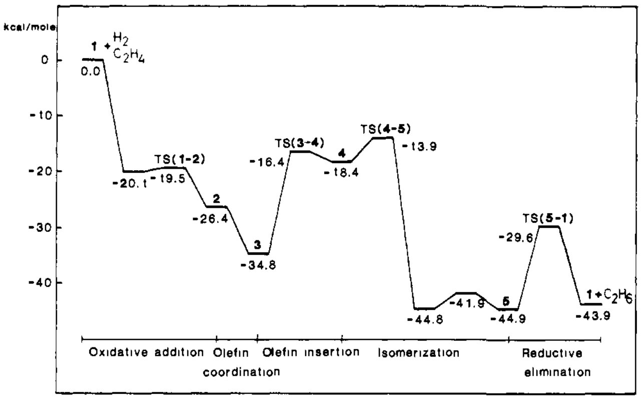

Figure 2. Potential energy profile of the entire catalytic cycle, in kilocalories per mole.

shown in Figure 1. The potential energy profile for the full cycle is shown in Figure 2. The energy difference between both ends of the profile corresponds to the energy of the reaction $H_2 + CH_2{=}CH_2 \rightarrow CH_3{-}CH_3$.[11] We find in Figure 2 that the potential energy profile is smooth, without excessive barriers and without too stable intermediates. This is, of course, the way it has to be for any good catalytic process, but it is heartening to find it out in a theoretical calculation.

The first two reactions, oxidative addition of H_2 and coordination of olefin, are found to be exothermic with little or no activation barrier. Olefin insertion, followed by isomerization of the trans ethyl hydride complex **4** to a cis complex, is the rate-determining step with a barrier height of about 20 kcal/mol. These two reactions, exothermic overall, may actually take place as one combined step with little stability in the trans intermediate **4**.[12] The final step of reductive elimination of ethane from the cis complex **5** is nearly thermoneutral with a substantial barrier (~15 kcal/mol).

Some specific features of the geometries and the energetics of the intermediates and the transition states may be noted in Figures 1 and 2. In the oxidative addition of H_2, formation of an H_2 complex is followed by a transition state, noted as TS(**1**→**2**), with a very small barrier (<1 kcal/mol). TS(**1**→**2**) is very late, with the Rh-H distances nearly as short as in the product **2**. The barrier being small, these two steps should be considered to take place as a combined step without a barrier. Olefin prefers to coordinate to the Y-shaped (trigonal bipyramidal) intermediate **2** from the HRhCl end, rather than from the HRhH end, to give **3** without a barrier. The Rh-C bond is long in **3**, probably due to the strong trans influence of the hydride as well as the electronic and steric effect of the chloride. The intermediate **3** is in a valley of the potential energy profile and may be detectable experimentally. The olefin insertion product **4** shows signs of a very strong agostic interaction, with a small RhCC angle (~80°), a short Rh···H distance, and a long CH bond (1.18 Å compared to normal 1.08 Å) interacting with Rh. The isomerization of the trans complex **4** to a cis complex, from which the reductive elimination can take place, has several possible routes and intermediates. Among them, the hydride migration from **4**, followed by the chloride migration to give **5**, seems to be the most favorable. The large exothermicity of the hydride migration brings the potential energy profile down, and the chloride migration takes place with a small (~3 kcal/mol) barrier. The ethyl migration which leads **4** directly to **5** has a higher barrier (not shown) and is unfavorable.

Detailed analysis of the geometries and the energetics of reactants, intermediates, and transition states, as well as a comparison with similar reactions studied previously, will be published elsewhere. The study of the solvent effect on the potential energy profile is also in progress.

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(10) The use of the Hartree–Fock method is justifiable for all the present complexes, where at least two phosphines and a chloride stabilize the closed-shell ground state. We use a valence double-ζ basis set for Rh with a relativistic effective core potential, the 3-21G set for hydrides and hydrocarbons, and the STO-2G set for the spectator ligands Cl and PH_3.

(11) The experimental value from the standard heat of formation is 32.7 kcal/mol,[11a] compared with the present HF/3-21G value of 43.9 kcal/mol. The 6-31G* RHF and MP2 calculations have given 44.0 and 41.1 kcal/mol, respectively.[11b] (a) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data, Suppl. 2* **1982**, 11. (b) *Carnegie-Mellon Quantum Chemistry Archive*; Whiteside, R. A., Frisch, M. J., Pople, J. A., Eds.; Carnegie-Mellon University: Pittsburgh, 1983.

(12) An electron correlation (MP2) calculation with a larger basis set at the optimized geometries of Figure 1 gives the energy of **4** higher than that of TS(**3**→**4**).

