(β-OH and β'-OH) O atoms have a progressively adverse inductive effect on the ability of the α-OH and carboxyl donor groups to form strong attachments. Note that the change in K_1/K_2 ratios also supports the concept of a change from bidentate to tridentate ligancy at about the radius of gadolinium. The attenuation of bidentate bonding (by β-OH O atoms) is a more regular phenomenon than the enhancement of tridentate bonding ability. The first β-OH converts the HIB moiety from a bidentate to a possibly tridentate ligand, whereas the introduction of a second β-OH only increases availability of groups which can furnish the requisite third donor O atom. Opposing this statistical effect is the fact that an unused β-OH or β'-OH O atom exerts a detrimental inductive effect on tridentate (as well as on bidentate) bonding.

In a previous paper[2] it was shown that adding one β-CH_3 group to DHIB (designated DHMP in that article) to give 2,3-dihydroxy-2-methylbutanoic acid (DHMB) enhanced the affinity of the ligand for lanthanons whenever the anion functioned tridentately (e.g., with Pr–Eu) but decreased the affinity when the anion exhibited bidentate attachment. Thus a β-CH_3 has a positive effect on the ability of a β-OH to be utilized but a negative (probably steric as opposed to inductive) effect when the β-OH is unused. We propose to investigate the rare earth bonding behaviors of ligand anions derived from 2,3-dihydroxy-2,3-dimethylbutanoic, 2,3-dihydroxy-2-hydroxymethylbutanoic, 2,3-dihydroxy-2-(1-hydroxyethyl)-butanoic, and other highly substituted acids, if these acids can be synthesized in sufficient amounts. It appears that none of these more complex reagents has been prepared to date and that synthesis of at least some of them (in good yield) might prove to be a formidable task.

Registry No. La(THIB)$_3$, 57606-49-2; Pr(THIB)$_3$, 57606-50-5; Nd(THIB)$_3$, 57606-51-6; Sm(THIB)$_3$, 57606-52-7; Eu(THIB)$_3$, 57606-53-8; Gd(THIB)$_3$, 57606-54-9; Tb(THIB)$_3$, 57606-55-0; Dy(THIB)$_3$, 57606-56-1; Ho(THIB)$_3$, 57606-57-2; Er(THIB)$_3$, 57606-58-3; Tm(THIB)$_3$, 57606-59-4; Yb(THIB)$_3$, 57606-60-7; Lu(THIB)$_3$, 57606-61-8; Y(THIB)$_3$, 57606-62-9.

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A Bonding Model for Transition Metal–Sulfur Dioxide Complexes[1]

AIC503733

Sir:

The bonding of the nitrosyl ligand in transition metal complexes has recently been a topic of considerable interest and a general molecular orbital model has been proposed which accounts for the geometry of the M–NO moiety (linear or bent) in terms of the number of d electrons in the system and the transition metal coordination polyhedron.[2] The central theme for the model is developed around the existence in the isolated NO^+ ligand of a σ orbital and degenerate π* orbitals which, when the ligand is attached to a transition metal in a linear fashion, produces a strong interaction with d_{z^2} (z = M–N–O axis) and the d_{xz}, d_{yz} orbitals, respectively. The resulting molecular orbital scheme contains a σ-type antibonding orbital (z^2, σ*) and a degenerate (in a molecule with a threefold or higher symmetry axis) pair of antibonding π* orbitals [(π*, d_{xz}) and (π*, d_{yz})]. If they lie sufficiently close to one another in energy, the two sets of orbitals (σ*, π*) will interact strongly upon bending the nitrosyl group to give stabilized and destabilized orbitals of the same symmetry (a') and a little perturbed orbital of different symmetry (a"). If the lowest of these orbitals is at least partially filled, the conformation with a bent nitrosyl will be stabilized. Previous authors have pointed out that the approach outlined above is applicable to other ligands, including SO_2,[3,7] with bonding characteristics similar to those of NO^+. It has not been emphasized, however, that the SO_2 ligand not only has orbitals of the proper symmetry and energy to fit into the framework of this model but also has the requisite structural credentials; i.e., it exhibits both planar and pyramidal coordination about the sulfur atom in its transition metal complexes (see Table I).[4-10]

