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

$$NHOH^- + C_2H_5O^{15}NO_2 \longrightarrow C_2H_5O^- + HONH^{15}NO_2 \xrightarrow{-2H^+} ON^{15}NO_2{}^{2-} \quad (3)$$

$$ON^{15}NO_2{}^{2-} + Ag^+ \longrightarrow {}^{15}NO_2{}^- + [AgNO] \longrightarrow Ag + NO \quad (4)$$

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.

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[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.

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

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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

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[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).

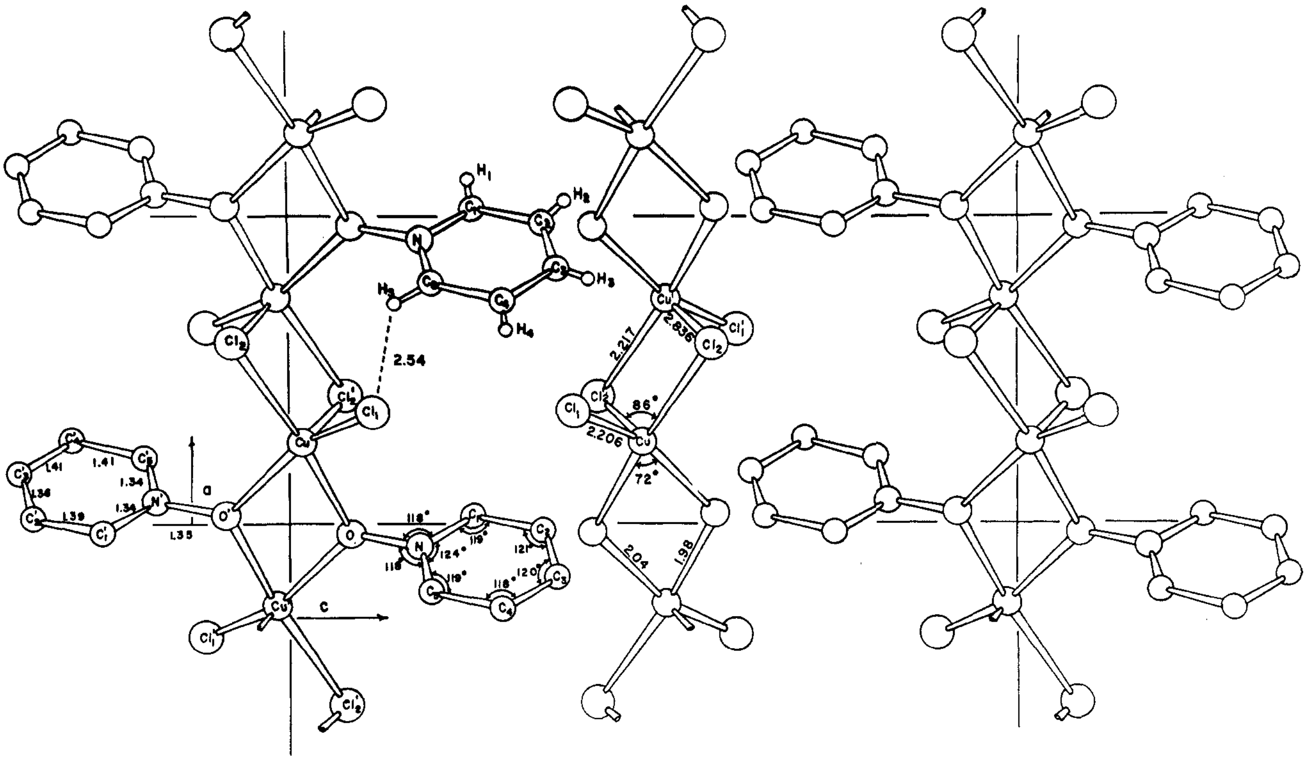

Figure 1.—A projection of the structure of $[(C_5H_5NO)CuCl_2]_n$ down the *b* axis showing the weak chloride bridges which bind the dimers together in infinite chains. The pyridine rings have been omitted from the central chain to show more clearly the hydrogen interactions.

ion from an adjacent dimer is situated at the apex 2.836 ± 0.005 Å from the copper ion.

