> -H), v(C <sub>(2)</sub> -H), v (NH <sub>2</sub> )	3117s	-	3198m	3194m	3192m	3194m	3200m
v (N-H)	-	3160m	-	-	-	-	-
v C <sub>(2)</sub> =O	-	1714s	1658s	1658s	1658s	1656s	1654s
δ(NH <sub>2</sub> ), v (C <sub>(4)</sub> =O), v (C=C) in phase	1674s	1674s 1658s	1642s 1644s	1634s 1650s	1644s 1648s	1640s	1640s 1650s
v (C <sub>(4)</sub> -C <sub>(5)</sub> ), v(N <sub>(3)</sub> -C <sub>(4)</sub> -C <sub>(5)</sub> )	1560s	-	1544m	1578m	1572m	1648s 1578m	1570w
Δ (N <sub>(1)</sub> -H)	-	1510m	1512w	1510w	1508w	1510w	1510w
δ (C <sub>(2)</sub> -H)+ v(C <sub>(8)</sub> -N <sub>(9)</sub> ) +δ (C <sub>(6)</sub> -H)	1449s	-	1455s	1454s	1457s	1456s	1454s
δ(N <sub>(1)</sub> -C <sub>(6)</sub> N <sub>(6)</sub> )	1420s	-	1402m	1402m	1406m	1412m	1404m
δ(N <sub>(3)</sub> -H)	-	1417s	1402m	1402m	1406s	1412m	1404m
v (C <sub>(5)</sub> -N <sub>(7)</sub> -C <sub>(8)</sub> )	1335s	-	1340m	1336m	1340m	1352w	1352w
v (N <sub>(9)</sub> -C <sub>(8)</sub> )+ v(N <sub>(3)</sub> -C <sub>(2)</sub> )+ δ (C-H)	1309 1300	-	1312m 1282m	1316m	1314m	1306w 1304w	1304s 1301m
δ (C <sub>(8)</sub> -H)+ v( N <sub>(7)</sub> -C <sub>(8)</sub> )	1232sh	-	1214m	1272m 1198s	1316m -	-	-
v (C <sub>(8)</sub> -N <sub>(7)</sub> )+ δ (C <sub>(6)</sub> -N <sub>(6)</sub> -H)+ v (C <sub>(1)</sub> -N <sub>(2)</sub> )	1156w	-	1145m	1138m	1147m	1152m	1142m
v (C <sub>(2)</sub> -N <sub>(3)</sub> )+ v (N <sub>(9)</sub> -R)	1126m	-	1115w	1116w	1114w	1114w	1111w
(NH <sub>2</sub> )	1023m	-	1030m	1020m	1038m	1026m	1032m
(NH <sub>2</sub> )+ v( N <sub>(1)</sub> -C <sub>(6)</sub> )	939s	-	920w	922m	936m	934w	944m
δ(N <sub>(1)</sub> -C <sub>(2)</sub> -N <sub>(3)</sub> )+ v (C <sub>(5)</sub> N <sub>(7)</sub> ),(H)	871m	-	834m	827w	834w	834w	832w
v (M-OH <sub>2</sub> )	-	-	410w	416mb	420m	380m	346m
v (M-O)	-	-	243s 238m	244s -	242s 239s	276wb -	271m -
v (M-N)	-	-	258m 236s	239s 220w	256m -	282wb 268w	270m 245s

**Table 3 X-ray data of the complexes**

		<b>Powder</b>	<b><math>\theta</math></b>	<b>d<sub>value</sub></b> <b>Q<sub>calc</sub></b>	<b>Q<sub>obs</sub></b> <b>hkl</b> <b>pattern line</b>
1	6.9	15.9618	0.0046	0.0046	100
2	8.5	11.0365	0.0088	0.0088	010
3	10.4	8.7852	0.0130	0.0130	001
4	12.5	6.6011	0.0234	0.0234	310
5	14.3	6.1866	0.0262	0.0262	002
6	17.8	5.2718	0.0361	0.0361	012
7	17.7	4.7396	0.0444	0.0444	701
8	18.8	4.6893	0.0455	0.0454	511
9	21.2	4.2252	0.0561	0.0559	032
10	22.0	4.0353	0.0613	0.0614	503
11	22.8	3.9125	0.0654	0.0655	005
12	25.7	3.5026	0.0816	0.0817	261
13	27.3	3.2054	0.0973	0.0974	430
14	29.5	3.0653	0.1065	0.1066	154
15	30.3	2.9367	0.1158	0.1160	952
16	31.4	2.8543	0.1225	0.1227	707
17	34.6	2.6337	0.1442	0.1442	574
18	36.9	2.4396	0.1681	0.1680	395
19	44.2	2.0424	0.2394	0.2385	799

