method of determining triplet energies of molecules which do not photophosphoresce. We are currently exploring the potential of this direct application of triboluminescence.

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(*N*-Methylsalicylaldiminato)(*N*-methylsalicylaldiminium)nickel(0). A Novel Example of a π-Coordinated Azomethine Group ($>C{=}NH-$)

Sir:

Salicylaldimine is known as one of the useful ligands which affords a rich family of transition metal complexes.[1] Without exception, to our knowledge, the Schiff base is incorporated in metal complexes as a chelating anion. We found a novel class of nickel(0) complexes in which the Schiff base was disproportionated into the anion and the protonated species. Here we report the crystal and molecular structure of the *N*-methyl derivative.

Two moles of *N*-methylsalicylaldimine were added to a toluene solution of $Ni(cod)_2$ (cod = 1,5-C_8H_{12}) at room temperature. On standing, the red reaction mixture gave a good yield (90%) of wine red air-sensitive well-developed crystals $Ni(CH_3N{=}CHC_6H_4OH)_2 \cdot C_6H_5CH_3$ (**1**),[2] mp 145–150°. Similarly, *N*-α-phenethylsalicylaldimine gave an analogous complex, mp 145°. The structure of **1** was studied by a single-crystal three-dimensional X-ray analysis.

Crystal data: $Ni(C_{16}H_{18}N_2O_2) \cdot C_7H_8$; $M = 421.2$; $a = 13.776$ (2), $b = 12.159$ (2), $c = 12.724$ (2) Å; $\beta = 91.97$ (2)°; space group $P2_1/n$; $Z = 4$; $D_x = 1.313$ g cm^{-3}. The X-ray diffraction data were collected on a computer-controlled Rigaku four-circle diffractometer with a maximum 2θ value of 45°, and Zr-filtered Mo Kα radiation was used. The structure was solved by the heavy atom method and refined by the least-squares method to an R value of 0.060 for 1340 nonzero reflections. Anisotropic thermal vibrations were assumed for all the non-hydrogen atoms. The location of the somewhat disordered methyl group of the toluene molecule was not established definitely. Nevertheless all the hydrogen atoms of the complex molecule were revealed from a difference Fourier map.

Figure 1 shows the structure of the complex molecule, two of which form a cyclic dimer as a result of hydrogen bonding between O(2) and O(1)(O(2)–O(1) distance = 2.61 Å). The crystallographic symmetry of the dimer of **1** is *Ci*. In each molecule the hydroxyl proton of one of the Schiff base ligands may be regarded as being transferred to the nitrogen atom of the other. The deprotonated ligand (ligand A) is then described as a *N*-methylsalicylaldiminato anion and the protonated one (ligand B) as a *N*-methylsalicylaldiminium ion. The ligand B bonds to the Ni atom through the N(2)=C(15) group. Thus the Ni atom has a trigonal planar coordination, if the N(2)=C(15) group is taken to be a monodentate ligand. The atoms, Ni, O(1), N(1), N(2), and C(15), are almost coplanar within the mean atomic deviation of 0.03 Å; the dihedral angle between the planes defined by O(1)–N(1) and that by N(2)–Ni–C(15) atoms is only 4.4°. The angle compares with the values in Ni(*t*-BuNC)$_2$Un, Un:PhN=NPh[3] (**2**) (1.2°), $(NC)_2C{=}C{=}N$-*t*-Bu[4] (**3**) (7.9°), and $C_2(CN)_4$[5] (**4**) (23.9°). In ligand A the Ni–N(1) distance of 1.875 (10) Å is shorter than the Ni–O(1) distance, 1.929 (8) Å; these relative lengths are different from those observed in several salicylaldiminato Ni(II) complexes[6] (Ni–N, 1.92–2.05 Å, Ni–O, 1.84–2.01 Å). In ligand B, the Ni–N, 1.867 (10) Å, and Ni–C distances, 1.917 (14) Å, are longer than the corresponding values, 1.843 (3) and 1.855 (4) Å, found in **3** and may be compared with the values 1.894 (4) Å for Ni–N in **2** and 1.954 (4) Å for Ni–C in **4**. The N(2)=C(15) bond length of 1.43 (2) Å is considerably longer than the N(1)=C(7) distance and rather close to the normal single-bond distance of N–C. A distortion from planarity of the C(16)N(2)H=C(15)-HC(14) fragment is observed as in π-bonded olefin complexes; the H[N(2)]–N(2)–C(16) and the H[C(15)]–C(15)–C(14) planes bend away from the Ni atom. The N(2)=C(15) vector forms angles of 55 and 77°, respectively, with the normals of those planes. The bond angles around the π-coordinated C=N bond indicates a contribution of sp^3 hybridization at the C and N atoms. It appears that the presence of intermolecular hydrogen bonds is important to the stability of the solid.

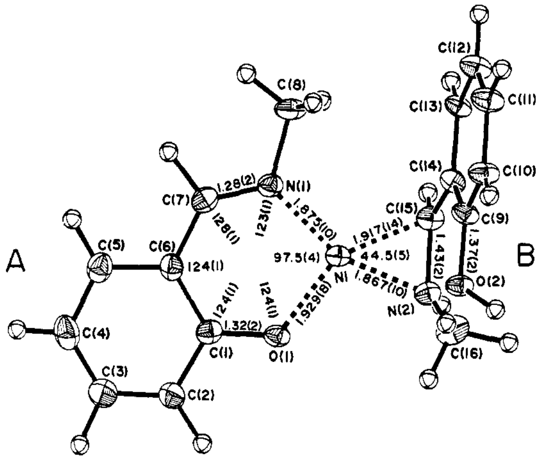

Figure 1. Stereochemistry of and important bond lengths and angles in (*N*-methylsalicylaldiminato)(*N*-methylsalicyaldiminium)-nickel(0).