Table I. Known Structures of Compounds with Terminal M–SO_2 Moieties

Compd	Coordination type	No.[b] of d electrons	M–S dist, Å	Angle between M–S vector and SO_2 plane,[a] deg
[Ru(NH_3)$_4$$SO_2$Cl[4]	Octahedral	6	2.072 (3)	180
CpMn(CO)$_2$$SO_2$[5]	Octahedral	6	2.037	180
IrCl(CO)SO_2(Ph_3P)$_2$[6]	Tetragonal pyramidal	8	2.49 (1)	121.5 (1.5)
RhCl(CO)SO_2(Ph_3P)$_2$[7]	Tetragonal pyramidal	8	2.450 (2)	120.3 (3)
(Ph_3P)$_3$PtSO_2[8,9]	Tetrahedral	10	2.36 (3)	120.3 (3)
(Ph_3P)$_2$Pt(SO_2)$_2$[17]	Tetrahedral	10	2.45 (1)	117.0 (3)

[a] See text. [b] Nitrosyl is considered to be NO^+.

Table II. Model Systems Investigated for L_nIrA (A = NO, SO_2)

L	n	A	Geometry	Position of A	d^6, d^8, d^{10} [a]
Cl	4	SO_2	Square pyramidal	Axial	p, b, –
Cl	4	SO_2	Trigonal bipyramidal	Axial	p, p, –
Cl	4	SO_2	Trigonal bipyramidal	Equatorial	p, b, –
Cl	5	SO_2	Octahedral		p, b, –
Cl	2	SO_2	Trigonal planar		p, b, b
Cl	3	SO_2	Square planar		p, b, b
Cl	3	SO_2	Trigonal pyramidal	Axial	p, b, b
Cl	3	SO_2	Tetrahedral		–, –, b
Cl	3	NO	Tetrahedral		–, –, b
CO	3	SO_2	Tetrahedral		–, –, p
CO	3	NO	Tetrahedral		–, –, p

[a] p denotes planar M–SO_2 or linear M–NO; b denotes bent.

We report here the results of some extended Hückel molecular orbital calculations on L_nM–A complexes (A = NO, SO_2) performed with a version of Hoffmann's program which uses Slater-type double-ζ orbitals.[2b] In order to allow a direct comparison between NO and SO_2 complexes we have used the structural and H_{ii} values from ref 2b with the following additions: for the S(3s) and S(3p) orbitals, H_{ii} = −20.77 and −11.63 eV, respectively, with a Slater exponent of 2.05, S–O = 1.45 Å, O–S–O = 114°, and Ir–S = 2.49 Å. The model systems examined are shown in Table II.

Two approaches to understanding the bonding in L_nMNO complexes have proven to be especially useful. (1) The perturbations of the transition metal d orbitals by the NO ligand are introduced first and the splittings produced by the

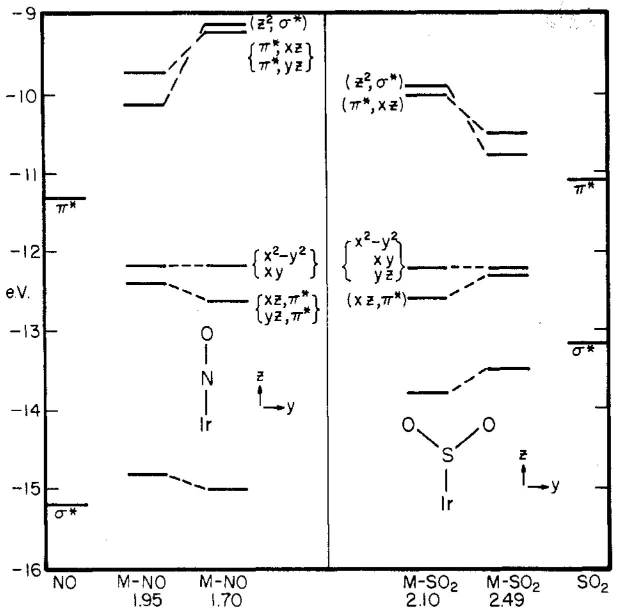

Figure 1. Calculated MO diagrams for Ir–NO and Ir–SO_2 at typical bonding distances using only metal 5d orbitals for Ir.

