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*Note*

# Suitability of the Topological Index $W^{1/3}$ for Estimation of the Stability Constants of Coordination Compounds

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The cubic root of the Wiener number, $W^{1/3}$, was correlated to stability constants of copper(II) chelates with naturally occurring amino acids and their *N*-alkylated derivatives. The results were compared to similar correlations obtained by other topological indices (*W* and Randić's connectivity indices). $W^{1/3}$ yielded the best result in four out of nine cases, and in all cases yielded better results than topological index *W*.

*Key words*: copper(II) complexes, amino acids, Wiener number.

In an attempt to develop a model suitable for prediction of the gas-chromatographic behavior of alkanes and cycloalkanes, Croatian chemists fitted the regression parameters, $a$ and $b$, to the function,

$$\mathrm{RI} = a[W(\mathrm{G})]^b \tag{1}$$

where RI and *W* are the GC retention and the Wiener index (number), respectively.[1] They noticed that parameter $b$ converged to a value very close to 1/3 ($b = 0.325 \pm 0.0004$ for alkanes, $b = 0.292 \pm 0.003$ for cycloalkanes), which led them to the assumption that $W^{1/3}$ had a physical meaning by itself – it is related to the radius of the molecule, since the authors assumed *W* to be roughly proportional to molecular volume.

TABLE I

Linear regression of stability constants[a] on the Wiener ($W$) and valence-connectivity indices ($\chi^v$) – $N$, number of complexes, $r$, the correlation coefficient

| Index | $N$ | Slope (S.E.) | Intercept (S.E.) | $r^2$ | Set[b] |
|---|---|---|---|---|---|
| | | Dependent variable: log $\beta_{110}$ | | | |
| $W^{1/3}$ | 6 | –0.729(0.127) | 9.906(0.485) | 0.892 | a2 |
| $W^{2/3}$ | 6 | –0.0989(0.0201) | 8.636(0.318) | 0.858 | a2 |
| W | 6 | –0.0172(0.0041) | 8.221(0.279) | 0.818 | a2 |
| $^1\chi^v$ | 6 | –0.761(0.169) | 8.967(0.417) | 0.834 | a2[c] |
| $W^{1/3}$ | 6 | –0.767(0.172) | 10.010(0.656) | 0.833 | a1 |
| $W^{2/3}$ | 6 | –0.104(0.026) | 8.672(0.409) | 0.802 | a1 |
| $W$ | 6 | –0.0182(0.0050) | 8.234(0.347) | 0.764 | a1 |
| $^2\chi^v$ | 6 | –0.624(0.161) | 8.328(0.346) | 0.789 | a1[c] |
| $W^{1/3}$ | 8 | –0.598(0.169) | 9.589(0.632) | 0.677 | b |
| $W^{2/3}$ | 8 | –0.0775(0.263) | 8.479(0.393) | 0.591 | b |
| $W$ | 8 | –0.0131(0.005) | 8.112(0.321) | 0.514 | b |
| $^2\chi^v$ | 8 | –0.954(0.184) | 8.740(0.276) | 0.836 | b[c] |
| | | Dependent variable: log $\beta_{120}$ | | | |
| $W^{1/3}$ | 5 | –1.189(0.280) | 17.975(1.010) | 0.857 | a3 |
| $W^{2/3}$ | 5 | –0.169(0.042) | 15.985(0.588) | 0.845 | a3 |
| $W$ | 5 | –0.0309(0.0081) | 15.338(0.473) | 0.828 | a3 |
| $^2\chi^v$ | 5 | –1.186(0.138) | 15.668(0.247) | 0.961 | a3[c] |
| $W^{1/3}$ | 8 | –0.976(0.270) | 17.230(1.010) | 0.686 | b |
| $W^{2/3}$ | 8 | –0.127(0.042) | 15.425(0.628) | 0.604 | b |
| $W$ | 8 | –0.0215(0.0083) | 14.827(0.513) | 0.529 | b |
| $^2\chi^v$ | 8 | –1.582(0.314) | 15.898(0.473) | 0.808 | b[c] |
| $W^{1/3}$ | 5 | –0.0428(0.0059) | 15.291(0.056) | 0.946 | c |
| $W^{2/3}$ | 5 | –2.22 (0.41) $10^{-3}$ | 15.107(0.044) | 0.908 | c |
| $W$ | 5 | –1.46 (0.03) $10^{-4}$ | 15.051(0.044) | 0.867 | c |
| $^3\chi^v$ | 5 | –0.110 (0.005) | 15.496(0.026) | 0.994 | c[c] |
| | | Dependent variable: $\beta_{110}$ – p$K_2$ | | | |
| $W^{1/3}$ | 6 | –1.130 (0.123) | 1.238(0.468) | 0.955 | a1 |
| $W^{2/3}$ | 6 | –0.155(0.020) | –0.707(0.309) | 0.940 | a1 |
| $W$ | 6 | –0.0273(0.0041) | –1.342(0.284) | 0.916 | a1 |
| $^1\chi^v$ | 6 | –1.194(0.179) | –0.184(0.441) | 0.917 | a1[c] |
| $W^{1/3}$ | 6 | –1.126(0.124) | 1.226(0.475) | 0.954 | a2 |
| $W^{2/3}$ | 6 | –0.155(0.020) | –0.719(0.920) | 0.938 | a2 |

