Hydrating the nucleophile with one water reduces the reaction efficiency,[9] but we show here that it *increases the negative temperature dependence*. Hydrating the nucleophile with two waters reduces the reaction efficiency by another 2 orders of magnitude,[9] but we show in Figure 1 that a similar negative temperature dependence is maintained.

The product distributions, reported in Figure 2, show that *Cl^- is the principal product*, whether the OD^- reactant has 0, 1, or 2 waters of hydration. Reactions efficiencies are approximately 50%, 10%, and 0.1%, respectively, to form Cl^- and 1% and 0.1% to form $Cl^-\cdot D_2O$[17] (Figure 1). The least exothermic channel is favored: strongly exothermic channels are avoided and, rather than follow them, there is no reaction at all. These systematic trends predict that *for the higher hydrates, solvation quenches reaction*, as confirmed experimentally. Similar trends have been established for both methyl bromide[18] and iodide.[19]

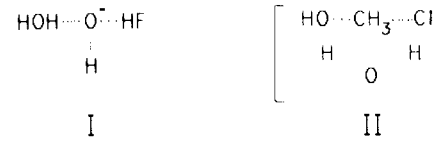
Three results require explanation: (1) Hydration reduces reactivity. (2) Hydration accentuates the negative temperature dependence of the reaction efficiency. (3) Hydrated reactants do not form hydrated products. These are discussed in turn.

(1) Wherever hydration of the reactant channels the reaction into a single product (Figure 2), hydration must progressively reduce the reaction exothermicity. If hydration decreases reactivity, this can then be expressed in terms of a reactivity/exothermicity relationship. The simplest of these is the Marcus relationship which has been applied successfully to nucleophilic displacement reactions in the gas phase *at a single temperature*.[20] This relationship describes *qualitatively*[21] the present result that, at any particular temperature, hydration reduces reactivity.

(2) Consider next how hydration affects the temperature dependence of the reaction efficiency. If hydration reduces the exothermicity (vide supra), how does the reduced exothermicity affect the temperature dependence? Analysis by Kebarle and colleagues[8] suggests that decreasing exothermicity should make the temperature dependence more negative[22] and data from a sequence of reactions of varying exothermicity demonstrate this trend.[8e] The results in Figure 2 exhibit this same trend: *hydration increases the negative temperature dependence of the reaction efficiency*.

(3) The failure to form $Cl^-\cdot D_2O$ efficiently parallels our previous study on CH_3Br,[18] suggesting again[23] that the transition state (II)—energetically and entropically unfavorable—frustrates solvate transfer from nucleophile to leaving group.

In conclusion, nucleophilic displacement and proton transfer[10] are contrasted. First, proton transfer occurs on every collision (irrespective of temperature and hydration): nucleophilic displacement does not; and efficiencies decrease with increasing hydration and temperature. This kinetic behavior can be modeled with the double-minimum potentials used to describe the two reactions.[20d] Second, hydrated products are formed efficiently for proton transfer but not for nucleophilic displacement: progressive hydration quenches nucleophilic displacement but not proton transfer. In the transition state for proton transfer (I), the polar solvate lies at the center of charge (a low-energy pathway);[10] for nucleophilic displacement (II), the solvate must span the nucleophile and leaving group, as the charge travels down



I II

the molecular backbone (a higher energy pathway, entropically disfavored).[18]

Registry No. OH^-, 14280-30-9; CH_3Cl, 74-87-3; $OH^-(H_2O)$, 23138-14-9; $OH^-(H_2O)_2$, 34118-36-0.

Supplementary Material Available: Table of numerical values of experimental and theoretical rate constants used in Figure 1 (1 page). Ordering information is given on any current masthead page.

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(22) The analysis considers how the reaction exothermicity affects the height of the central barrier in the double-minimum potential.[7,20] The temperature dependence becomes positive as the energy of the tip of the barrier exceeds that of the reactants.
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Polymetallic Systems with Subtle Spin Orders

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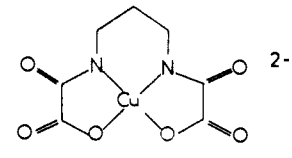
We have recently witnessed and been among the actors of a renaissance in molecular magnetism. One of the most important elements of this renaissance is the possibility of designing polymetallic systems exhibiting predictable magnetic properties.[1] Heteropolymetallic compounds play an important role along this line. Indeed, they offer a larger diversity than the homopolymetallic compounds, as for the exchange pathways between nearest-neighbor metal ions.[2-5] The goal of this paper is to emphasize that quite novel magnetic behaviors may be obtained in carefully designed polymetallic systems. For that, we present a few of the examples recently investigated in our group.

