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Ring Size Effects in Phenol–Phenolate Tungsten (VI) Chelates

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A growing number of hydrogen-bonded metal diol complexes, many of which contain catechol as a ligand, have been isolated.[1] Based on the significance of hydrogen-bonding interactions in the design of molecular receptors and the potential utility of transition-metal-containing hydrogen-bonded molecules in materials synthesis, new and synthetically flexible examples of such precursors would be highly interesting.[2] In our ongoing research using substituted binaphthol (R_2BINOH_2) as a chiral auxiliary,[3] we have discovered an interesting class of complexes of the formula $W(=X)Cl_3(OArOH{\cdot}OEt_2)$ ($X = O$ and NC_6H_3-2,6-Me_2), derived from monoanionic aromatic diol ligands.[1a] We have extended our study to include a range of aromatic diols to determine the effect of the chelate ring size and steric characteristics of phenol substituents on the strength of the hydrogen bond.

The formation of the phenol-phenoxide complexes is solvent dependent. Alcoholysis reactions between aromatic diols and $W(=X)Cl_4$[4] in THF generate the expected dianionic aryloxide product $[W(=X)(OArO)Cl_2(THF)]$ as dark purple to brown solids. The THF ligand in these molecules is presumably *trans* to the X and is highly labile, exhibiting rapid exchange with free THF on the NMR time scale. Similar alcoholysis reactions performed in Et_2O produce purple crystalline products of the formula $W(=X)Cl_3(OArOH{\cdot}OEt_2)$ where $X = O$ and dark purple to brown solids where $X = NC_6H_3$-2,6-Me_2.[5] Despite the appearance that the phenol–phenolate derivatives are merely kinetically-trapped intermediates in the formation of the bisaryloxide complexes, many of them show substantial stability in noncoordinating solvents. Titrating the ether complexes with THF at ambient temperature initially generates a hydrogen-bonded THF complex, which quickly decomposes into uncharacterized products and free diol. Depending on the identity of the aromatic diol derivative employed (Figure 1), the products possess either rigorous C_s or C_1 symmetry in variable temperature NMR studies and exhibit an uncoupled proton resonance ranging between $\delta = 15$ and 6, consistent with the terminal phenol ligand.[6] Like the THF ligands in the dianionic chelates, the hydrogen bonded Et_2O rapidly exchanges with free ether. The chemical shift of the hydrogen bonding proton is both temperature and concentration dependent, although the magnitude of this dependence varies markedly with the identity of the ligand.

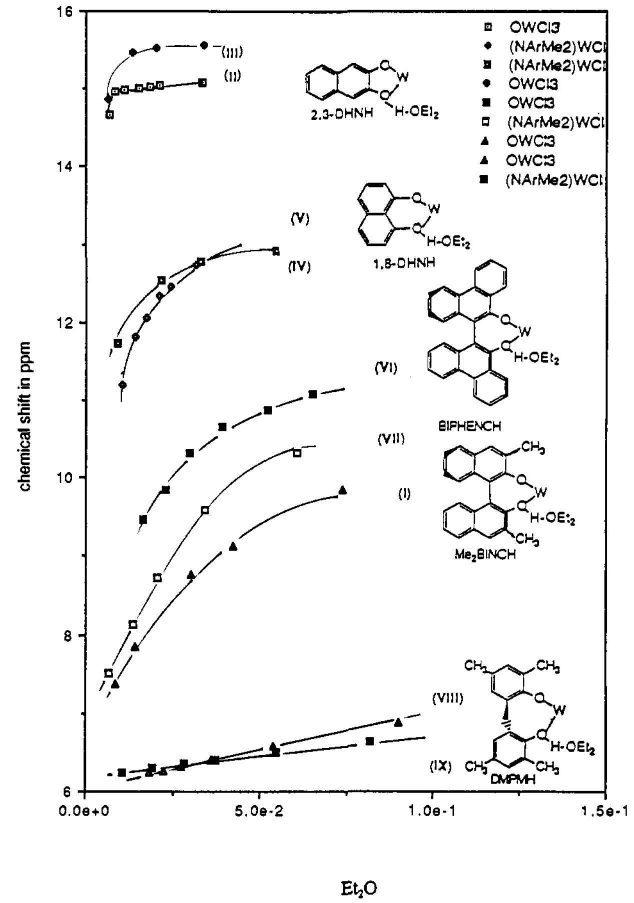

Figure 1. Variations in the chemical shift of the hydrogen bonded proton as a function of the Et_2O concentration for various $W(=X)Cl_3(OArOH{\cdot}OEt_2)$ complexes at ambient temperature.