L ligands are then considered.[2a] (2) The perturbations on the d orbitals are introduced in the opposite order, i.e., the L ligands first and then the NO ligand.[2b] Although both methods have unique advantages, we chose the former for the present discussion.

In comparing the bonding in nitrosyl– and sulfur dioxide–transition metal complexes it is significant that the calculated energy of the LUMO (lowest unoccupied molecular orbital) for free SO_2 (−11.10 eV) is similar to that calculated for NO (−11.29 eV) and has the proper symmetry to interact with a d_{xz} orbital of a transition metal (*z* along the M–S bond and *x* perpendicular to the SO_2 plane). The HFMO (highest filled molecular orbital) for SO_2 has the proper symmetry and energy (−13.10 eV) to provide a strong σ interaction with d_{z^2}. The HFMO for NO lies at significantly lower energy (−15.2 eV)

The ordering schemes for the Ir–NO and Ir–SO_2 moieties, for two sets of distances spanning the known range of M–N and M–S distances, are depicted in Figure 1. Notice that for NO both the σ* and π* interactions are stronger compared to SO_2, even though the energy match is better between the d orbitals and the SO_2 σ orbital. This is, of course, a consequence of better overlap in the NO case.

Before proceeding to the discussion of the effect of introducing the L ligands, we interject the observation that in the absence of significant π interactions from L or the introduction of different ligands (L and L') into the complex, there is a low barrier to rotation of the SO_2 ligand about the M–S bond and the conclusions concerning the local geometry observed at the sulfur atom are independent of this parameter. The actual potential minimum for rotation is in general agreement with the available structural evidence and in the calculations reported here the orientation of the SO_2 was chosen accordingly.

The effect of introducing σ-type perturbations on the M–NO diagrams (Figure 1) has been extensively reviewed elsewhere[2a] and the result of introducing π interactions from these ligands has been convered by Hoffmann et al.[2b] We note only that if the above-mentioned differences between NO and SO_2 are taken into account, the resulting MO diagrams for L_nMSO_2 complexes of various geometries are quite similar to those for the corresponding L_nMNO complex. We find, therefore, that the rules for predicting geometries for SO_2 complexes are generally transferable from those for nitrosyls (see Table II).

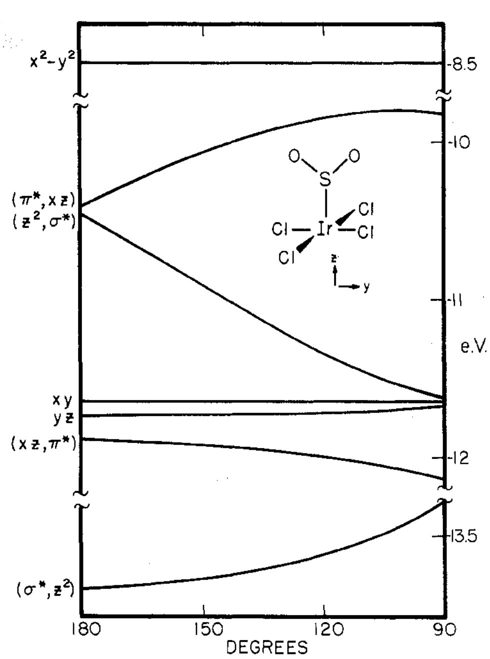

Figure 2. Walsh diagram for the square-pyramidal Cl_4IrSO_2 moiety.

To illustrate this point we present the L_4IrSO_2 results. If L introduces only σ-type interactions, then the primary difference between this diagram and the leveling scheme shown in Figure 1 is a major perturbation of the $x^2 - y^2$ orbital and a minor perturbation for z^2. The Walsh-type diagram, as a function of the M–SO_2 angle, for Cl_4IrSO_2 is shown in Figure 2. The M–SO_2 angle is defined as the angle between the M–S vector and the resultant of the two S–O vectors.