Some years ago, Monoyama et al.[6] described the copper(II) mononuclear dianion **1**, derived from the 1,3-propylenebis(oxamate) and noted here $[Cu(pba)]^{2-}$.



1

We have found that slow diffusion of aqueous solutions of $Na_2[Cu(pba)]$ and of $M(ClO_4)_2\cdot 6H_2O$, M = Mn or Ni, affords the ordered bimetallic chains $MCu(pba)\cdot nH_2O$. When M is manganese(II), the compound $MnCu(pba)(H_2O)_3\cdot 2H_2O$ (**2**) was obtained in the form of well-shaped light-blue single crystals. The crystal structure was determined. **2** crystallizes in the orthorhombic system, space group *Pnma*. The lattice parameters are $a = 12.945$ (1) Å, $b = 21.250$ (4) Å, and $c = 5.2105$ (8) Å, with $Z = 4$ MnCu units. A perspective view of the structure is shown in Figure 1. The Mn^{2+} ions are in elongated octahedral surroundings with two water molecules in apical positions and the Cu^{2+} ions are in square-pyramidal surroundings with a water

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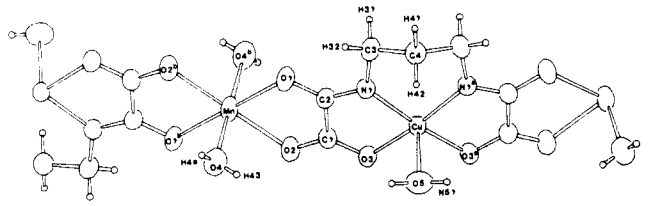


Figure 1. Perspective view of the bimetallic chain MnCu(pba)$(H_2O)_3 \cdot 2H_2O$ (**2**). The Mn atom is located at a center of symmetry and the Cu atom in a mirror plane. Selected bond lengths: Mn–O1 = 2.165 (1), Mn–O2 = 2.169 (1), Mn–O4 = 2.197 (2), Cu–N1 = 1.933 (1), Cu–O3 = 1.990 (1), Cu–O5 = 2.281 (2).

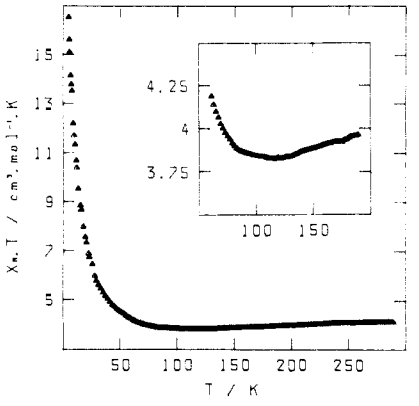


Figure 2. Temperature dependence of $\chi_M T$ for the bimetallic chain MnCu(pba)$(H_2O)_3 \cdot 2H_2O$ (**2**) in the 300–4.2 K temperature range. In the inserted frame, we expanded the $\chi_M T$ axis in the 50–200 K temperature range to give evidence of the minimum of $\chi_M T$.

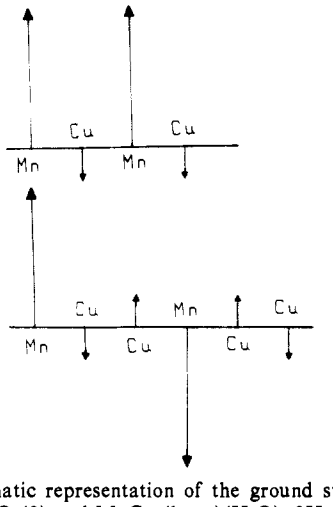


Figure 3. Schematic representation of the ground state for MnCu(pba)$(H_2O)_3 \cdot 2H_2O$ (**2**) and $MnCu_2$(bapo)$(H_2O)_4 \cdot 2H_2O$ (**4**).

