

$[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{CH}_3\text{CN})]^+\text{BF}_4^-$ (96%) and $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{Cl})$ (98%). From these data, **4** was assigned as the bridging chloride complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\mu\text{-Cl})(\text{PPh}_3)(\text{NO})\text{Re}(\eta^5\text{-C}_5\text{H}_5)]^+\text{BF}_4^-$. Complex **4** was further assigned as a *dl* (*SS,RR*) as opposed to a meso diastereomer on the basis of the following observations: (1) decomposition of (*S*)-**2** yielded *optically active* (+)-(*SS*)-**4**, $[\alpha]^{22}_{589} = 549^\circ$ ($c = 0.71$ mg/mL); (2) the optically active chloride complex (+)-(*S*)- $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{Cl})$ reacted *rapidly* (-60°C , 2–3 h) with (*S*)-**2** to give (+)-(*SS*)-**4** (74%), $[\alpha]^{22}_{589} = 528^\circ$; (3) efforts to prepare (*SR,RS*)-**4** (meso) from (–)-(*R*)- $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{Cl})$ and (*S*)-**2**, which reacted only slowly at 0°C , were unsuccessful.

In summary, we have demonstrated the ready availability of a chiral, optically pure, transition-metal Lewis acid. In future reports, we will describe the mechanism of formation of these species, their configurational stability, and important applications in organic synthesis.¹⁵

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Trivalent Nickel: Sulfur Coordination ($\text{NiN}_2\text{O}_2\text{S}_2$) vs. Oxygen Coordination (NiN_2O_4)

Sir:

The high (>2) oxidation levels of nickel and their redox reactions are of current interest.^{1,2} The low-spin ($S = 1/2$) trivalent state is now known to be present³ in several bacterial hydrogenases, at least two of which having been shown⁴ to have sulfur ligation

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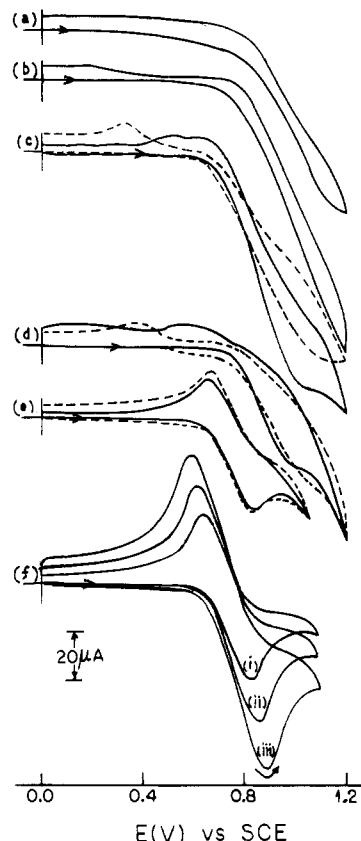


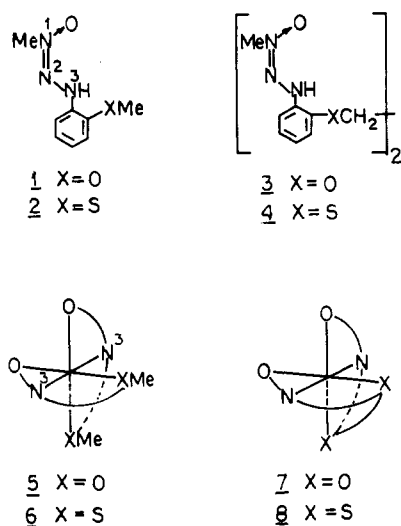
Figure 1. Cyclic voltammograms in dichloromethane (0.1 M TEAP) at a platinum electrode (unless otherwise stated, the scan rate is 50 mV/s and the temperature is 298 K for solid lines and 263 K for broken lines): (a) Zn(II) analogue of **5**, (b) Zn(II) analogue of **6**, (c) **5**, (d) **7**, (e) **6**, (f) **8**, with a scan rate of (i) 50, (ii) 100, or (iii) 200 mV/s.

to nickel. In this context we wish to report for the first time the results of some experiments designed to answer this important question: Does sulfur coordination make nickel(III) more easily accessible than oxygen coordination in similarly constituted species? Lower reduction potential of the nickel(III)–nickel(II) couple and better thermal stability of the nickel(III) species are taken as criteria of accessibility.

