

3.08 (3 H, singlet, =NCH₃), 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=N(CH₃)) and a broad peak at δ 5.40 (1 H, CH=N(CH₃)). 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 NO₂⁻ Ion

Sir:

Charge transfer experiments¹ have resulted in a value of (2.38 ± 0.06) eV as the best estimate of the electron affinity of NO₂. Photodetachment experiments using conventional light sources determined a vertical detachment energy of ≤ 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 NO₂⁻ and NO₂. The transition NO₂⁻(0,0,0) → NO₂(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 NO₂⁻ which photo detaches at energies below the electron affinity of NO₂.^{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 ¹A₁ NO₂⁻ or (2) an excited electronic state of NO₂⁻; considerations of effective temperature, energy separation, method of formation, and long trapping times in the ICR discuss possibilities 1 and 2.

A third and more likely possibility would be an isomer of NO₂⁻. This possibility is consistent with an anomalous NO₂⁻, formed by the reaction of NO with a cluster ion of O⁻, CO₃⁻ + NO = NO₂⁻ + CO₂, which has been reported⁴ and is expected to be several elec-

tron volts less stable than the symmetric, normal NO₂⁻. It is quite conceivable that the anomalous NO₂⁻ could be a peroxy isomer. A peroxy form of NO₃⁻, formed by a similar reaction of NO with a cluster ion of O₂⁻, has also been suggested.⁴ A peroxy form of NO₂⁻ would also be isoelectronic with the recently reported NOF.⁵ It has been suggested³ that the anomalous NO₂⁻ 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 that of O⁻.⁶

There is at least one other plausible isomer of NO₂⁻. We draw this conclusion from the simple observation that NO₂⁻ 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 Buenker⁷ was the first to suggest that the equilateral triangle form of O₃ lies quite close energetically to the accepted geometry,¹¹ $\theta = 116.8^\circ$, $r(\text{O}-\text{O}) = 1.278 \text{ \AA}$. More recently, Hay, Dunning, and Goddard¹² 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 $\theta = 60^\circ$, $r(\text{O}-\text{O}) \approx 1.45 \text{ \AA}$.

We have carried out *ab initio* self-consistent-field calculations to investigate the relative energies of the various NO₂⁻ isomers. Atom-optimized primitive Gaussian basis sets¹³ 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 $\sim 116^\circ$ in analogy with ozone) ground state is⁸

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

The peroxy form of NO₂⁻ has only a plane of symmetry (point group C_s), with resulting electron configuration

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

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

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

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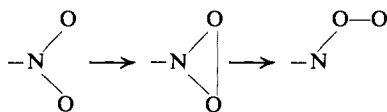
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The present study, then, centered about a series of non-empirical self-consistent-field computations, with electron configurations 1, 2, and 3 representing the three expected isomers. A helpful qualitative discussion of the analogous states of ozone has been given by Goddard and coworkers.¹⁵

One important qualitative conclusion may be drawn prior to the calculations. This concerns the possible interconversion of the "normal" and peroxy forms of NO_2^- . The most likely pathway for this conversion would be (schematically)



In fact, such a path is highly improbable, since the ring state has three occupied π (or a'') orbitals ($1b_1$, $2b_1$, and $1a_2$) while the normal and peroxy forms have only two occupied π orbitals. Thus, orbital symmetry suggests that there should be a substantial barrier preventing access to the ring state from either direction.

The structure of each isomer has been predicted by minimizing the total energy with respect to the various geometrical parameters. The results are summarized in Table I. Note first that the expected ground state

Table I. Geometries, Energies, and Mulliken Populations for Three Isomers of NO_2^- ^a

Property	Isomer		
	Normal	Peroxy	Ring
$r(\text{N-O})$	1.264	1.245	1.502
$r(\text{O-O})$		1.493	
θ (deg)	117.0	118.5	58.5
E (hartrees)	-204.0336	-203.9161	-203.8736
E (eV)	0.00	3.20	4.35
Atomic populations			
N	6.83	7.21	7.24
O ₁	8.58	8.22	8.38
O ₂	8.58	8.57	8.38

^a Bond distances are in Å. O₁ is the central atom in the peroxy isomer.

geometry is indeed remarkably close to that of ozone, the difference in bond angles being less than 1° . The difference in bond distances is less than 0.02 Å, another indication of the validity of isoelectronic arguments.¹⁶ Finally, this geometry agrees quite well with the experimental structure of the NO_2^- ion in crystalline sodium nitrite.¹⁷ The peroxy form has a similar bond angle, 118° , and NO bond distance, 1.25 Å. However, the O-O bond distance is much longer than in ozone. In fact, the O-O distance is slightly greater than in hydrogen peroxide,¹⁸ 1.475 Å. Thus the labeling of this second isomer as the peroxy form is quite appropriate. The peroxy form lies 3.20 eV above the

normal isomer. The ring isomer is indeed very nearly an equilateral triangle, the ONO bond angle being 58° . The NO bond distance is 1.50 Å, or 0.05 Å longer than the predicted bond distance¹² for the comparable isomer of O_3 . However, the ring isomer is seen to lie much higher (4.4 eV) for the NO_2^- system than for O_3 (1.6 eV). Thus our isoelectronic analogy is not very accurate in this particular regard.

Since it has been suggested³ that the anomalous NO_2^- is the result of a weak electrostatic interaction between NO and O^- , we report in Table I Mulliken populations for the three isomers. There it is seen that the terminal oxygen is indeed the most negatively "charged," in a simple picture. However, the other two atoms account for nearly half of the ion's -1 charge.

In conclusion, the peroxy form of NO_2^- corresponds to a well-defined minimum in the potential energy surface. Consequently, its postulation by experimentalists is given substantive theoretical support. Moreover, the fact that the peroxy and normal forms of NO_2^- do not appear²⁻⁴ to interconvert can be understood in terms of the relatively high energy of the ring state, the superficially logical intermediate for such an interconversion.

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Synthesis of Heteropoly Anions in Aprotic Solvents. Tungstoselenates(V), -(VI), and -(VII)

Sir:

The characterization of "substituted" heteropoly Keggin anions, $\text{XMZ}_{11}\text{O}_{40}^{n-}$, where X is the central tetrahedrally coordinated atom, Z is molybdenum or tungsten, and M is a second heteroatom occupying one of the 12 equivalent "octahedral" sites, was first reported by Baker, *et al.*¹ Numerous examples of such complexes have since been described.² When M is in a high formal oxidation state (+5, +6), further substitution is possible and it is difficult to isolate pure

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