molecule at the apex. Within the chains, two nearest-neighbor metal ions are bridged by an oxamato group with a Mn···Cu separation of 5.412 Å. The variation vs. the temperature T of the product $\chi_M T$, χ_M being the molar magnetic susceptibility per MnCu unit for **2**, is shown in Figure 2. The magnetic curve exhibits a rounded minimum at 115 K, which is the signature of this kind of antiferromagnetically coupled bimetallic chains,[4,5,7] and below 115 K a very fast increase of $\chi_M T$ upon cooling down. At 4.2 K, $\chi_M T$ reaches the extremely high value of 17 cm^3 mol^{-1} K. This low-temperature magnetic behavior is due to the fact that the ground state of the chain may be symbolized by $[S_{Mn} = {}^5/_2, S_{Cu} = -{}^1/_2]_n$ (see Figure 3), which is qualitatively equivalent to a chain of ferromagnetically coupled $S = 2$ local spins.

One of the main challenges in the area of the molecular materials is the design of molecular ferromagnets.[8,9] The first step

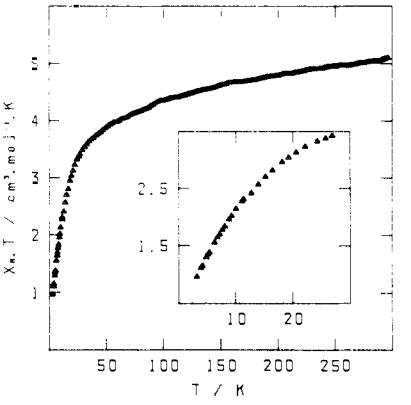
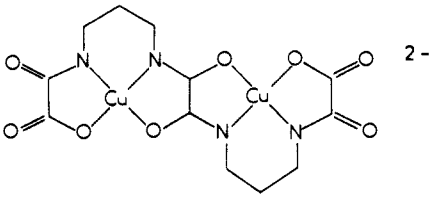


Figure 4. Temperature dependence of $\chi_M T$ for $MnCu_2$(bapo)$(H_2O)_4 \cdot 2H_2O$ (**4**) in the 300–3 K temperature range. In the inserted frame, we expanded the T axis in the 0–30 K temperature range to emphasize the decrease of $\chi_M T$ toward zero upon cooling down to 0 K.

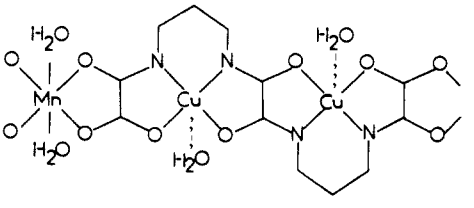
along this line is to find a strategy to stabilize a state of high-spin multiplicity. The orthogonality of the magnetic orbitals is such a strategy,[2,3] but it is often difficult to achieve. In a certain sense, it requires going against a natural trend which favors the pairing of the electrons in molecular orbitals of low energy. An alternative strategy consists of imposing the parallel alignment of local spins ${}^5/_2$ (Mn^{2+} or Fe^{3+}) owing to an antiferromagnetic interaction with local spins ${}^1/_2$ (Cu^{2+}) as in **2**.

We also synthesized the copper(II) binuclear anion **3** derived



3

from the *N,N'*-bis(oxamato-1,3-propylene)oxamide, denoted here $[Cu_2(bapo)]^{2-}$. An aqueous solution of $Na_2[Cu_2(bapo)]$ reacts with an aqueous solution of $M(ClO_4)_2 \cdot 6H_2O$, M = Mn or Ni, to give chain compounds with the so far unknown MnCuCu arrangement. When M = manganese(II), the compound $MnCu_2(bapo)(H_2O)_4 \cdot 2H_2O$ (**4**) was obtained. Anal. Calcd for $C_{12}H_{24}N_6O_{14}Cu_2Mn$ (**4**): C, 22.88; H, 3.84; N, 8.89; O, 35.53; Cu, 20.16; Mn, 8.72. Found: C, 22.64; H, 3.96; N, 9.19; O, 35.13; Cu, 20.11; Mn, 8.39. Its structure is most likely as shown below:



4

The magnetic properties of **4** are shown in Figure 4, again in the form of a $\chi_M T$ per MnCuCu unit vs. T plot. $\chi_M T$ continuously decreases upon cooling down and tends to zero when T approaches zero. This arises from the fact that now the ground state of the $[MnCuCu]_n$ chain is $[+{}^5/_2, -{}^1/_2, +{}^1/_2, -{}^5/_2]_{n/2}$ as schematized in Figure 3, and at 0 K, there is no magnetic moment.