Triazene 1-oxide ligands^{5–7} **1–4** were used in this work. The basis of this choice is twofold: (i) there is systematic replacement of ether oxygen (**1**, **3**) by thioether sulfur (**2**, **4**) such that NiN_2O_4 and $\text{NiN}_2\text{O}_2\text{S}_2$ coordination spheres could be constructed; (ii) should tridentate ligation (**1**, **2**) fail to sustain metal oxidation, hexadentate ligation (**3**, **4**) might still be successful. Ligands **1** and **2** afford⁶ pseudooctahedral paramagnetic ($S = 1$) bis complexes of nickel(II) (**5**, **6**) and similarly **4** furnishes⁸ **8**. Species **3** and **7** are new,^{9,10} and both have the same magnetic moment ($3.08 \mu_B$) in the solid state at 298 K. The gross stereochemical similarity of the complexes in dichloromethane (this solvent is used

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- (9) The ligand (**3**) was synthesized by condensing *N*-methylhydroxylamine with the diazotized diamine,¹⁰ and the nickel(II) chelate was prepared in the usual manner⁶ from nickel(II) acetate and **3**. Anal. Calcd for $\text{NiC}_{16}\text{H}_{20}\text{N}_6\text{O}_4$: C, 46.07; H, 4.31; N, 20.15. Found: C, 46.17; H, 4.31; N, 19.87.
- (10) Jaunin, R.; Holl, R. *Helv. Chim. Acta* **1958**, *41*, 1783–1792.

in all studies in this work) is reflected in their ligand field spectra.^{6,11}



To assess the feasibility of metal oxidation (nickel(II) \rightarrow nickel(III)) complexes **5–8** were subjected to cyclic voltammetry (298 and 263 K) in dichloromethane solution at a platinum electrode with tetraethylammonium perchlorate (TEAP) used as the supporting electrolyte and a saturated calomel electrode (SCE) used as the reference electrode. The zinc(II) analogues¹² of **5–8** were used as controls to sort out possible ligand oxidations. Representative voltammograms are shown in Figure 1. The zinc(II) analogues of **5** and **6** (those of **7** and **8** behave similarly) do not display any characteristic peaks in the range up to 0–1.2 V. The anodic current however begins to increase progressively above ~ 0.7 V, possibly due to the onset of bound ligand oxidation. Complexes **5** and **7** behave similarly, but there are signs of an ill-defined anodic peak at ~ 1 V associated with little cathodic response (even at 263 K) on scan reversal. If the ill-defined anodic peak is at all due to metal oxidation, the oxidized complex must be very unstable.

In contrast both **6** and **8** display one well-defined cyclic response with the following $E_{1/2}$ values:^{13,14} **6**, +0.75 V; **8**, +0.74 V. The one-electron nature of the response is corroborated by coulometric data.¹⁵ We thus have the electrode processes 1 and 2, where 6^+



and 8^+ represent the oxidized complexes. The solution color of both **6** and **8** is yellow while that of 6^+ and 8^+ is brown. Complex 6^+ is much less stable^{15,16} than 8^+ . Isolation of either cation in

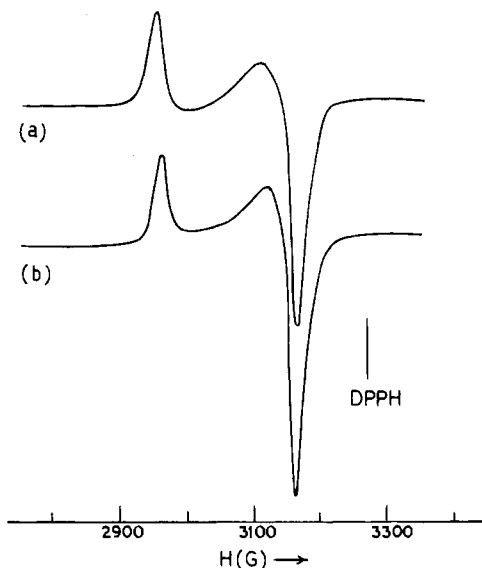


Figure 2. Frozen-solution (77 K) X-band EPR spectra of (a) 6^+ and (b) 8^+ .

the solid state as salts has not been achievable so far.

