TABLE II

RESULTS OF CALCULATIONS

π-Electron density		Bond order		Transition energy, eV		λ, Å	Oscillator strength	Symmetry	Polarization
q_1	1.4174	P_{12}	0.4954	${}^1E_{5\rightarrow6}$	3.644	3403	0.49	B_2	Y
q_2	1.3776	P_{23}	0.6426	${}^1E_{5\rightarrow7}$	4.619	2684	0.72	A_1	X
q_3	1.2496	P_{34}	0.4810	${}^1E_{4\rightarrow6}$	4.655	2669	0.88	A_1	X
q_4	1.6641	P_{45}	0.2660						

imposes the restriction that a maximum of three types of transition will be symmetry allowed. Our calculations give three transitions that correspond closely with those observed experimentally: ${}^1E_{5\rightarrow6}$, ${}^1E_{5\rightarrow7}$, and ${}^1E_{4\rightarrow6}$. The latter two transitions are very close to each other in energy and intensity and have the same predicted polarization. The observed shorter wavelength band may then possibly be an overlapping doublet. The observed spectra, which show some variation with solvent, are tabulated along with a mean value for the solution spectra. Correlation with the calculated transition energies is remarkably good and may be taken as evidence of a well-developed π-electron system including the disulfide bond. The calculated oscillator strengths are higher than the observed values, particularly for the long-wavelength transition.

TABLE III[3]

OBSERVED UV SPECTRA

Solvent	Band 1[a]	Band 2[a]
HCl (12 M)	3420 (0.051)	2700 (0.40)
H_2SO_4 (18 M)	3320 (0.049)	2600 (0.41)
$HClO_4$ (12 M)	3340	2580
Mean	3360	2627
Calcd	3403 (0.49)	2684 (0.72) 2669 (0.88)

[a] Wavelength given in ångströms; oscillator strength in parentheses.

^{15}N Nmr Spectra.—An nmr study of the ^{15}N thiotrithiazyl cation in 70% nitric acid showed two multiplets that were readily assigned to N(1) and N(3) on the basis of multiplicity and relative areas. The positions of these absorptions, relative to $^{15}NH_4^+$, were −343 ppm for the N(1) triplet and −355 ppm for the N(3) doublet. Qualitatively this implies that N(1) has less π bonding around it and a higher π-electron density. The calculated values support this: N(1) ($P_{12} + P_{27}$), 0.991, q_1, 1.4174; N(3) ($P_{23} + P_{34}$), 1.124, q_3, 1.250.

Bonding.—The dominant features of the structure of thiotrithiazyl are its planarity and its short N–S bonds. The results of our calculations encourage us to accept the assumptions of conjugation throughout the entire ring, although limited in extent across the S–S bond, and of donation of two electrons from each of the sulfurs to the π-electron system. Undoubtedly the 3d orbitals of sulfur must participate in bonding in this molecule, but it does not seem useful at this stage to try to describe a scheme for the bonding based on the geometric requirements of $3d_{xz}$ or $3d_{yz}$ orbitals or to envision a particular hybridization involving 3d (and possibly 4s) orbitals because such speculation is not subject to test or verification. Similarly the assignment of sp hybridization to N(3)[3] does not afford any advantage over sp^2 or some intermediate hybridization in terms of the semiempirical methods being employed in our calculations. The treatment of the disulfide bond that we have used should hopefully be effective in studies of the related 1,2-dithiolium ion systems.[8]

Acknowledgment.—The author wishes to thank the Pratt Institute Computer Research and Education Center for its cooperation and generous donation of computer time.

---

[8] H. Prinzbach and E. Futterer, *Advan. Heterocycl. Chem.*, **7**, 39 (1967)

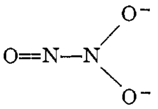
CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA, AND THE INORGANIC MATERIALS
RESEARCH DIVISION, LAWRENCE RADIATION LABORATORY,
BERKELEY, CALIFORNIA 94720

The Structure of the Oxyhyponitrite Ion

BY DAVID N. HENDRICKSON AND WILLIAM L. JOLLY

Received September 12, 1968

The structure of the anion of Angeli's salt[1] ($Na_2N_2O_3$) has never been unequivocally determined. Three structures have been considered



I

$O{=}N{-}O{-}N^-{-}O^-$

II

${}^-O{-}N{=}N{-}O{-}O^-$

III

The ultraviolet spectrum,[2] the infrared spectrum,[3] the heat of formation,[4] and the pK values[5] have all been interpreted as favoring structure I. In this study, we have obtained further evidence for structure I by asymmetrically labeling the $N_2O_3^{2-}$ ion with ^{15}N

---

[1] A. Angeli, *Gazz. Chim. Ital.*, **26**, 17 (1896).

