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(15) This type of decomposition reaction may be responsible for the relative scarcity of early transition metal "perphenyl" complexes, M(phenyl)$_x$.[14b] (See also ref 5 and 6.)
(16) Calcd for $TaC_{19}H_{29}$: C, 52.06; H, 6.66. Found: C, 52.09; H, 6.40. ^1H NMR (τ, C_6D_6): 2.60–3.30 (m, 5, C_6H_5), 8.53 (s, 15, C_5Me_5), 8.87 (s, 9, $TaMe_3$). The methyl groups are equilibrating rapidly on the NMR time scale at this temperature, presumably by a "reverse" pseudorotation (tetragonal pyramid to tetragonal pyramid; cf. TaCp″Me_3Cl in text).
(17) Calcd for $TaC_{18}H_{25}$: C, 51.19; H, 5.96. Found: C, 52.10; H, 6.02. ^1H NMR (τ, C_6D_6): 1.50 and 2.48 (AA′BB′ pattern, 4, C_6H_4), 8.20 (s, 15, C_5Me_5), 9.79 (s, 6, $TaMe_2$).
(18) ^{13}C NMR (parts per million downfield of Me_4Si in C_6D_6, ^1H decoupled): 11.0 (q, $^1J_{CH}$ = 127 Hz, C_5Me_5), 52.7 (q, $^1J_{CH}$ = 120 Hz, $TaMe_2$), 115.3 (s, C_5Me_5), 131.8 (d, $^1J_{CH}$ = 159 Hz, C_6H_4), 132.4 (d, $^1J_{CH}$ = 159 Hz, C_6H_4), 230.5 (s, $^2J_{CH}$ = 8 Hz, C_6H_4).
(19) Red crystalline $Nb(C_5Me_5)Me_3Cl$ is prepared in 87% yield by the addition of solid LiC_5Me_5 to an ethereal solution of $NbMe_3Cl_2$[14b] followed after 1 h by filtration and concentration in vacuo. ^1H NMR (τ, C_6D_6): 8.30 (s, 15, C_5Me_5), 8.60 (s, 9, 3Me). Reaction with phenyllithium gives **4** in 60% isolated yield.
(20) ^1H NMR (τ, C_6D_6): 1.65 and 2.55 (AA′BB′ pattern, 4, C_6H_4), 8.22 (s, 15, C_5Me_5), 9.40 (s, 6, $NbMe_2$). ^{13}C NMR (parts per million, $CDCl_3$, −40 °C, ^1H decoupled): 10 (s, $C_5\mathit{Me}_5$), 44 (s, $NbMe_2$), 115 (s, C_5Me_5), 129 (s, C_6H_4), 130 (s, C_6H_4), 213 (s, C_6H_4).
(21) (a) Anal. Calcd for $TaC_{20}H_{29}$: C, 53,34; H, 6.48. Found: C, 53.42; H, 6.54. (b) ^1H NMR (τ, C_6D_6, 80 °C, except phenyl protons): 5.92 (t, 2, $^2J_{HH}$ = 6 Hz, $TaC\mathit{H}_2CH_2C_6H_4$), 7.95 (t, 2, $^2J_{HH}$ = 6 Hz, $TaCH_2C\mathit{H}_2C_6H_4$), 8.38 (s, 15, C_5Me_5), 9.30 (s, 6, $TaMe_2$). ^{13}C NMR (parts per million, ^1H gated decoupled, C_6D_6): 11.2 (q, $^1J_{CH}$ = 128 Hz, $C_5\mathit{Me}_5$), 44.4 (t, $^1J_{CH}$ = 124 Hz, $TaCH_2\mathit{C}H_2C_6H_4$), 74.4 (br q, $^1J_{CH}$ = 123 Hz, $TaMe_2$), 96.1 (t, $^1J_{CH}$ = 117 Hz, $Ta\mathit{C}H_2CH_2C_6H_4$), 119.5 (s, C_5Me_5), 124.6 (d, $^1J_{CH}$ = 160 Hz, C_6H_4), 126.7 (d, $^1J_{CH}$ = 159 Hz, C_6H_4), 127.3 (d, $^1J_{CH}$ = 158 Hz, C_6H_4), 137.6 (d, $^1J_{CH}$ = 163 Hz, C_6H_4), 158.6 (s, C_6H_4), 213.9 (s, C_6H_4).
(22) At −52 °C two methyl peaks are found at 69.8 and 79.0 ppm in the $^{13}C\{^1H\}$ NMR spectrum in toluene-d_8. $\delta\nu_\infty$ for the two methyl groups is 138 ± 10 Hz and $k_c = 308\ s^{-1}$ at $T_c = 288 \pm 10$ K or $\Delta G^{\ddagger} = 13.6 \pm 0.5$ kcal mol^{-1}.
(23) By ^{13}C NMR, if $\delta\nu_\infty$ is estimated as 70 Hz and T_c = 193 K, then $\Delta G^{\ddagger}$ (maximum) = 9.2 kcal mol^{-1}. By ^1H NMR, if $\delta\nu_\infty$ is estimated as 81 Hz, J_{HH} = 10 Hz and T_c = 178 K, then $\Delta G^{\ddagger}$ (maximum) = 8.4 kcal mol^{-1}.
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Received August 3, 1978