Cocomplexation of Urea and UO_2^{2+} in a Schiff Base Macrocycle: A Mimic of an Enzyme Binding Site

Catherina J. van Staveren,† David E. Fenton,‡
David N. Reinhoudt,*† Johan van Eerden,§ and
Sybolt Harkema§

Laboratories of Organic Chemistry and
Chemical Physics, University of Twente
7500 AE Enschede, The Netherlands
Department of Chemistry, The University
Sheffield S3 7HF, U.K.

Received February 3, 1987

The single-crystal X-ray structure of the ternary complex of a Schiff base macrocycle **1** shows that the electrophilic uranyl cation and urea both complex cooperatively in the cavity of the macrocycle.

As part of our work on the complexation of neutral molecules by macrocyclic ligands,[1] we are particularly interested in the complexation of urea. We have shown that urea can form complexes with (aza-)18-crown-6[2,3] but the association constants of these complexes in water are very small (18-crown-6–urea, log $K_s = 0.1$).[4]

Protonation of urea effects stronger binding especially when the crown ether is sufficiently large to form an encapsulated complex (e.g., the complex benzo-27-crown-9–urea–$HClO_4$).[5] Protonation of the weakly basic urea ($pK_a = 0.1$, water, 25 °C) requires strongly acidic conditions and to avoid this we have introduced a covalently linked carboxylic group in the cavity of the macrocycle. A strong hydrogen bond of urea with 2-carboxyl-1,3-xylyl-30-crown-9 resulted in an encapsulated complex.[6]

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† Laboratory of Organic Chemistry, University of Twente.

‡ Department of Chemistry, The University.

§ Laboratory of Chemical Physics, University of Twente.

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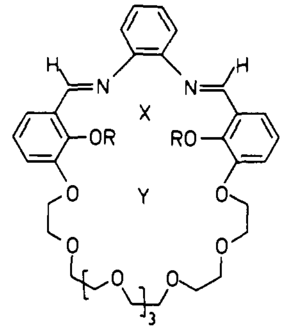
The concept of using an electrophilic center to bind urea in the cavity of a crown ether proved to be a more general concept. A metal cation can serve as the electrophile as was shown by the isolation and single-crystal X-ray analysis of the 2,6-pyrido-27-crown-9–urea–$LiClO_4$ (1:2:1) complex in which one of the urea molecules is encapsulated.[6]

In an effort to bind an electrophilic metal ion in the crown ether irreversibly we have concentrated our work on macrocycles of type **1**, since the strong binding of quadridentate (salen type) Schiff bases with soft metal ions is well-known.[7] Furthermore urea forms many complexes with such metal salts and X-ray structure determinations show that in these complexes the urea is coordinated to the metal ion via oxygen.[8] The complexation of urea by **1** would involve coordination of the carbonyl oxygen to the metal ion and additional stabilization by hydrogen bonding between the NH_2 groups of urea and polyether oxygens.



1: R = H; X = –; Y = –
2: R = H; X = –; Y = $Ba(ClO_4)_2$
3: R = –; X = Ni; Y = urea
4: R = –; X = UO_2; Y = $7H_2O$
5: R = –; X = UO_2; Y = urea

This type of cocomplexation of a neutral guest by a host molecule both by hydrogen bonding and coordination with a metal ion is frequently observed in (metallo) enzymes. Urease is believed to bind urea at the active site of the enzyme both through a coordinative bond to a nickel ion and by means of hydrogen bonds with carboxylate groups of the polypeptide chain.[9]

Reaction of 2-(allyloxy)-3-hydroxybenzaldehyde with heptakis(ethylene glycol) ditosylate, followed by removal of the protecting allyl group, and condensation with *o*-phenylenediamine with $Ba(ClO_4)_2$ as a template afforded **2** in good yield.[10]

Reaction of **2** with $Ni(OAc)_2$ in MeOH followed by removal of $Ba(ClO_4)_2$ with guanidinium sulfate and subsequent reaction with urea in MeOH afforded the complex **3** with one urea bound per nickel complex. However X-ray crystal structure determination showed that urea is only hydrogen bonded to the polyether moiety and to one of the phenolic oxygens.[10] There is no short contact between nickel and urea, owing to the preferred square-planar coordination of nickel. This prevents a planar pentagonal coordination required for the cocomplexation of urea with assistance by the polyether moiety. Therefore a cation with preferential planar pentagonal coordination was used.