An X-ray crystallographic study of $W(=O)Cl_3(Me_2BINOH{\cdot}OEt_2)$ confirms that, like the analogous catechol derived compound,[1a] the molecule adopts an octahedral geometry with the chloride ligands in a *mer* arrangement (Figure 2).[7] The binaphthol ligand chelates in a previously unobserved naphtholate–naphthol bonding mode, with a dihedral angle between the naphthyl rings of 63°. The naphthol unit adopts the expected *trans* relationship to the oxo ligand, and the 2.262(6)-Å W–O(3)

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[5] A representative procedure for preparation of $W(=X)Cl_3(OArOH{\cdot}OEt_2)$: under N_2, $W(=X)Cl_4$ is slurried in dry Et_2O. For $X = O$, the aromatic diol is added by an addition tube at 0 °C and stirred overnight. For $X = NC_6H_3$-2,6-Me_2, the aromatic diol is added by an addition tube, and the mixture is refluxed overnight. The solvent is removed *in vacuo*. The solid is washed with Et_2O and filtered, and the residual solvent is removed *in vacuo*.

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[7] $W(=O)Cl_3(Me_2BINOH{\cdot}OEt_2)$ forms prism-like black crystals in the space group *Fdd*2 on crystallization from CH_2Cl_2/hexane $a = 23.094(4)$ Å, $b = 37.724(7)$ Å, $c = 11.707(3)$ Å, $V = 10199(6)$ Å^3, and $Z = 16$. Single crystal data were collected using Cu Kα radiation on a Rigaku AFC5R diffractometer. The structure was solved by a combination of Patterson and direct methods. Isotropic refinement for 1777 observed reflections ($I > 0.01(I)$) gave $R = 0.027$. Anisotropic refinement gave $R_w = 0.042$. Complete details of the structure and refinement are contained in the supplementary materials.

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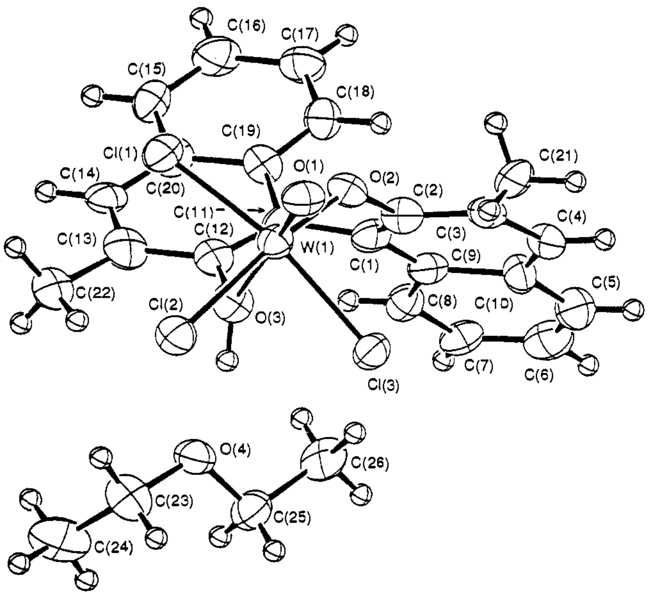

Figure 2. ORTEP representation of $W({=}O)Cl_3(Me_2BINOH{\cdot}OEt_2)$, showing the arbitrary numbering scheme and employing 30% thermal ellipsoids. Selected bond angles and distances: angles (deg), Cl(1)–W(1)–O(1) = 96.4(2), Cl(3)–W(1)–O(1) = 97.7(2), Cl(2)–W(1)–O(1) = 95.5(2), O(1)–W(1)–O(3) = 176.7(3), O(1)–W(1)–O(2) = 101.2(3), W(1)–O(1)–C(2) = 135.3(6). W(1)–O(3)–C(12) = 122.4(5); distances (Å), W(1)–O(1) = 1.712(6), W(1)–O(3) = 2.262(6), O(3)–O(4) = 2.59; torsional angle (deg), C(2)–C(1)–C(11)–C(12) = –63(1).