Synthesis and Structure of the Imidazolate Bridged Dicopper(II) Ion Incorporated into a Circular Cryptate Macrocycle

Sir:

Discrete imidazolate (im) bridged binuclear metal complexes are of interest to prepare and characterize since units of this kind are known[1] or proposed[2] to exist in metalloproteins. Previously we described a number of imidazolate bridged dicopper(II) complexes.[3] Related bis[methylmercury(II)],[4] bis[porphyrinatoiron(II)] and -[porphyrinatomanganese(II)],[5] cobalt and ruthenium ammine,[6] as well as additional dicopper(II)[7] compounds are also known. Some of these compounds have been shown to undergo pH dependent imidazolate bridge splitting reactions,[3,4] of relevance to proposed enzyme mechanisms.[8] Additional solution studies would be greatly facilitated if the imidazolate bridged bimetallic center were incorporated into a ligating cavity that would prevent the two metal ions from migrating away from each other when the bridge is broken. The ligand 4,5-bis[2-(2-pyridyl)ethyliminomethyl]-imidazolate (bpim) was synthesized for this purpose, but the imidazolate bridge in Cu_2bpim^{3+} (**1**) is too stable, remaining intact down to pH 4.25.[3a] Examination of the structure of the $[(Me_4dien)_2Cu_2(im)(ClO_4)_2]^+$ cation[3c] (**2**) suggested that circular cryptate macrocycles such as **3** (macrocycle A), in which two five-atom chains link the two diethylenetriamine moieties, would be ideally suited to girdle the $[Cu_2(im)]^{3+}$ ion. Here we report the synthesis and X-ray crystal structure of one such compound, $[Cu_2(imH)_2(im)\subset A](ClO_4)_3$.[10]

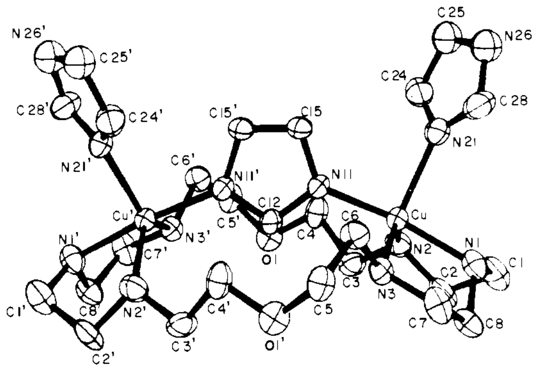
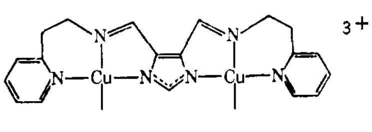
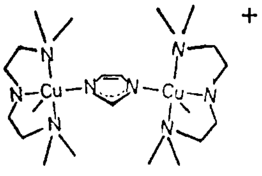