Reaction of the $Ba(ClO_4)_2$ complex **2** with 1 equiv of uranyl acetate in refluxing methanol yielded the uranyl complex **4** as deep red crystals which formed upon cooling to room temperature (yield 80%, mp 110–112 °C). The mass spectrum shows a molecular ion peak at *m/e* 906.298 (calcd 906.308 for $C_{34}H_{40}N_2O_{12}U$), which indicates that the UO_2^{2+} ion is tightly bound. In the ^1H NMR spectrum (Me_2SO-d_6), the signals for the phenolic OH which are present in the $Ba(ClO_4)_2$ complex at 13.13 ppm have disappeared, indicating that the hydroxy groups are deprotonated. These observations show that the uranyl cation occupies the Schiff base cavity. From the elemental analysis we calculated that seven water molecules are coordinated to the complex. (Anal. Calcd for $C_{34}H_{40}N_2O_{12}U{\cdot}7H_2O$: C, 39.54; H, 5.27; N, 2.71. Found: C, 39.32, H, 4.84; N, 2.63.) Treatment with guanidinium sulfate in $H_2O/CHCl_3$ gave no $BaSO_4$.[10] The IR spectrum shows strong bands at 897 cm^{-1} (ν_{as}(O—U—O)) and 1602 cm^{-1} (ν(C=N)) and a strong broad band at 3450 cm^{-1} (H_2O).

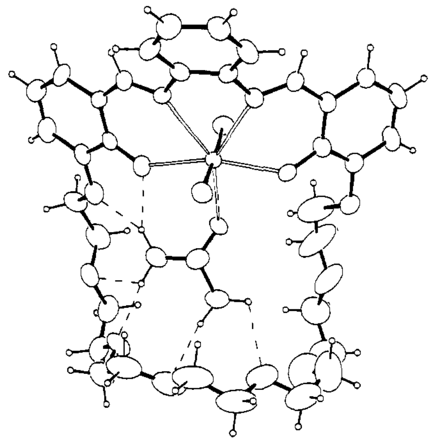


Figure 1. View of the structure of **5** showing the coordination of the U atom (U–O_{uranyl} 1.78 Å, U–$O_{phenolic}$ 2.24–2.30 Å, U–O_{urea} 2.37 Å, U–N 2.55–2.59 Å) and the hydrogen bonding of urea to the macrocycle (N···O distances 2.94–3.14 Å, N–H···O angles 109–170°).

When a solution of **4** in MeOH was treated with 1 equiv of urea in MeOH, the complex **5** precipitated immediately as a red powder (yield 70%, mp 247–249 °C). In the ^1H NMR spectrum (Me_2SO-d_6) a broad singlet at 5.4 ppm indicates the presence of urea. The mass spectrum exhibited a signal at 906.299 which corresponds to the mass of the complex without urea, but at *m/e* 60 a strong signal was present, which was not observed for the complex **4**. Satisfactory elemental analysis for $C_{34}H_{40}N_2O_{12}$-$U{\cdot}CH_4N_2O$ was obtained. The IR spectrum shows strong bands at 1640 cm^{-1} (ν(C=O)), 1602 cm^{-1} (ν(C=N)), and 896 cm^{-1} (ν_{as}(O—U—O)). The signal at 1640 cm^{-1} is also observed in infrared spectra of metal complexes of urea[11] and indicates a strong interaction of urea with the uranyl cation.

X-ray structure determination[12] (Figure 1) proved that urea is coordinated to the uranyl cation via a lone pair of electrons of the carbonyl oxygen (C=O···U angle 141°).[8] Together with the coordination of urea to one of the phenolate oxygens and five oxygens of the polyether chain via hydrogen bonds, this results in a highly structured complex. The Schiff base moiety deviates substantially from planarity, the angles between the mean planes of adjacent aromatic rings being 37° and 46°, respectively. This deformation is necessary to accomodate the large uranyl cation.[7c]

Our results show that the concept of complexation of neutral molecules assisted by electrophilic centers present in the cavity can be extended to ternary complexes. Extension to other (metallo) enzyme mimicks is in progress.

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(12) $C_{34}H_{40}N_2O_{10}{\cdot}UO_2{\cdot}CH_4N_2O$, monoclinic, space group $P2_1/c$, a = 16.280 (5) Å, b = 11.734 (3) Å, c = 20.531 (5) Å, β = 109.11 (3)°, V = 3706 (4) Å^3, Z = 4, D_c = 1.73 g cm^{-3}, μ(Mo Kα) = 42.2 cm^{-1}. Measured, 6467 unique reflections (3° < θ < 25°), T = 180 K. Position of U atom obtained from Patterson synthesis. Structure completed by successive difference Fourier syntheses. Full-matrix least-squares refinement of 3331 observed reflections ($F_o^2 > 3\sigma(F_o^2)$). After isotropic refinement of the non-H atoms an empirical absorption correction[13] was applied. Refinement was completed with anisotropic thermal parameters for the non-H atoms; all H atoms were put in calculated positions. Final R = 2.8%, R_w = 3.4%, 478 variables, largest residual peak 0.7 e Å^{-3}. All calculations were done using SDP.[14]

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Supplementary Material Available: Tables of positional and thermal parameters and bond distances and angles of the structure of **5** (6 pages). Ordering information is given on any current masthead page.