Table I

ligand	K_{Et_2O} (M^{-1}) (±8%)	X
2,3-dihydroxynaphthalene	4000	O (II)
(2,3-DHNH)	2500	NArMe$_2$ (III)
1,8-dihydroxynaphthalene	220	O (IV)
(1,8-DHNH)	260	NArMe$_2$ (V)
10,10′-biphenanthrol (BIPHENOH)	89	O (VI)
3,3′-dimethyl-1,1′-bi-2-naphthol	25	O (I)
(Me$_2$BINOH)	33	NArMe$_2$ (VII)
bis(4,6-dimethylphenol)methane	1.5	O (VIII)
(DMPMH)	0.50	NArMe$_2$ (IX)
pamoic acid (PAMH$_2$)	3700 (252 K)	O (X)
catechol (CATH$_2$)	3.4	

distance betrays the strong *trans* influence of the oxo group. The O(3)–O(4) distance of 2.59 Å, with an O(3)–H(1) distance of 1.42 Å, is consistent with the hydrogen bonding between ether and naphthol. Uncharacteristically, the short W–O(2) distance of 1.793(6) Å is indicative of significant aryloxide π-donation to tungsten. This observation is supported by the related catechol-containing structure, which possesses a shorter W=O distance (1.65 Å) and a significantly longer $W{-}O_{Ar}$ distance (1.89 Å).[1a]

Diethyl ether titrations of this series of compounds in $CDCl_3$ at 298 K indicate that the ring size of the chelate correlates directly to the strength of the hydrogen bond (Table I).[8] **II** and **III**, which are prepared with 2,3-dihydroxynaphthalene (2,3-$DHNH_2$), have a chelate ring size of five and exhibit the largest binding constants for the ether substrate. Increasing the ring size by one carbon increments systematically decreases the binding constant by approximately 1 order of magnitude. This trend may stem partially from steric effects,[9] as the complexes containing

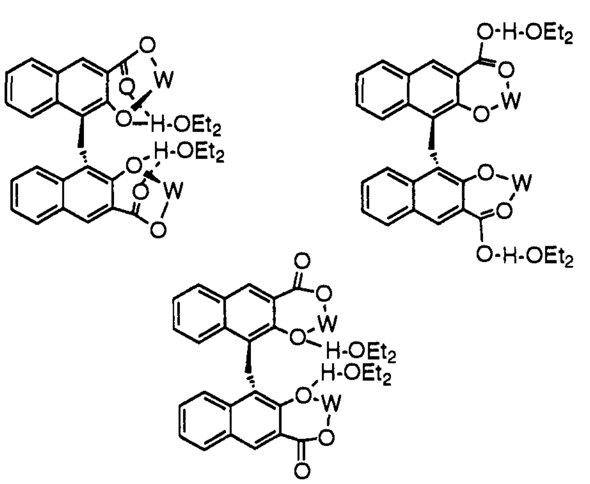

Figure 3. Possible binding modes of Et_2O in $[W({=}O)Cl_3](PAMH_2{\cdot}2OEt_2)$.

Me_2BINOH and DMPMH ligands display the smallest binding constants. The extremely sterically encumbered ligand ethylidenebis(4,6-di-*tert*-butylphenol) ($EDBPH_2$) is not trapped as the hydrogen-bonded chelate but directly proceeds to the bis(aryloxide) chelate, $W({=}O)Cl_2(EDBP)$ (**XI**). It does not, however, appear that steric constraints alone can account for the consistent decrease in the binding constant. Dramatic variations of hydrogen bond strength between Me_2BINOH and BIPHENOH are not observed, although the compounds vary in steric characteristics. Changes in the ring size could also have an influence on the electronic environment at the phenol oxygen. Rigorously planar rings, such as 2,3-DHNH, force the π system of the aromatic ring and the single pπ lone pair of the phenol into an orientation favoring the greatest overlap. As the ring size is increased, the aromatic π system is forced toward an orthogonal arrangement with the oxygen lone pair.[10] The result of this conformational change should be to systematically diminish the ability of the aromatic ring to delocalize electron density from the oxygen, and this could further reduce the efficacy of the hydroxyl group in hydrogen-bonding interactions.

The hydrogen bond chelates occur for ligands other than simple aromatic diols. For example, $\{[W({=}O)Cl_3]_2(PAMH_2{\cdot}2Et_2O)\}$, which exhibits noncooperative hydrogen bonding, has binding constant of 3700 M^{-1} at 252 K, extends this interaction to salicylate-like ligands (Figure 3). An examination of the extent to which other hydrogen bonded metal complexes can be tuned by variations in ligand type will aid in elucidating the probable role of steric and electronic effects. Studies to establish the potential utility of these compounds in synthetic and materials applications are currently in progress.

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Supplementary Material Available: Experimental details and characterization data (23 pages); listing of observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

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[8] The data from the Et $_2$O titration studies were fit by two methods: an iterative Scatchard plot and a least-squares curve fit program (MINSQ). The equations used in these methods are described in Conners, *Binding Constants*; John Wiley & Sons: New York, 1987.

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