Letters to the Editor

Oxidative addition of ethylene oxide to Pt^{II} in neutral aqueous solutions. Evidence for bifunctional behavior of $PtCl_4^{2-}$

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The complexes $PtCl_i(H_2O)_{4-i}^{2-i}$ (i = 2 to 4) are readily alkylated[1] by protonated ethylene oxide (EO) to give β-ethanolplatinum, isolated as $Cs_2Pt^{IV}(CH_2CH_2OH)Cl_5$. The activity of Pt^{II} increases in the order $PtCl_2(H_2O)_2 << PtCl_3(H_2O)^- \approx PtCl_4^{2-}$, in conformity with an S_N2 mechanism of oxidative addition. When this reaction was carried out in neutral aqueous solutions, different regularities were unexpectedly found. At 323 K and a constant ionic strength of 0.5 M, the equation $-d[EO]/d\tau = k_2[EO][PtCl_2(H_2O)_2] + k_4[EO][PtCl_4^{2-}]$, where $k_2 = 0.10 \pm 0.02$ and $k_4 = (4.2 \pm 0.3) \cdot 10^{-3}$ mol L^{-1} s^{-1}, holds; the $PtCl_3(H_3O)^-$ complex is inert. The alkylation of Pt^{II} (0.1 M) with an excess of EO (1 M) at 298 K results in the simultaneous accumulation of two organometallic derivatives. The ^1H NMR spectrum of one of these [(D_2O), δ: 3.89 (t, α-H, $^3J_{HH}$ = 7.15 Hz, $^2J_{^{195}Pt-^1H}$ = 84.5 Hz); 3.35 (t, β-H, $^3J_{^{195}Pt-^1H}$ = 12 Hz) (*cf.* Ref. 1)] corresponds to $Pt^{IV}CH_2{}^{\alpha}CH_2{}^{\beta}OH$ (product **A**) and does not change when the solution is acidified. In an alkaline medium (pH > 7.6), this complex rapidly decomposes ($k > 10^{-3}$ s^{-1}) to recover EO. The signals of the second product (**B**) [(D_2O), δ: 3.78 (t, H(α), $^3J_{HH}$ = 6.30 Hz, $^2J_{^{195}Pt-^1H}$ = 86.2 Hz); 3.16 (t, β-H, $^3J_{^{195}Pt-^1H}$ = 21 Hz)] disappear when D_2SO_4 is added; as this takes place, the intensities of the signals of complex **A** increase. When Pt^{II} is alkylated in a 0.6 M solution of NaCl, complex **B** is the only organometallic product. Complexes **A** and **B** do not decompose in an NaCl solution for several hours.

Since the addition of Cl^- suppresses the reaction of EO with $PtCl_2(H_2O)_2$, it may be concluded that product **A** results from the reaction with this complex. The increase in the acidity of H_2O in the coordination sphere of Pt^{II} makes it possible to attribute structure **C** to the transition state (TS) of this reaction. Taking into account the fact that **B** is converted into **A** when the solution is acidified and that practically no reverse reaction is observed when a solution of compound **A** is alkalified (this reaction is apparently suppressed by the rapid elimination of EO), one should attribute structure **D** to product **B**, and structure **E** should be attributed to the corresponding TS. The dissimilarity of the structures of **A** and **B** is confirmed by the substantial difference between the $^3J_{^{195}Pt-^1H}$ values.

The formation of product **B** indicates the bifunctional behavior of $PtCl_4^{2-}$: Pt^{II} in TS **E** exhibits properties of both a nucleophile and an electrophile. If we assume that the bifunctional behavior is inherent in

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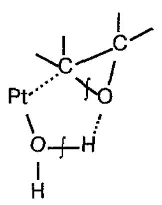

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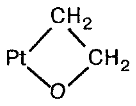

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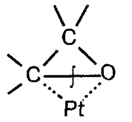

E

many metal-centered nucleophiles, we can understand why the reactivities of RI and ROTs toward the above mentioned and "normal" nucleophiles are essentially different. The higher relative rates of the reactions of RI with metal-centered nucleophiles result from the additional nucleophilic assistance to heterolysis, whereas in the case of ROTs, the leaving group has no affinity to metal complexes, and therefore, only nucleophilicity of the latter is significant.

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Intermolecular interactions in aqueous solutions of mebicar

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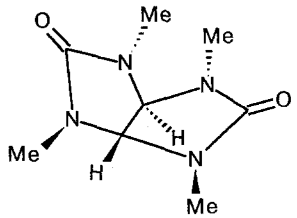
2,4,6,8-Tetramethyl-2,4,6,8-tetraazabicyclo[3.3.0]-octane-2,7-dione (mebicar, **1**) is an efficient daytime tranquilizer with a broad spectrum of activity.[1]



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Mebicar is extremely soluble in media of various polarities (g L^{-1}): 530 (H_2O), 225 (MeOH), 155 (DMSO), 250 (CH_2Cl_2), 90 ($CHCl_3$). It has been suggested that the amphiphilic nature of **1** may be associated with its pharmacological activity.[2] We studied the effects of **1** on the structure of water and on the structures and activities of model macromolecular biological systems of a protein nature.

By differential scanning calorimetry we found that **1** can be hydrated by various mechanisms simultaneously. The specific heat capacity of **1** in a 1 % aqueous solution and its temperature increment (298—373 K) are $\bar{c}_p{}^{25}$ = 2.88 J g^{-1} K^{-1} and $\Delta c_p \cdot \Delta T_m{}^{-1} = 1.46 \cdot 10^{-3}$ J g^{-1} K^{-2}. The value of the increment for **1** is comparable to that for *L*-leucine (**2**) $\Delta c_p \cdot \Delta T_m{}^{-1} = 1.1 \cdot 10^{-3}$ J g^{-1} K^{-2} (in the hydration of **2**, hydrophobic effects predominate). The low value of $\bar{c}_p{}^{25}$ for this compound, as also that for urea (**3**) ($\bar{c}_p{}^{25}$ = 1.55 J g^{-1}), characterizes the ability of these substances to break the structure of water; for compound **2**, $\bar{c}_p{}^{25}$ = 1.92 J g^{-1} K^{-1}.

Using millimeter absorption spectroscopy[4] we quantitatively evaluated the composition of the hydration shell of molecule **1**. We measured absorption (α/dB mm^{-1}) of electromagnetic radiation by aqueous solutions of **1** at the frequencies ν = 1.05, 1.40, 1.71 cm^{-1} and in the 4—7 cm^{-1} range in the 287—333 K temperature interval. The $\alpha(\nu)$ dependence at 293 K indicates that molecule **1** binds nine water molecules with lifetimes in the hydration shell $\tau \geq 10$ ps. As measurements

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