Intermolecular Influences on M–M Multiple Bonds from Thin-Film UPS Studies of Group VI $M_2(O_2CCH_3)_4$ Complexes

Dennis L. Lichtenberger* and John G. Kristofzski

Laboratory for Electron Spectroscopy and Surface Analysis
Department of Chemistry, University of Arizona
Tucson, Arizona 85721

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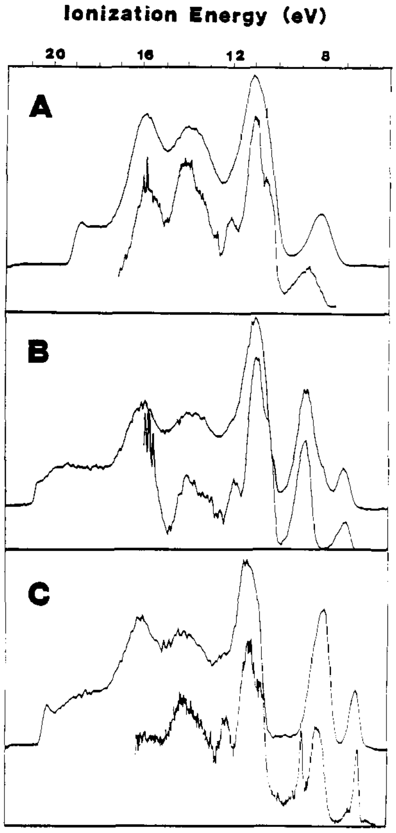

Figure 1. Valence He I photoelectron spectra of $M_2(O_2CCH_3)_4$ for (A) M = chromium, (B) M = molybdenum, and (C) M = tungsten. In each case the top spectrum is from the thin film and the bottom spectrum is from the gas phase.

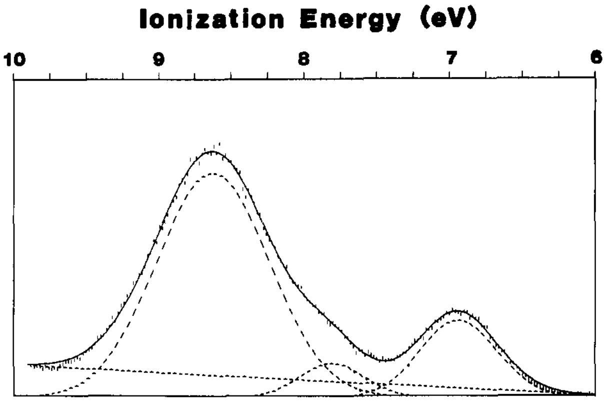

Figure 2. Close-up He I spectra of the $Mo_2(O_2CCH_3)_4$ metal ionization region for the thin film. The vertical lines indicate experimental data. The solid line is the sum of three asymmetric Gaussian peaks, shown as dashed lines.

Dimetal tetracarboxylate complexes have provided a rich arena for study of metal–metal bonding since the presence of σ-, π-, and δ-orbital symmetry interactions was first explained in 1964.[1] The title compounds have proven particularly fruitful for investigating these interactions because the volatility of these compounds makes them suitable for gas-phase photoelectron studies, thus allowing detailed experimental examination of the theoretical principles of bonding.[2-10] Development of the basic bonding description for these complexes has been accompanied by numerous studies of the effects of bridging ligands and axial interactions on the metal–metal bond strength and bond length. The Cr–Cr bond length is especially sensitive to the bridging ligand type and axial interactions.[11] The importance of axial interactions is illustrated by comparison of the hydrous and anhydrous single-crystal[12] structures of $Cr_2(O_2CCH_3)_4$ and by a further comparison of these structures to the recent gas-phase electron diffraction results of Fink and Ketkar.[13] These structures yield Cr–Cr bond lengths of 2.362 (1), 2.288 (2), and 1.966 (14) Å, respectively. In contrast, the Mo_2^{4+} and W_2^{4+} cores show minimal change in metal–metal bond length despite the use of a wide variety of bridging and axial ligands.[14,15] As one step to examining the electronic effects of axial occupation on the metal–metal bond, we have obtained the photoelectron spectra of thin films of anhydrous group VI tetraacetates. In these thin films the axial positions of the metal–metal bonds are occupied by neighboring molecules. With appropriate preparation[16] of these films in ultrahigh vacuum conditions, we are able to obtain spectra which exhibit only slight broadening as compared to the gas-phase spectra, indicating that each molecule contributing to the observation is in a similar electronic environment. The axial positions of the metal–metal

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