to room temperature. Urea (21 mg.) and HNF_2 (24.6 cc.) were held at 0° for 68 hr. in a 7-ml. high pressure ampoule; HNF_2 (10.1 cc.) was recovered but the remainder had been converted to N_2F_4 (5.5 cc.) in 95% yield according to (1). The solid remaining gave qualitative tests for NH_4^+ and F^-. HNF_2 (4.5 cc.) was condensed into an 80-ml. stainless steel ampoule. After 6

days at room temperature the ampoule contained 1.1 cc. of HNF_2 and 0.8 cc. of N_2F_4. This represents a 59% yield of N_2F_4 based on 1.

The Structure of Gaseous Copper(II) Nitrate as Determined by Electron Diffraction

BY R. E. LaVILLA[1a,b] AND S. H. BAUER[1a]

Anhydrous copper(II) nitrate has a sufficient vapor pressure at 180–200° to permit the recording of electron diffraction photographs. That this gas is monomeric has been demonstrated by Addison, et al., by means of vapor density measurements and confirmed with mass spectrometry; its range of stability has also been ascertained. Visually estimated intensities of the electron diffraction patterns were used for the Fourier inversion to a radial density function and were compared with computed intensity curves for many models. The analysis indicates the molecular structure of gaseous copper(II) nitrate to be of the bidentate form with the copper atom occupying the center of inversion. The central copper atom has four nearest oxygen atoms at 2.00 ± 0.02 Å. and two Cu–N distances of 2.30 ± 0.03 Å., $\angle$O–N–O = 120 ± 2° and $\angle$O–Cu–O ≈ 70°.

A. Introduction

Addison and Hathaway[2] reported the preparation of anhydrous copper(II) nitrate and found it to have an unexpected volatility. When heated to 150–225°, it sublimes with a vapor pressure of 0.3 to 3.5 mm.; the vapor density corresponds to monomeric $Cu(NO_3)_2$. An analysis of the mass spectrum[3] of gaseous copper(II) nitrate with the solid sample at 88° supports the monomeric nature of the molecular gas and suggests that the nitrogen and oxygen atoms are bonded as in the nitrate groups. The infrared spectra[4] of the solid and vapor phases are typical of covalently bonded nitrate groups, but there are significant differences between the spectra of the two phases. A preliminary report[5] of the crystal structure of anhydrous $Cu(NO_3)_2$ lends further support to the presence of covalent bonding in the solid phase.

Of considerable interest are the recently prepared anhydrous ferric and mercuric nitrates[6a] and copper perchlorate[6b] which also show high volatilities. Thus, it appears that copper(II) nitrate is a typical member of an interesting group of compounds.

We hope that this preliminary electron diffraction investigation of copper(II) nitrate vapor provides a structural basis for the interpretation of its interesting properties. Owing to an unfortunate error in the reduction of photographic intensities between the third and sixth maxima, an incorrect structure was at first deduced for gaseous copper(II) nitrate.[7] The diffraction pattern predicted for that structure differs substantially from the experimental one, following correct reduction of data, and hence may be dismissed from further consideration.

B. Experimental

Anhydrous $Cu(NO_3)_2$ was furnished by C. C. Addison in sealed glass vials. These were opened in a nitrogen-filled drybox and the sample transferred to the reservoir of a special designed nozzle assembly. Nonsectored electron diffraction photographs were taken with the camera described by Hastings and Bauer,[8] with the nozzle assembly maintained between 175 and 185°