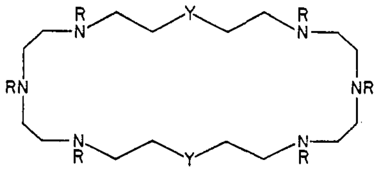
Figure 1. Structure of $[Cu_2(imH)_2(im)\subset A]^{3+}$ showing the 40% probability thermal ellipsoids. The primed and unprimed atoms are related by a crystallographically required twofold symmetry axis. Selected bond distances (in ångstroms; esd, ~0.01 Å) follow: Cu-N(1), 2.033; Cu-N(11), 1.946; Cu-N(2), 2.251; Cu-N(3), 2.131; Cu-N(21), 2.133. Selected bond angles (in degrees; esd, ~0.4°) follow: N(11)-Cu-N(1), 171.5; N(11)-Cu-N(21), 94.2; N(11)-Cu(N(2), 98.9; N(11)-Cu-N(3), 89.6; N(1)-Cu-N(2), 83.2; N(1)-Cu-N(3), 83.0; N(1)-Cu-N921), 93.7; N(21)-Cu-N(2), 97.6; N(21)-Cu-N(3), 127.9; N(2)-Cu-N(3), 133.1. The copper atom is displaced from the plane defined by N(2), N(3), and N(21) by 0.15 Å toward N(11).



Cu_2bpim^{3+} **1**



$[(Me_4dien)_2Cu_2(im)(ClO_4)_2]^+$ **2**



Macrocycle A
Y = CH_2, O
R = H, alkyl
3

The ligand A[10] was prepared as a colorless oil in 77% yield by detosylation of the monocycle amine tetratosylate (compound **10** in ref 9) using HBr, 40% in acetic acid, in the presence of 12 equiv of phenol at 80 °C for 24 h. A 60 mM solution of the macrocycle in 1.25 mL of methanol was slowly added to 3 mL of a 50 mM methanolic solution of $Cu(NO_3)_2 \cdot 3H_2O$. To the resulting deep blue solution was added 1.3 mL of 0.1 N sodium imidazolate in 90% methanol followed by an excess

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of methanolic sodium perchlorate. After removal by filtration of a small amount of purple powder, diamond-shaped blue platelets grew slowly from the deep blue filtrate.

The compound crystallizes in the monoclinic system, space group $C2/c$ or Cc, with four formulas in a unit cell of dimensions a = 15.008 (3), b = 10.186 (2), c = 26.062 (3) Å; β = 100.48 (1)°; ρ_{calcd} = 1.654, ρ_{obsd} = 1.68(1) g/cm^3. The structure, shown in Figure 1, was solved by standard Patterson and Fourier methods using 1727 independent reflections ($2\theta \leq 45°$, $F_o > 4\sigma(F_o)$) collected on a Picker FACS-I-DOS diffractometer at 23 °C using monochromatized Mo Kα radiation. The value for the conventional discrepancy index, $R_1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$, at the present stage of refinement in $C2/c$ is 0.077. Further work, to test refinement in Cc and to choose the best model for refining a disordered perchlorate anion, is currently in progress and will be reported with full details of the structure determination at a later date.