This distorted geometry may be attributed to several factors. The oxygen bridge causes the O–Cu–O angle to be compressed from its preferred value of 90 to 72°, and the center of symmetry in the bridge indicates the copper–oxygen ring is planar with a Cu–O–Cu angle of 108°. This can be rationalized in terms of a bond angle compromise between the 120° sp^2 hybridized oxygen orbitals and the 90° copper d orbitals which form the bonds in the bridge.

The restrictions on Cl(2) imposed by the chloride bridge are another source of distortion. The basal plane of the square-based pyramid is chosen to be coincident with the copper–oxygen plane, and the basal chloride, Cl(2), associated with one copper ion is the apical coordinating ligand for the adjacent ion. The chloride ion Cl(2) lies 0.38 Å out of the basal plane owing to its interaction with the adjacent copper ion along the *a* axis. Its position is a compromise between the two ideal square-pyramidal sites. The apical Cu–Cl(2) bond makes an angle of 82° with the basal plane of the square pyramid.

An additional cause for the distorted geometry around the copper ion arises from the steric interaction of chloride Cl(1) with the pyridine ring. To evaluate this interaction, hydrogen atom positions were assigned by considering the hydrogen atoms to be coplanar with the pyridine ring and 1.08 Å from the carbon atoms to which they are attached. The Cl(1)–H(5) distance was calculated to be 2.5 Å and represents the interaction between Cl(1) on one dimer and H(5) on the adjacent dimer in the same chain. If Cl(1) were in its normal square-pyramidal position, H(5) would be on a line with the Cu–Cl(1) bond, and the steric repulsion would be large. This interaction results in the Cu–Cl(1) bond bending 33° from the basal plane.

Although the hydrogen atoms H(1) and H(5) can effectively shield the sixth coordination site on the copper ions, the molecular structure found in the solid does not provide maximum shielding or represent a minimum with respect to steric interaction within the dimer unit. A rotation of the pyridine ring about the N–O bond would bring the *o*-hydrogen atoms within the region of the vacant sixth coordination site at a distance of approximately 2.8 Å. A similar type of shielding has been reported for $RuCl_2[P(C_6H_5)_3]_3$.[3] This effect should be more pronounced when methyl groups replace the *o*-hydrogen atoms. In the complex $(2\text{-}CH_3C_5H_4NO)_2Cu_3Cl_6(H_2O)_2$ a similar dimeric structure is found,[4] but the heterocyclic rings are oriented with the methyl groups in the region of the sixth coordination site. The methyl hydrogen atoms may be much nearer to the copper ion than the *o*-hydrogen atoms in the pyridine complex. Specific hydrogen atom distances were not calculated for the methyl group, but separations on the order of 2.5 Å are possible.

A square-planar bridged dimer would be susceptible to further coordination along the axial positions, and a strongly coordinating ligand can readily occupy one

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(3) S. J. La Placa and J. A. Ibers, *Inorg. Chem.*, **4**, 778 (1965).

(4) R. S. Sager and W. H. Watson, *ibid.*, **7**, 2035 (1968).

of the axial sites. The pyridine rings would be restricted in their thermal motion and provide a more effective shielding of the sixth coordination site. This restriction would make the *trans* site on the adjacent copper ion available for coordination. This model is consistent with the reaction of the 1:1 complexes with coordinating ligands, such as water or dimethyl sulfoxide, and with the existence of the 2:1 dimeric pyridine N-oxide complex, $[(C_5H_5NO)_2CuCl_2]_2$.[5]

The *o*-hydrogen atoms on the pyridine ring do not provide maximum shielding of the sixth coordination site in the solid, but the hydrogen H(3) on one chain occupies this site on an adjacent chain. The Cu–H(3) separation is 2.8 Å, and although the distance is too long to be considered a normal bond, the electrostatic interaction should affect the electron distribution around the copper ion.