TABLE I

Max.	Min.	q_{obs}	I_{vis}	$q[V_h-(22T)]$	$\dfrac{q[V_h-(22T)]}{q_{obs}}$	$q[V_d-(19T)]$	$\dfrac{q[V_d-(19T)]}{q_{obs}}$
1		11.9	7.5	12.0	1.008	12.0	1.008
	1	16.0	−8.9	16.0	1.000	15.8	0.988
2		20.2	8.5	20.5	1.015	20.8	1.030
Shoulder		22.2	3.0	23.0	1.036	23.0	1.036
	2	27.5	−7.5	26.3	0.956	26.2	0.953
3		30.7	5.0	31.1	1.013	31.0	1.010
	3	33.0	−3.4	33.0	1.000	33.0	1.000
4		35.4	7.0	34.8	0.983	34.8	0.983
	4	37.9	−1.7	38.0	1.003	37.9	1.000
5		40.1	1.3	41.2	1.027	40.6	1.013
	5	43.2	−2.6	43.0	0.995	43.0	0.995
6		46.0	2.5	45.2	.983	45.6	.991
	6	49.0	−2.4	48.2	.984	48.0	.980
7		52.3	6.0	52.6	1.006	52.3	1.000
Shoulder		54.1	1.8	55.0	1.017	54.5	1.007
	7	58.2	−5.2	58.1	0.998	58.4	1.003
8		63.5	7.0	62.9	.991	63.2	0.995
	8	68.6	−4.5	67.8	.988	68.2	.994
9		74	6.0	72.5	.980	72.7	.982
	9	79	−5.5	77.0	.975	77.0	.975
10		84	7.0	82.1	.977	82.1	.977
				Mean	0.997		0.996
				Av. dev.	0.015		0.014

(vapor pressure 0.6 to 1.0 mm.). Photographs were taken over a period of 6 days, with different loadings of sample. No differences were noted in the diffraction patterns. The Medium Lantern Slide Kodak plates which were used were processed in Kodak D-76, and the exposures ranged from 0.3 to 8.0 min. The sample–plate distance was ≈18 cm., electron wave length ≈0.053Å; gold foil served for calibration patterns.

C. Analysis of the Photographs

The positions of the maxima and minima in the diffraction pattern of ten selected photographs were measured with an optical comparator. The intensities of all the diffraction features were estimated visually. In addition, three plates selected for proper density were microphotometered to supplement the visual estimate of the intensities between the third and sixth halos, whose narrow breadth and close spacing made a reliable visual estimate difficult. The results are summarized in Table I.

(1) (a) Cornell University; (b) National Bureau of Standards.

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(6) (a) C. C. Addison, B. J. Hathaway, and N. Logan, *ibid.*, 51 (1958); (b) B. J. Hathaway, *ibid.*, 344 (1958).

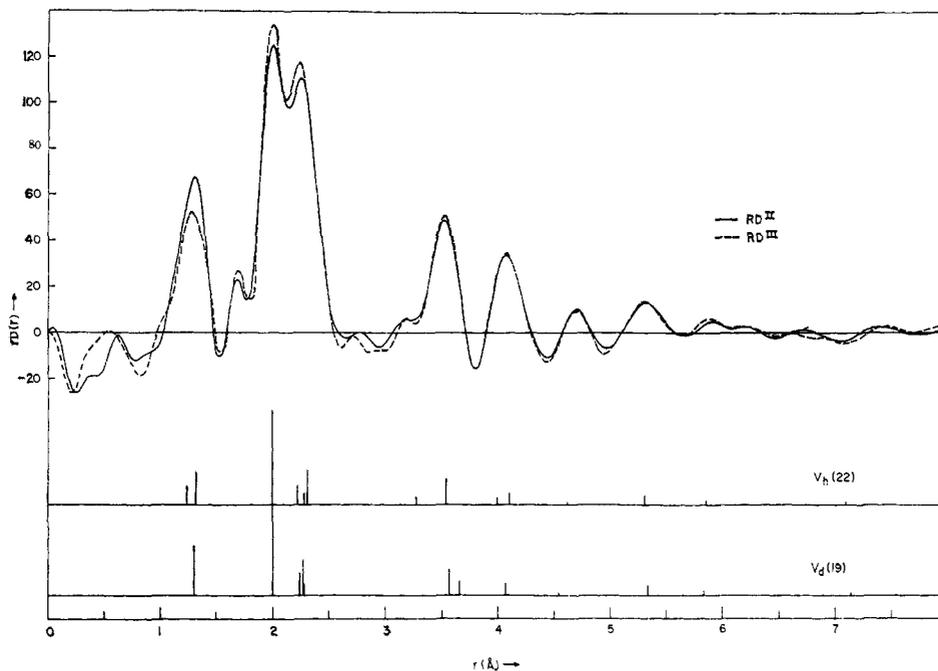(7) S. H. Bauer and C. C. Addison, *ibid.*, 251 (1960).