In this paper, we focused on the design of polymetallic systems exhibiting unusual or so far unknown spin arrangements. Some

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(10) **3** was prepared as follows: the action of 2 mol of ethyl oxamate on 1 mol of 1,3-propylenebis(oxamate) affords the 1,3-oxamidobis(propyleneoxamate), which reacts with 2 mol of $Cu(OH)_2$ in the presence of 4 mol of OH^- to give, after hydrolysis of the terminal primary groups, **3**.

of these systems, like the $Mn^{2+}Cu^{2+}$ bimetallic chains, could represent quite an important step in the perspective of molecular ferromagnets. The quantitative interpretation of the magnetic properties as well as the investigation of the other physical properties will be developed in a subsequent paper.

Registry No. 1·2Na, 61344-73-8; 2, 101935-07-3; 3·2Na, 101954-74-9; 4, 101935-08-4; NiCu(pba)·$3H_2O$, 101935-09-5; ethyl oxamate, 617-36-7; *N,N'*-bis(aminopropylene)oxamate, 19980-60-0; *N,N'*-bis(oxamato-1,3-propylene)oxamide, 101954-75-0.

Supplementary Material Available: Atomic parameters and listing of structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

Evidence for an Enol Intermediate in the 3-Oxo-Δ^5-steroid Isomerase Catalyzed Isomerization of Δ^5 Ketones

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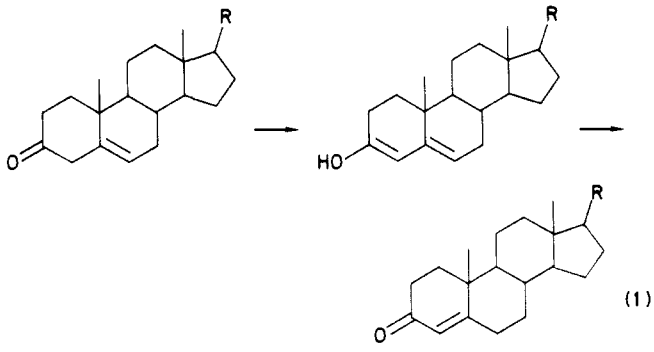
Received January 21, 1986

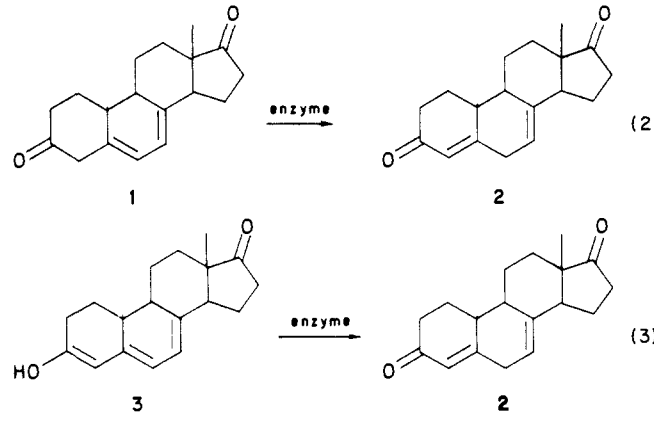
The 3-oxo-Δ^5-steroid isomerase (EC 5.3.3.1) from *Pseudomonas testosteroni* catalyzes the isomerization of a variety of $\Delta^{5,6}$ and $\Delta^{5,10}$ steroids to their Δ^4 isomers.[1,2] This enzyme is of particular interest due to its extremely high activity ($k_{cat} = 4.4 \times 10^6$ min^{-1} at pH 7 and 25 °C with 5-androstene-3,17-dione as the substrate).[1] The mechanism has been extensively investigated and both Asp-38 and Asn-57 have been identified at the active site.[3-7] The proposed catalytic mechanism involves protonation of the carbonyl followed by proton transfer of the 4β-hydrogen to the 6β-position through the intermediate formation of a dienol (eq 1).[9] Although model



(1)

reactions have demonstrated that a mechanism involving a Schiff base intermediate can account for a substantial fraction of the catalytic activity,[10-12] no evidence has been found which confirms an intermediate of this type.[1]

We now wish to report that the isomerase catalyzes the interconversion of 5,7-estradiene-3,17-dione (**1**) to 4,7-estradiene-3,17-dione (**2**). Furthermore, the putative intermediate trienol **3** also serves as a substrate for the isomerase, implicating an enol intermediate in the overall catalytic process.