The important question of whether the geometry around the sulfur atom is planar or pyramidal can be answered by examination of two orbitals in the molecular orbital diagram, labeled (π*, *xz*) and (z^2, σ*). If, as is the case here, these antibonding orbitals are sufficiently close in energy, they interact as the SO_2 is bent out of the M–SO_2 plane so that the stability of the initially more stable orbital, (z^2, σ*) for Cl_4IrSO_2, is enhanced and the remaining orbital (π*, *xz*) is destabilized. For d^6 systems the orbitals will be filled only through the nonbonding *xy* orbital and a planar M–SO_2 group is predicted. In the d^8 system, where the (z^2, σ*) orbital is filled, we calculate a minimum energy conformation at an M–SO_2 angle of 120°, in pleasing agreement with the structural results obtained for two known examples of square-pyramidal d^8 SO_2 adducts.[6,7] The hypothetical d^7 case shows an intermediate geometry, with an angle of ca. 135°. For a pseudo-octahedron (Cl_5IrSO_2) the ordering of (π*, *xz*) and (z^2, σ*) is inverted compared to the square pyramid, but the same conclusions hold concerning the SO_2 geometry as a function of the number of d electrons. For both pseudo-octahedral and square-pyramidal geometries, we find the conclusions to be remarkably independent of the choice of d-orbital parameters.

The pseudo-tetrahedral $ML_3(NO)$[2b] and $ML_3(SO_2)$ cases are especially interesting for both ligands (SO_2 and NO) since the ordering and energy difference of the z^2 and π-type antibonding MO's are sensitive to the computational and geometric parameters assumed in the calculation. Although the trends as these parameters are varied are readily explicable within the framework of the model, we feel that the results of our calculations for L_3IrA (L = Cl, CO; A = NO, SO_2) are interesting and significant. We find that the tetrahedral Cl_3IrA (d^{10}) model systems favor a bent geometry for NO as well as for SO_2 although comparison of the sum of the one-electron energies for the planar (linear) geometries to those of the bent models shows a slightly larger difference for SO_2 than for NO. It has been pointed out that substitution of a π acceptor in the equatorial positions of square pyramids containing the NO ligand at the axial position tends to stabilize the linear M–NO geometry.[2b] This is also true for the tetrahedral models and those with L = CO predict linear M–NO and planar $M–SO_2$ moieties. It is indeed interesting, then, that with the one notable exception $[Ni(NO)(N_3)(PPh)_2]$, all of the four-coordinate transition metal nitrosyls exhibit a nearly linear M–NO geometry[2a,11–16] and tetrahedral environment about the metal atom. In contrast, the one known structure of a pseudotetrahedral mono(sulfur dioxide) complex $(Ph_3P)_3PtSO_2$[8] has recently been reexamined[9] and can be interpreted in terms of a bent $M–SO_2$. Further, the monomeric complex $(Ph_3P)_2Pt(SO_2)_2$ has recently been determined by single-crystal x-ray techniques[17] and clearly contains *two* strongly bent $M–SO_2$ moieties, while all of the known bisnitrosyl–transition metal complexes exhibit linear or nearly linear M–NO geometries. In general it appears that the tendency to bend is greater for $M–SO_2$ complexes than for nitrosyls, a consequence of the smaller energy separation between π^* and σ^* orbitals in SO_2.

In conclusion, the SO_2 ligand promises to be at least as useful a probe to the bonding of transition metal complexes as NO has been and no doubt this ligand deserves considerably more attention than it has received in the past.

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Registry No. SO_2, 7446-09-5.

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Electron-Transfer Reactions of Excited States. Reductive Quenching of the Tris(2,2'-bipyridine)ruthenium(II) Luminescence

AIC50522H

Sir:

Recently reported quenching[1,2] and flash photolysis[3,4] experiments have demonstrated the operation of electron-transfer processes in the photochemistry of the charge-transfer excited state of tris(2,2'-bipyridine)ruthenium(II), $^*Ru(bpy)_3^{2+}$. To date these studies have dealt with reactions in which this excited state, which is a very strong reducing agent, gives up an electron to yield $Ru(bpy)_3^{3+}$ and reduced quencher. The reduction potential for the couple $Ru(bpy)_3^{3+}–^*Ru(bpy)_3^{2+}$ (eq 1) implicated in these processes has recently been