Ni <sub>2</sub> (ADN)(5FURL)(OH) <sub>4</sub> (H <sub>2</sub> O).2H <sub>2</sub> O					
1	11.0	8.0337	0.0155	0.0155	100
2	12.7	6.9619	0.0206	0.0206	010
3	13.5	6.5511	0.0233	0.0233	001
4	15.3	5.7842	0.0299	0.0310	200
5	16.5	5.3661	0.0347	0.0361	110
6	18.8	4.7145	0.0450	0.0361	110
7	22.7	3.9126	0.0653	0.0646	021
8	24.5	3.6290	0.0759	0.0749	211
9	25.6	3.4755	0.0853	0.0854	112
10	26.0	3.4230	0.0853	0.0854	103
11	27.5	3.2396	0.0953	0.0956	221
12	29.0	3.0753	0.1057	0.1058	041
13	30.2	2.9558	0.1145	0.1138	014
14	32.5	2.7517	0.1417	0.1420	105
15	33.7	2.6564	0.1417	0.1420	151
16	35.1	2.5536	0.1534	0.1526	115
17	36.0	2.4918	0.1611	0.1604	016
18	38.4	2.3414	0.1824	0.1832	171
19	40.0	2.2513	0.1973	0.1966	126
20	41.2	2.1885	0.2088	0.2090	091
21	42.6	2.1197	0.2226	0.2225	118
22	45.0	2.0121	0.2470	0.2477	490
23	48.2	1.9233	0.2703	0.2710	491
24	50.0	1.8857	0.2812	0.2813	681
25	52.3	1.8220	0.3012	0.3020	961
26	57.22	1.7471	0.3865	0.3278	981



1	9.8	9.140	0.0123	0.0123	100
2	12.6	7.016	0.0203	0.0203	010
3	15.8	5.602	0.0318	0.0318	001
4	16.4	5.398	0.0343	0.0326	110
5	18.2	4.868	0.0421	0.0441	101
6	19.0	4.665	0.0459	0.0449	210
7	21.8	4.072	0.0603	0.0609	030
8	23.6	3.765	0.0790	0.0695	410
9	25.0	3.557	0.0790	0.0810	401
10	25.4	3.502	0.0815	0.0812	040
11	26.0	3.422	0.0853	0.0855	230
12	26.6	3.347	0.0892	0.0898	420
13	27.6	3.228	0.0959	0.0954	003
14	28.6	3.117	0.1029	0.1021	520
15	29.8	2.994	0.1115	0.1107	900
16	30.6	2.918	0.1174	0.1173	231
17	31.8	2.810	0.1266	0.1254	141
18	34.0	2.633	0.1442	0.1446	403
19	35.0	2.560	0.1525	0.1526	313
20	36.0	2.491	0.1935	0.1932	223
21	36.5	2.4588	0.1654	0.1654	018
22	43.4	2.082	0.2306	0.2301	633
23	45.8	1.978	0.2555	0.2547	833

$Zn_2(ADN)(URL)(OH)_4(H_2O).2H_2O$					
1	8.0	11.038	0.0082	0.0082	100
2	9.4	9.397	0.0113	0.0113	010
3	14.4	6.143	0.0264	0.0264	001
4	15.6	5.673	0.0310	0.0308	120
5	17.4	5.673	0.0310	0.0308	220
6	18.6	4.764	0.0440	0.0441	410
7	20.6	44.306	0.0539	0.0541	211
8	21.2	4.185	0.0570	0.0572	121
9	23.0	3.862	0.0670	0.0674	501
10	24.8	3.585	0.0778	0.0774	302
11	25.8	3.449	0.0840	0.0842	260
12	26.4	3.372	0.08/9	0.0873	170
13	27.4	3.251	0.0946	0.0942	061
14	28.0	3.182	0.0987	0.0987	113
15	28.8	3.096	0.1043	0.1037	370
16	29.4	3.034	0.1086	0.1093	052
17	29.8	2.994	0.1115	0.1119	470
18	30.4	2.936	0.1160	0.1168	081
19	31.0	2.881	0.1204	0.1213	133
20	32.0	2.793	0.1281	0.1281	091
21	33.2	2.695	0.1376	0.1370	262
22	34.0	2.633	0.1442	0.1441	732
23	35.6	2.518	0.1577	0.1579	514
24	38.0	2.365	0.1787	0.1785	254
25	39.4	2.284	0.1916	0.1918	544
26	42.8	2.110	0.2246	0.2244	365



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1	13.2	6.699	0.0222	0.0222	100
2	14.8	5.978	0.0279	0.0279	010
3	15.8	5.602	0.0318	0.0318	001
4	18.6	4.764	0.0440	0.0444	200
5	20.6	4.306	0.0539	0.0540	101
6	24.0	3.703	0.0729	0.0723	210
7	27.2	3.274	0.0932	0.0945	310
8	29.0	3.075	0.1057	0.1059	130
9	30.4	2.936	0.1160	0.1167	410
10	32.6	2.743	0.1329	0.1320	221
11	33.0	2.711	0.1360	0.1359	212
12	34.4	2.560	0.1525	0.1512	023
13	37.0	2.426	0.1699	0.1695	132
14	37.8	2.377	0.1769	0.1764	421
15	39.0	2.306	0.1880	0.1878	241
16	40.0	2.251	0.1973	0.1974	142
17	40.2	2.240	0.1992	0.1986	521
18	42.4	2.129	0.2206	0.2208	621
19	46.8	1.938	0.2662	0.2661	514
20	47.6	1.908	0.2746	0.2748	722
21	50.6	1.801	0.3082	0.3075	416