That 6^+ and 8^+ are genuine nickel(III) complexes (low-spin d^7) and not nickel(II)-stabilized ligand radicals is demonstrated by X-band EPR spectra¹⁶ of frozen (77 K) solutions. Both spectra (Figure 2) are effectively axial: for 6^+ , $g_{\parallel} = 2.213$ and $g_{\perp} = 2.076$; for 8^+ , $g_{\parallel} = 2.217$ and $g_{\perp} = 2.076$. Hyperfine splitting due to ligand nitrogens is not observed. The uncommon $g_{\parallel} > g_{\perp}$ situation corresponds to axial compression (unpaired electron in the $d_{x^2-y^2}$ orbital).^{17–19}

In summary we note that while the formation of the nickel(III) state is uncertain in NiN_2O_4 coordination (**5**, **7**) this state is smoothly achieved in $\text{NiN}_2\text{O}_2\text{S}_2$ chelation (**6**, **8**). In spite of their equal $E_{1/2}$ values 8^+ is much more stable^{15,16} than 6^+ , presumably due to the extra chelate effect of the hexadentate ligand. The accessibility of nickel(III) is then in the order $8^+ > 6^+ \gg 7^+$, 5^+ . In a grossly covalent situation the ability of a donor atom to transfer²⁰ negative charge to an oxidized metal center should stabilize¹ the metal–ligand ensemble, affording relatively low $E_{1/2}$ values for metal oxidation. On this count sulfur donors are expected to work better than oxygen donors (other things remaining the same) for covalent bonding to higher oxidation states not having excessive electron demand.²⁰ The superior accessibility of the nickel(III) state in the $\text{N}_2\text{O}_2\text{S}_2$ coordination sphere as compared to the N_2O_4 sphere can be viewed this background.^{21,22}

- (11) The $\text{NiN}_2\text{O}_2\text{X}_2$ coordination sphere is sufficiently distorted to create observable splitting of the ν_1 band. Band maxima (λ , nm) and extinction coefficients (ϵ , $\text{M}^{-1} \text{cm}^{-1}$) presented as λ (ϵ) are as follows: **5**, 1400 (sh (33), 1150 (45), 675 (sh (31), 525 (sh (255)); **6**, 1500 (sh (39), 1000 (88), 625 (61), 525 (sh (88)); **7**, 1350 (sh (49), 1100 (58), 675 (sh (43), 500 (sh (215)); **8**, 1400 (25), 1000 (70), 625 (42), 500 (sh (82) (sh = shoulder). For all complexes a band is observed in the range $\lambda = 625\text{--}675$ with $\epsilon = 31\text{--}61$. This is most probably the ν_2 band or a component thereof.
- (12) Zinc(II) analogues are white to light yellow crystalline solids and were prepared by reacting the ligands (**1–4**) in stoichiometric proportions with zinc(II) acetate in ethanol. The complexes were characterized by elemental analyses and IR spectra.
- (13) Values of $E_{1/2}$ are calculated as the average of anodic and cathodic peak potentials. For a reversible process the peak–peak (ΔE_p) separation is expected to be ~ 60 mV. The observed ΔE_p values lie in the range 150–200 mV. High ΔE_p values occur quite commonly in dichloromethane solution.¹⁴
- (14) Chakravarty, A. R.; Chakravorty, A. *Inorg. Chem.* **1981**, *20*, 3138–3143.
- (15) Electrolysis was done at 0.9 V. Experimental n values are 0.97 (**6**) and 1.02 (**8**) (average of three readings). In the case of **6** the oxidized complex is stable at 298 K on the cyclic voltammetric time scale. However decomposition occurs at this temperature on the coulometric time scale, and coulometric data for **6** were collected at 263 K. For **8** data were collected at 298 K.

- (16) Coulometrically produced solutions (6^+ , 263 K, and 8^+ , 298 K) were immediately frozen to 77 K and spectra taken. When **6** is electrooxidized at 298 K, no EPR signals are observed in the frozen solution, showing that 6^+ is unstable at 298 K.
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- (20) The transfer of charge from the polarizable ligand must not proceed to an unrestricted extent since that would be tantamount to ligand oxidation rather than metal oxidation. Such a situation will arise when the electron demand of the metal is very high (e.g., manganese(VII)). Thermodynamically this can occur whenever the reduction potential of the oxidized metal exceeds that of the oxidized ligand (both metal and ligand in the bound form).
- (21) An organic analogue of this situation is the case of sulfur-stabilized carbocation.²²
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Further work directed toward the generalization of these themes with the help of other examples is in progress. We strongly suspect that the relative paucity¹ of synthetic sulfur-ligated nickel(III) species may actually be due more to the lack of a systematic search than to inherent instability.^{23,24}

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- (23) One reason for this situation is no doubt the inertia of the prevalent view that only hard donors are suited for binding higher oxidation states. The recent discovery²⁴ of thiolato complexes of, e.g., manganese(III) and cobalt(III) is a good indication of things to come.
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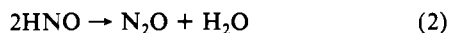
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Photolysis of the N=N Bond in Trioxodinitrate: Reaction between Triplet NO⁻ and O₂ To Form Peroxonitrite