Trienol **3** was synthesized according to a published procedure[13] by quenching the enolate of 4,6-estradiene-3,17-dione (**4**) in acetic acid–water (1:1). Although **3** is unstable in solution, it can be stored for several days as a solid under vacuum. The ultraviolet spectrum of our sample showed $\lambda_{max}^{MeOH} = 320$ nm, ϵ 13 000 (lit.[13] 320 nm, ϵ 15 000) with no evidence of substantial absorbance due to contamination by **1** (λ_{max}^{MeOH} 281 nm, ϵ 8600),[13] **2** (λ_{max}^{MeOH} 238 nm, ϵ 14 950),[13] or **4** (λ_{max}^{MeOH} 280 nm, ϵ 26 300).[14] Quenching the enolate of **4** in acetic acid/benzene (1:2) gave a mixture of **1**, **2**, and **4**, with **1** as the major product on the basis of the ultraviolet spectrum.[13] Alternatively, **1** could be prepared in situ from trienol **3**. When **3** is added to acetate buffer at 25 °C and pH 4.5, the predominant product formed after about 5 min is **1** (ca. 90%) with some contamination by **4** (ca. 10%). This latter procedure proved to be the most convenient, as **1** decomposes to **4** when stored in solution. Reproducible results were most easily obtained by generating **1** in situ immediately before the kinetic measurements.

The 5,7-dienone **1** was examined as a substrate for the isomerase (pH 4.49, 0.034 M acetate, 1.7% methanol) at 25.0 and 10.0 C.[15] Initial rates were determined at substrate concentrations ranging from 20 to 150 μM and an enzyme concentration of 4.3×10^{-11} M (10 °C) or 2.9×10^{-11} M (25 °C) by monitoring the increase in absorbance due to appearance of the 4,7-dienone **2** (λ_{max}^{MeOH} = 246 nm). Values of k_{cat}/K_m were determined from weighted least-squares analysis of plots of $1/V$ vs. $1/[S]$ and found to be $(6.6 \pm 0.5) \times 10^9$ M^{-1} min^{-1} (25 °C) and $(2.5 \pm 0.2) \times 10^9$ M^{-1} min^{-1} (10 °C). Although the unavoidable presence of small amounts of the competitive inhibitor **4** ($K_I = 18$ μM) complicates the interpretation of the kinetics, the ratio k_{cat}/K_m may be obtained from the slope of a plot of $1/V$ vs. $1/[S]$.[16] Lower limits for both k_{cat} and K_m are given by k_{cat}^{app} (6.2×10^5 min^{-1} at 25 °C and 1.90×10^5 min^{-1} at 10 °C) and K_m^{app} (95 μM at 25 °C and 75 μM at 10 °C). A comparison with k_{cat}/K_m at pH 4.5 and 25 °C

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(15) Both **1** and **3** are quite labile to isomerization, particularly in neutral and basic solutions. In order to minimize the background rate it was necessary to examine the enzyme-catalyzed reaction of **2** and **3** at pH 4.5 and, in the case of **3**, 10.0 °C. The isomerase activity at pH 4.5 is approximately half of that at pH 7 toward a variety of other substrates.
(16) If the ratio [I]/[S] is constant then

$$V = \frac{V_{max}[S]}{[S] + K_m(1 + [I]/K_i)} = \frac{V_{max}[S]}{[S] + C[S]K_m/K_i + K_m}$$

where $C = [I]/[S]$. Inverting gives

$$\frac{1}{V} = \frac{K_m}{V_{max}}\frac{1}{[S]} + \frac{1}{V_{max}}\left(C\frac{K_m}{K_i} + 1\right)$$

A plot of $1/V$ vs. $1/[S]$ gives K_m/V_{max} as its slope. The intercept divided by the slope is equal to $1/K_m^{app} = 1/K_m + C/K_i$. Accurate determination of k_{cat} and K_m requires a knowledge of the exact value of C. Our value is not sufficiently precise to allow a meaningful calculation.

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