$$Ru(bpy)_3^{3+} + e^- = {}^*Ru(bpy)_3^{2+} \quad E_{1/2} = -0.81\ V^4 \tag{1}$$

$$Ru(bpy)_3^{3+} + e^- = Ru(bpy)_3^{2+} \quad E_{1/2} = +1.29\ V^4 \tag{2}$$

evaluated using rate comparisons.[4] From eq 1 and 2 (where both $E_{1/2}$ values were determined in acetonitrile vs. SCE) the excited-state free energy of $^*Ru(bpy)_3^{2+}$ (eq 3) is calculated

$$Ru(bpy)_3^{2+} = {}^*Ru(bpy)_3^{2+} \tag{3}$$

to be 2.10 V in acetonitrile. If the free energy content of the excited state is the same in water and acetonitrile, the above value may be combined with the $E°$ value for the $Ru(bpy)_3^{3+}–Ru(bpy)_3^{2+}$ couple (1.27 V[5]) in water to give $E°_{III,*II} = -0.83$ V for the couple $Ru(bpy)_3^{3+}–^*Ru(bpy)_3^{2+}$ in water. The latter is in excellent agreement with the value −0.84 V calculated from spectroscopic considerations.[2,6]

The above processes involve loss of an electron from $Ru(bpy)_3^{2+}$ or $^*Ru(bpy)_3^{2+}$ to give $Ru(bpy)_3^{3+}$. The ion $Ru(bpy)_3^{2+}$ may also take on an electron to give $Ru(bpy)_3^+$. This reduction (eq 4) occurs electrochemically in *N,N*-dimethylformamide at $E_{1/2} = -1.25$ V vs. SCE[7] and in acetonitrile at $E_{1/2} = -1.33$ V[8] vs SCE. The reduction product (in which the added electron probably resides in ligand-centered π^* orbitals[7–9]) has been observed in pulse radiolysis studies of aqueous $Ru(bpy)_3^{2+}$ solutions as well.[9] As is the one-electron oxidation product, the one-electron reduction product of $Ru(bpy)_3^{2+}$ is, in principle, more readily attained from $^*Ru(bpy)_3^{2+}$ by the excited-state free energy.[10] Combining the values from ref 4 and ref 8 for reactions 3 and 4, respectively, the $E_{1/2}$ for reduction of the excited state (eq 5)

$$Ru(bpy)_3^{2+} + e^- = Ru(bpy)_3^+ \tag{4}$$

$$^*Ru(bpy)_3^{2+} + e^- = Ru(bpy)_3^+ \tag{5}$$

is estimated to be +0.77 V vs. SCE in acetonitrile. Upon correction for the liquid junction potential,[11] the value +0.84 V relative to hydrogen is obtained as $E°_{*II,I}$ for the couple. Thus the charge-transfer excited state $^*Ru(bpy)_3^{2+}$ is expected to be a moderately strong *oxidizing* agent in addition to exhibiting the reducing properties already elucidated. In this paper, which describes the results of studies of the quenching of $^*Ru(bpy)_3^{2+}$ emission by several reducing agents, some observations which support this point of view are reported.

Emission intensity measurements were made on a Perkin-Elmer Model MPF4 spectrofluorimeter using exciting wavelengths between 452 and 530 nm with emission monitored at 608 nm and 10–20-nm slit widths. With the exception of $Co(phen)_3^{2+}$, all of the quenchers had negligible absorbance at 608 nm and at the excitation wavelength used. For $Co(phen)_3^{2+}$, absorption corrections were made according to published methods.[12] Solutions of $Co(phen)_3^{2+}$ were prepared in situ with 1,10-phenanthroline in 25% excess. Hexaammineruthenium(III) chloride (Matthey-Bishop, Inc.) was recrystallized according to published procedures.[13] Hexaammineruthenium(II) solutions were generated by reduction of hexaammineruthenium(III) with europium(II).[13,14] Europium(II) solutions were prepared by amalgamated zinc reduction of europium(III). Sodium dithionite (Fisher) was standardized using ferricyanide.[15] All intensity measurements were made at 25.0 ± 0.1° using deaerated solutions except where noted.

Stern–Volmer plots for the quenchers used are shown in Figure 1. From these plots, K_{SV}, the Stern–Volmer constant,