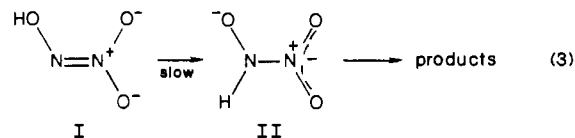
Sir:

Studies on the reaction of Na₂N₂O₃ (sodium trioxodinitrate, N-N) with hemoglobin¹ have led to the suggestion that the anion HN₂O₃⁻ decomposes by the formation of NO and HNO₂⁻ rather than nitrosyl hydride (HNO) and NO₂⁻ (eq 1, 2) as previously reported.²⁻⁷ This proposal was advanced without reference to



extensive kinetic and isotopic evidence^{5,6} that shows the existence of an equilibrium between HN₂O₃⁻ and its primary decomposition products (eq 1). Furthermore, the only reported evidence for occurrence of HNO₂⁻ in aqueous solution is as a transient product of the pulsed radiolysis of nitrite.⁸ In this paper we report studies on the photochemical decomposition of trioxodinitrate that provide further support for the mechanism of eq 1 and 2 and also show that the reactive intermediate NO⁻ can appear in solution in singlet and triplet states exhibiting distinct chemical properties, analogous to the isoelectronic case of O₂.

Important mechanistic implications arise from the reversibility of the decomposition of trioxodinitrate.⁵ Homolytic cleavage of the -N=N- bond would generate biradical NO₂⁻, but the reverse recombination reaction is observed upon addition of normal reagent nitrite, which cannot be in an excited, triplet electronic state. Therefore, by the principle of microscopic reversibility, the cleavage of trioxodinitrate must involve the generation of ground-state NO₂⁻ by the heterolytic cleavage of a -N-N- bond. The overall scheme must therefore include a tautomerization step (eq 3).⁵ Furthermore, the tautomerization step must be slow, as otherwise



substantial deviations from the observed first-order kinetics of decomposition would occur due to the buildup of nitrite in solution.⁵

The reported results of kinetic studies on the trioxodinitrate-hemoglobin reaction¹ provide support for eq 3, since they show the reaction to be first order in HN₂O₃⁻ and zero-order in hemoglobin, with rate constants similar to those found for the normal self-decomposition.⁴ Thus these authors were, in all probability, measuring the rate of tautomerization of trioxodinitrate. Hollocher et al.^{9,10} have also suggested a rate-determining conversion between two forms of trioxodinitrate to account for the kinetics of the trioxodinitrate-hemoglobin reaction.

Studies of different reactions in which HNO is an intermediate have led to the conclusion that it may exist in solution in two different forms^{11,12} and that these may correspond to the anions of HNO and NOH. The molecule HNO is known to have a singlet ground state,¹³ while that of NOH is expected to be a triplet.^{14,15} Both species should deprotonate rapidly in the pH range of interest here (pK_a = 4.7 for HNO;¹⁶ NOH should be more acidic); the multiplicity difference would be preserved in the two forms of the anion NO⁻. Heterolysis of tautomer II of HN₂O₃⁻ (eq 3) should produce singlet NO⁻ as well as singlet NO₂⁻; the former is known to be excited relative to its triplet ground state,¹⁷ in an energy level spacing similar to the isoelectronic case of O₂.¹⁸ Normal self-decomposition of HN₂O₃⁻ is thus expected to form singlet NO⁻, consistent with previously reported evidence that the undeprotonated intermediate in this reaction is HNO.¹⁹ Decomposition of the species tautomer I would lead to formation of triplet NO⁻, and this has now been shown photochemically.

There is good evidence that NO⁻ reacts with O₂ to give peroxonitrite (ONOO⁻), as has been demonstrated for the auto-oxidation of hydroxylamine.^{20,21} However, ONOO⁻ does not form when O₂ is bubbled through self-decomposing HN₂O₃⁻ solution,²² in which the form of NO⁻ produced is expected to be singlet. Since we expect O₂ to react with triplet NO⁻, the photolysis of trioxodinitrate has been studied both in O₂-free and in oxygenated solutions, in anticipation that peroxonitrite should form in the latter case.

The photochemical decomposition of trioxodinitrate was carried out in a reactor utilizing a Hanovia low-pressure mercury lamp, emitting light of wavelengths 253.7 and 184.9 nm. The latter line was screened by the use of a water jacket. Reaction was initiated by adding weighed Na₂N₂O₃ to the reaction solution, which was either O₂-saturated or N₂-saturated. The solution was stirred by the gas flow. The reaction was followed by withdrawing samples and measuring the trioxodinitrate concentration by UV absorption at either 248 or 233 nm, depending upon the pH.^{3,4}

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