The structure in solution was examined by the ^{1}H nmr spectrum of a pyridine-d_5 solution of **1**: δ(ppm, TMS) 2.65 (3 H, doublet, $J = 5.4$ Hz, $=NH(CH_3)$),

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3.08 (3 H, singlet, $=NCH_3$), 7.78 (1 H, singlet, $CH=N$ of ligand A), 9.05 (1 H, broad, OH). The presence of the protonated azomethine group π-coordinated to nickel is supported by a doublet at δ 3.83 (1 H, J = 7.8 Hz, $-CH=NH(CH_3)$) and a broad peak at δ 5.40 (1 H, $CH=NH(CH_3)$). Thus, the molecular structure of **1** in solution is essentially the same as in the crystal.

On exposure to air of **1**, bis(N-methylsalicylaldiminato)nickel(II) is formed. Treatment of **1** with 1,2-bis(diphenylphosphino)ethane (dp) in aromatic solvents quantitatively gave $Ni(dp)_2$ and the free N-methylsalicylaldimine, a result consonant with the zero-oxidation state of the nickel atom.

One of the conspicuous features of the present system is that the $C=N$ bond, which is prone to form a σ-type coordination through the nitrogen lone pair, can be made to act as a two-center π-acid by protonation.

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Three Isomers of the NO_2^- Ion

Sir:

Charge transfer experiments[1] have resulted in a value of (2.38 ± 0.06) eV as the best estimate of the electron affinity of NO_2. Photodetachment experiments using conventional light sources determined a vertical detachment energy of $\leq$2.8 eV.[2] The large difference between the electron affinity and vertical detachment energy is readily explained by the significant geometry change and hence poor Franck–Condon factors between NO_2^- and NO_2. The transition $NO_2^-(0,0,0) \rightarrow NO_2(0,0,0)$ has a Franck–Condon factor of 0.003.[3]

Photodetachment experiments with both a conventional light source–ion cyclotron resonance apparatus and a tunable dye laser have detected an anomalous NO_2^- which photo detaches at energies below the electron affinity of NO_2.[2,3] The apparent photodetachment threshold for this unusual ion is 1.8 eV. It is unlikely that this long wavelength photodetachment is the result of either (1) vibrationally excited X $^1A_1$ NO_2^- or (2) an excited electronic state of NO_2^-; considerations of effective temperature, energy separation, method of formation, and long trapping times in the ICR discount possibilities 1 and 2.

A third and more likely possibility would be an isomer of NO_2^-. This possibility is consistent with an anomalous NO_2^-, formed by the reaction of NO with a cluster ion of O^-, $CO_3^- + NO = NO_2^- + CO_2$, which has been reported[4] and is expected to be several electron volts less stable than the symmetric, normal NO_2^-. It is quite conceivable that the anomalous NO_2^- could be a peroxy isomer. A peroxy form of NO_3^-, formed by a similar reaction of NO with a cluster ion of O_2^-, has also been suggested.[4] A peroxy form of NO_2^- would also be isoelectronic with the recently reported NOF.[5] It has been suggested[3] that the anomalous NO_2^- is the result of a weak electrostatic interaction between NO and O^-, hence the close resemblance of the long wavelength photodetachment cross section and threshold to to that of O^-.[6]

There is at least one other plausible isomer of NO_2^-. We draw this conclusion from the simple observation that NO_2^- is isoelectronic with ozone, a molecule which has been the subject of several *ab initio* theoretical electronic structure studies.[7–10] The work of Peyerimhoff and Buenker[7] was the first to suggest that the equilateral triangle form of O_3 lies quite close energetically to the accepted geometry,[11] $\theta = 116.8°$, r(O–O) = 1.278 Å. More recently, Hay, Dunning, and Goddard[12] have reported extensive configuration interaction calculations which predict this "ring state" to lie 1.57 eV above the accepted ground state. We note that the ring state does represent a well-defined minimum in the potential energy surface and is the lowest electronic state of ozone at $\theta = 60°$, r(O–O) $\approx$ 1.45 Å.

We have carried out *ab initio* self-consistent-field calculations to investigate the relative energies of the various NO_2^- isomers. Atom-optimized primitive Gaussian basis sets[13] of size (9s 5p) were centered on the N and O nuclei. Although we usually contract this size basis to (4s 2p), in the present study a more flexible (5s 3p) contraction was chosen,[14] to allow for some of the distortion inherent in molecular negative ions. The electron configuration for the expected (bond angle $\sim$116° in analogy with ozone) ground state is[8]

$$1a_1^2\ 1b_2^2\ 2a_1^2\ 3a_1^2\ 2b_2^2\ 4a_1^2\ 5a_1^2\ 3b_2^2\ 1b_1^2\ 4b_2^2\ 6a_1^2\ 1a_2^2 \qquad (1)$$

The peroxy form of NO_2^- has only a plane of symmetry (point group C_s), with resulting electron configuration

$$1a'^2\ 2a'^2\ 3a'^2\ 4a'^2\ 5a'^2\ 6a'^2\ 7a'^2\ 8a'^2\ 1a''^2\ 9a'^2\ 10a'^2\ 2a''^2 \qquad (2)$$

The ring state is again of C_{2v} symmetry, with configuration

$$1a_1^2\ 1b_2^2\ 2a_1^2\ 3a_1^2\ 2b_2^2\ 4a_1^2\ 5a_1^2\ 3b_2^2\ 1b_1^2\ 6a_1^2\ 1a_2^2\ 2b_1^2 \qquad (3)$$

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