As anticipated, the $Cu_2(im)^{3+}$ ion is incorporated into the circular cryptate macrocycle A using the two diethylenetriamine units at the poles of the cavity. Each copper(II) ion is further coordinated to a neutral imidazole (imH) ligand, achieving overall pentacoordination. As may be seen from the N-Cu-N bond angles (Figure 1), the copper geometry is best described as distorted trigonal bipyramidal, with N(1) and N(11) nearly on the axis and N(2), N(3), and N(21) defining the equatorial plane. The Cu-N bond lengths are similar to those in **2**^{3c} except for Cu-N(2) which is somewhat elongated. The two ether oxygen atoms of macrocycle A do not coordinate to the metal ions, the closest nonbonded Cu···O contact being an intermolecular one of 4.67 Å. A crystallographically required twofold axis passes through atom C(12) of the bridging imidazolate ligand. Further details of the geometry are given in the caption to Figure 1.

The synthesis and structure determination of $[Cu_2(imH)_2(im)\subset A](ClO_4)_3$ demonstrates the propensity of a cryptate macrocycle to incorporate a ligand bridged bimetallic center. An unbridged pair of copper(II) ions located inside the cavity of a macrotricyclic ligand has been structurally characterized recently.[11] The present compound is of relevance to the 4-Cu(II) form of bovine erythrocyte superoxide dismutase.[12] Additional physical and chemical studies of the complex will enable its evaluation as a model for the known or postulated functions of the protein.

Acknowledgments. This work was supported at Columbia University by NIH Research Grant No. GM-16449 from the National Institute of General Medical Sciences and by Grant No. CHE 76-18434 from the National Science Foundation.

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(10) The symbol A is used to denote macrocycle A with Y = O and R = H: 1,4,7,13,16,19-hexaaza-10,22-dioxatetracosane.

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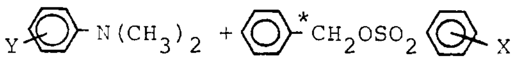
Received August 28, 1978

Carbon-14 Kinetic Isotope Effects in the Menschutkin-Type Reaction of Benzyl Benzenesulfonates with *N,N*-Dimethylanilines. Variation of the Effects with Substituents

Sir:

In 1975, we reported the first example of the bell-shaped behavior of carbon-14 isotope effects in the Menschutkin-type reaction of a series of benzyl benzenesulfonates with *N,N*-dimethyl-*p*-toluidine (eq 1, Y = *p*-CH_3).[1] The behavior indicated that the transition-state structure of the reaction varies with perturbation on the leaving group. The symmetry in terms of the force constants of two reacting bonds was demonstrated to be an important factor to determine the magnitude of the isotope effects as suggested by theoretical calculations.[2-6] Further study on the reaction has revealed that the magnitude of the effect varies not only with X but also with Y. In the present paper, the experimental results and an interpretation by means of the theory concerning the variations of transition state structures in S_N2 reactions are described.



$$\xrightarrow[45\ °C]{\text{acetone}} \text{ammonium salt} \quad (1)$$

The experimental procedure employed was the same as that reported in the previous paper.[1] The revised equation (eq 2) was used to calculate the isotope effects, where x is the fraction of reaction, A_x is the specific activity of the recovered product at x, and A_∞ is that at 100% reaction.[7] Isotope effects obtained are tabulated together with rate constants in Table I. The effects are plotted against substituent constants of X and Y in Figures 1a and 1b, respectively.[8]

$$A_x = A_\infty[1 - (1 - x)^{k^{14}/k^{12}}]/x \qquad (2)$$

The bell-shaped behavior is apparent in four cases out of six in Figure 1 including the one reported before (Figure 1a, Y = *p*-CH_3). Furthermore, it seems reasonable to regard the monotonous trends in Figure 1a in the cases of Y = H and *p*-CH_3O as parts of bell-shaped curves; for these two cases the maximum position presumably would be found at a more electron-withdrawing and a more electron-donating area of X, respectively. A shift of this type in the position of a maximum appears clearly in Figure 1b where the maximum for X = *m*-NO_2 occurs at a more electron-withdrawing area of Y compared with the maxima for X = H and *p*-Cl.

Since the magnitude of the kinetic isotope effects is connected directly with the transition-state structure, the variation of the isotope effect is expected to be explained as a result of variation of transition-state structures. According to Swain-

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