[2] C. C. Addison, G. A. Gamlen, and R. Thompson, *J. Chem. Soc.*, 339 (1952).

[3] R. D. Feltham, *Inorg. Chem.*, **3**, 900 (1964).

[4] H. R. Hunt, Jr., J. R. Cox, Jr., and J. D. Ray, *ibid.*, **1**, 938 (1962).

[5] P. E. Sturrock, J. D. Ray, J. McDowell, and H. R. Hunt, Jr., *ibid.*, **2**, 649 (1963).

and by then isotopically analyzing the products of an asymmetric decomposition of the ion.

We prepared ^{15}N-labeled $Na_2N_2O_3$ by the reaction of labeled ethyl nitrate with ordinary hydroxylamine[1,2]

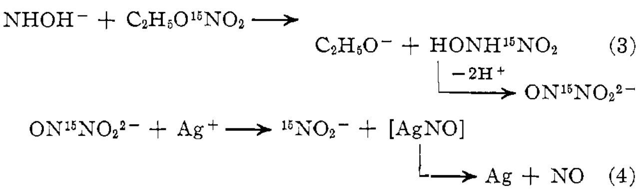
$$C_2H_5O^{15}NO_2 + NH_2OH + 2OH^- \longrightarrow O_2{}^{15}NNO^{2-} + C_2H_5OH + 2H_2O \quad (1)$$

The salt was decomposed by treatment with aqueous silver ion

$$O_2{}^{15}NNO^{2-} + Ag^+ \longrightarrow NO + {}^{15}NO_2^- + Ag \quad (2)$$

Essentially all of the ^{15}N ended up in the nitrite. The lack of scrambling of the nitrogen atoms during the synthesis and decomposition proves that the two nitrogen atoms in $N_2O_3{}^{2-}$ are structurally distinguishable. Therefore structure II is unequivocally eliminated. The fact that the ^{15}N was introduced in the form of an $-NO_2$ group and finally appeared in the form of an NO_2^- ion is persuasive evidence that the ^{15}N atom in the $N_2O_3{}^{2-}$ ion was attached to at least two oxygen atoms. Therefore we eliminate structure III.

Plausible mechanisms for the synthesis and decomposition reactions, based on structure I, can be written



$$NHOH^- + C_2H_5O^{15}NO_2 \longrightarrow C_2H_5O^- + HONH^{15}NO_2 \quad (3)$$

$$\xrightarrow{-2H^+} ON^{15}NO_2{}^{2-}$$

$$ON^{15}NO_2{}^{2-} + Ag^+ \longrightarrow {}^{15}NO_2^- + [AgNO]$$

$$\longrightarrow Ag + NO \quad (4)$$

Experimental Section

Synthesis.—Sodium oxyhyponitrite was prepared by the reaction of hydroxylamine with ethyl nitrate, as described by Addison, *et al.*[2] The compound was labeled asymmetrically with ^{15}N in a reduced-scale synthesis by using ^{15}N-labeled ethyl nitrate which had been synthesized by the following procedure. An aqueous solution of 2.47 g of ordinary potassium nitrate and 0.511 g of 95% ^{15}N potassium nitrate[6] (a total of 29.4 mmol) was passed through a column of AG 50W-X8 cation-exchange resin[6] (200–400 mesh) to give, upon evaporation of the eluate, 4.94 g (29.1 mmol) of labeled silver nitrate. This $AgNO_3$ was treated with 34 mmol of ethyl iodide in 10 ml of absolute ethanol at room temperature for 30 min. The resulting ethanol solution of labeled ethyl nitrate was then vacuum distilled at room temperature from the silver iodide precipitate and was treated with an ethoxide–ethanol solution of 43.0 mmol of hydroxylamine, according to the method of Addison, *et al.* The ^{15}N-labeled $Na_2N_2O_3$ was twice recrystallized by dissolving in a minimum of water and adding an excess of absolute ethanol and was then washed with ether and vacuum dried. A yield of 0.224 g (6.2%, based on KNO_3) was obtained.