The low magnetic moment of $[(C_5H_5NO)CuCl_2]_2$ is attributed to a superexchange mechanism. This is qualitatively described as a direct transfer *via* overlap of the odd-electron Cu(II) orbitals which have been expanded by a mixture with oxygen orbitals of appropriate symmetry. The magnetic electrons probably occupy orbitals of approximately $d_{x^2-y^2}$ symmetry, and the exchange interaction predominantly occurs through basal ligands of the pyramidal geometry. Attempts to correlate the exchange energy with substituents on the pyridine ring have not been too successful, and this may be due to intermolecular perturbations, such as the Cu–H(3) interaction, which affects the electron distribution.

The 2:1 dimeric complex $[(C_5H_5NO)_2Cu(NO_3)_2]_2$[6] also is an oxygen-bridged dimer with the geometry around the Cu(II) ions closely approximating a square-based pyramid; however, the magnetic moment is normal. Each bridging oxygen atom in this complex is at the apex of one of the pyramids, and the magnetic electron orbitals do not overlap significantly. The oxygen bridging in this complex may be rationalized in terms of the steric effect of the nitrate ligands rather than an electronic effect.

The two infrared bands in $[(C_5H_5NO)CuCl_2]_2$ assigned to Cu-Cl stretching vibrations[7] now can be understood. The band at 330 cm^{-1} is consistent with a nonbridged chloride ion, and the band at 311 cm^{-1}, with the weakly bridged chloride ion. The variation in solubilities and infared band positions for the 1:1 complexes can be related to the strength of the Cu-Cl bridging interaction. The complexes probably exist as dimers in solution, as indicated by molecular weight measurements.[8]

Acknowledgment.—We wish to thank The Robert A. Welch Foundation for its financial support and the American Chemical Society for Grant PRF No. 3240-D5 (to W. H. W.)

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The Kinetics of Nitrosyl Exchange in Some Metal Nitrosyls in the Gas Phase

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Received September 26, 1968

Carbonyl-exchange and -substitution reactions of metal carbonyls have been widely studied. The rates are first order in the metal compound and zero order in the attacking ligand for most simple metal carbonyls and related organometallics.[1,2] Some cyclopentadienylmetal carbonyls[3] and square-planar complexes of heavier transition metals[4] (*e.g.*, $Rh_2(CO)_4Cl_2$) exchange carbonyls by a second-order mechanism, presumably owing to the ease with which they form intermediates of higher coordination numbers.

The nitrosyl carbonyls that have been studied, $Co(CO)_3NO$ and $Fe(CO)_2(NO)_2$,[5] give different results. Carbonyl exchange is significantly slower than that of the isoelectronic $Ni(CO)_4$. NO is a three-electron donor that is supposed to increase the electron density on the metal more than CO does. This increase strengthens the M–C bonding and decreases the rate of carbonyl exchange. The conclusion is supported by the carbonyl stretching frequencies of the compounds.[6] Substitution of a carbonyl by a phosphine or an amine is a second-order process.[7] The great polarizability of the nitrosyl group may allow it to accept electron density from the metal upon the approach of a nucleophile and so increase the ease with which an intermediate of higher coordination number is formed. That no substitution of the nitrosyl group has been observed during these reactions is not unexpected, for the M–N bond is stronger than the M–C bond and also the compound formed by direct substitution would be reactive because it does not obey the "rule of eighteen." Little work has been done on the kinetics and mechanism of nitrosyl-exchange or -substitution reactions, not even on establishing that such reactions occur. We report a study of the nitrosyl-exchange reactions of $Fe(CO)_2(NO)_2$, $Co(CO)_3NO$, and $(C_5H_5)NiNO$ in the gas phase.

Experimental Section

Chemicals.—$Fe(CO)_2(NO)_2$,[8] $Co(CO)_3NO$,[9] and $(C_5H_5)NiNO$[10]

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