TABLE I (cont.)

| | | | | | |
|---|---|---|---|---|---|
| $W$ | 6 | –0.0264(0.0042) | –1.355(0.288) | 0.941 | a2 |
| $^1\chi^v$ | 6 | –1.159(0.133) | –0.224(0.327) | 0.950 | a2[c] |
| $W^{1/3}$ | 8 | –0.823(0.213) | 0.401(0.799) | 0.714 | b |
| $W^{2/3}$ | 8 | –0.110(0.033) | –1.085(0.495) | 0.647 | b |
| $W$ | 8 | –0.0187(0.0066) | –1.595(0.407) | 0.575 | b |
| $^1\chi^v$ | 8 | –0.823(0.162) | –0.647(0.409) | 0.812 | b[c] |

[a] The stability constants, $\beta$, are defined by the relation: $\beta_{klm} = [Cu_kL_lH_m]/[Cu]^k[L]^l[H]^m$. $K_2$ is the second protonation constant of the ligand, L (*i.e.,* amino acid); $pK_2 = -\log K_2$.

[b] Sets: a1, stability constants of copper(II) chelates with glycine and *N*-alkylated glycines (Me-, $Me_2$-, $Et_2$-, *t*Bu-, *t*BuMe-),[2] assuming $\log \beta_{110}$(*t*BuGly) = 6.059; a2, the same as a1 assuming $\log \beta_{110}$(*t*BuGly) = 6.303; a3, the same as a1 but the complex with *t*BuGly is missing; b, stability constants for the complex of glycine and *N*-alkylated glycines (Me-, $Me_2$-, Et-, $Et_2$-, Pr-, Bu-, *i*Pr-);[2,6] *c*, stability constants of binary complexes of naturally occurring amino acids (Gly, Ala, Val, Phe, Tyr),[3,7] measured at the same temperature and ionic strength. The topological indices for sets a1, a2, a3, and b were calculated from ligand (L) constitutional formulas, and for set c from constitutional formulas of the bis-complexes, $CuL_2$.

[c] The best result reffered in the respective paper (Ref. 2: a1, a2, a3, b; Ref. 3: c).

This notion inspired me to try to apply the molecular descriptor $W^{1/3}$ to the estimation of stability constants of coordination compounds. The constants of copper(II) chelates with *N*-alkylated glycines[2] and naturally occurring amino acids[3] were previously fairy well correlated with topological indices calculated for constitutional formulas (graphs, G) of ligands[2] and chelates.[3] The four indices (the Wiener number, *W*, and first-, second-, and third-order valence-connectivity indices, $\chi^v$),[4,5] were found suitable for the estimation of stability constants of coordination compounds, but, unfortunately, no general rule was derived for their best application. Still, valence-connectivity indices yield, in general, better results than the Wiener number.[2,3]

Linear regressions of stability constants on topological indices, Table I, clearly show that $W^{1/3}$ indiscriminately yields better $r^2$ values than *W*, and in four cases out of nine regressions on $W^{1/3}$ yielded the best results obtained so far. As variable $W^{1/3}$ factually improves the results obtained with *W*, the use of $W^{1/3}$ does not help too much if *W* itself yields poor results (*cf.* set b, Table I: $r^2 = 0.677$ for $W^{1/3}$, $r^2 = 0.514$ for *W*; $\log \beta_{110}$).

At the end, I owe the reader an explanation, at least hypothetical, why descriptor $W^{1/3}$ is better than index *W*. If $W^{1/3}$ is, as already said, generalized molecular length,* it has to be in correlation with interatomic distances. On

* It was later demonstrated that the Wiener index should be better interpreted as the area of the surface of the molecule,[8] but this does not alter the general conclusion of the discussion.

the other hand, the difference in the stability of structurally related coordination compounds, like those studied in this paper, is mostly due to nonbonding (van der Waals) interactions of atoms bonded to different coordination sites (with an increase of generalized length, $W^{1/3}$, the distance between ligands decreases). As the repulsive part of van der Waals potential (operating at short distances) could be approximated with a line, it implies that a function of the form $y = a\ W^{1/3} + b$ should fit the van der Waals potential among the ligands, and therefore corresponds to the increase of (steric) energy upon complexation (this energy is in turn proportional to $-\log \beta$).

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## SAŽETAK

### Prikladnost topološkog indeksa $W^{1/3}$ za procjenu konstanti stabilnosti kompleksnih spojeva

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Treći korijen Wienerova broja, $W^{1/3}$, koreliran je s konstantama stabilnosti bakrovih(II) kelata s prirodnim aminokiselinama i njihovim *N*-alkiliranim derivatima. Rezultati su uspoređeni sa sličnim korelacijama dobivenima s drugim topološkim indeksima (*W* i Randićevi indeksi). Indeks $W^{1/3}$ dao je najbolje slaganje u četiri od devet slučaja, a uvijek se pokazao boljim od indeksa *W*.