The unlabeled and labeled products were characterized by hydrogen and nitrogen analyses and by the uv spectra of their aqueous solutions. These data indicated that the samples were hydrated mixtures containing approximately 85% $Na_2N_2O_3$ and 5% $NaNO_2$.[7] (Sodium oxyhyponitrite is known to be very hygroscopic and is usually contaminated with sodium nitrite.[2]) Unlabeled material: *Anal.* Calcd for $Na_2N_2O_3$: N, 22.96. Found: H, 0.67; N, 20.04. Labeled material: *Anal.* Calcd for $Na_2N_2O_3$: N, 23.08. Found: H, 0.65; N, 19.22. The nitrite impurity explains why more nitrite than nitric oxide was obtained from the reactions with silver ion (see below). Its presence did not affect the validity of the results; the lack of appreciable labeling of the nitric oxide in reaction 2 is the principal evidence for an asymmetric $N_2O_3{}^{2-}$ ion.

Decomposition Reaction.—Reaction 2 was effected by tipping 0.3–0.4 mmol of $Na_2N_2O_3$ from a side arm during 5 min into an excess of a degassed aqueous $AgClO_4$ solution maintained at 0° while Toepler-pumping the evolved gas through a $-112°$ trap into a gas buret. The gas was measured and then analyzed mass spectrometrically. The remaining solution was then frozen at $-78°$; 1 ml of 60% H_2SO_4 was added, and the mixture was warmed and held at 70° for 12 hr. This procedure converted the nitrite to nitric oxide, which was pumped off and analyzed as described above.

$$2H^+ + NO_2^- + Ag \longrightarrow NO + Ag^+ + H_2O \quad (5)$$

Four samples of the unlabeled compound and three samples of the labeled compound were decomposed and analyzed by the above procedures. The total nitric oxide[8] formed in reactions 2 and 5 corresponded within 5% to the nitrogen contents of the samples. The amount of nitric oxide[8] from reaction 5 was generally 5–15% greater than that from reaction 2.

Isotopic Analysis.—The nitric oxide samples were analyzed with a Consolidated Engineering Corp. mass spectrometer (Model 21-620). The samples were found to contain 0–5% nitrous oxide. In the runs with labeled $Na_2N_2O_3$, the NO from reaction 2 was found to contain 1.1–1.5 atom % ^{15}N,[9] and the NO from reaction 5 was found to contain 14.2–15.0 atom % ^{15}N.

Acknowledgment.—This research was supported by the U. S. Atomic Energy Commission.

---

[6] Bio-Rad Laboratories, Richmond, Calif.

[7] Based on the reported[2] extinction coefficients for $N_2O_3{}^{2-}$ and NO_2^- at 250 and 365 mμ.

[8] Corrected for the presence of N_2O.

[9] Ordinary nitrogen contains 0.36 atom % ^{15}N.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
TEXAS CHRISTIAN UNIVERSITY, FORT WORTH, TEXAS 76129

Chloride Bridging in Di-μ-(pyridine N-oxide)-bis(dichlorocopper(II))

BY R. S. SAGER, R. J. WILLIAMS, AND W. H. WATSON

Received September 13, 1968

The crystal structure of di-μ-(pyridine N-oxide)-bis-(dichlorocopper(II)), $[(C_5H_5NO)CuCl_2]_2$, has been reported,[1,2] and the molecular structure was described as an oxygen-bridged dimer. The atomic parameters listed in these reports are correct, but a significant interaction was not discussed. The structure is described more accurately as consisting of oxygen-bridged dimers held together in infinite chains by weak chloride bridges, Figure 1.

The highly distorted geometry around the copper ions may be rationalized with the inclusion of this additional interaction. The coordination may be described roughly as a square-based pyramid where the two bridging oxygen atoms and the two chloride ions form the distorted square base, and the chloride

---

(1) H. L. Schafer, J. C. Morrow, and H. M. Smith, *J. Chem. Phys.*, **42**, 504 (1965).

(2) R. S. Sager, R. J. Williams, and W. H. Watson, *Inorg. Chem.*, **6**, 951 (1967).