(8) J. M. Hastings and S. H. Bauer, *J. Chem. Phys.*, **18**, 13 (1950).

Fig. 1.—Radial distribution curves. The solid curve is an inversion of the solid intensity curve V, and the dashed curve of the dashed intensity curve V, Fig. 2. The heavy lines underneath the R.D. curves indicate the interatomic distances weighted by nZ_iZ_j/r_{ij} for models $V_h(22)$ and $V_d(19)$.

Theoretical intensity curves were calculated according to

$$\left(\frac{\pi}{10}\right) qI(q) = \sum_{i,j}' \frac{Z_iZ_j}{r_{ij}} \sin r_{ij} \left(q\,\frac{\pi}{10}\right) \qquad (1)$$

for the three symmetric models suggested by Addison and Hathaway.[2]
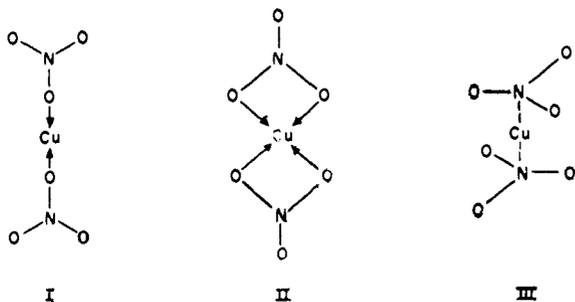
(THE NITRATE GROUPS WERE ASSUMED TO BE COPLANAR)

In these preliminary computations, we assumed N–O = 1.25 Å. and that the short Cu–O or Cu–N distances were 1.95 Å. The correlation of these curves with the observed intensity pattern was in general poor for all the models; however, the planar bidentate ligand model II was the best, particularly in the region of the first two halos. To obtain a zero-order approximation, the intensity curve for this bidentate model was matched to the experimental curve for the region $q \lesssim 12.0$, and the composite intensity curve was inverted according to

$$rD(r) = \sum_{q=1}^{q_{max}} \left(\frac{q\pi}{10}\right) I(q)\, e^{-\gamma q^2} \sin r\left(\frac{q\pi}{10}\right) \qquad (2)$$

with $e^{-\gamma q^2} = 0.1$ at $q_{max} = 88$; the resulting approximate radial distribution curve was designated R.D.[I]. Prominent peaks appeared at 1.30, 3.57, and 4.08 Å., a double peak at 2.00 and 2.25 Å., and lesser peaks at larger distances. The 1.30-Å. peak, which was relatively broad, may be identified with the N–O distances, while the

peaks at 2.00 and 2.25 with the Cu–N, Cu–O, or O–O, or combinations of these distances.

On the basis of R.D.[I], the computed portion of the composite experimental curve, $0 \leq q \leq 12$, was changed to that for a planar bidentate structure with the four N–O distances around the central Cu at 1.32 Å., the remaining two N–O at 1.24 Å., Cu–O at 2.00 Å., and the Cu–N at 2.33 Å. R.D.[II] (Fig. 1) was computed from this modified experimental curve (Fig. 2, curve V), using the same weighting function. No essential changes appeared in the peak positions, but there was an improvement in smoothness and a decrease in the spurious behavior at $r < 1.0$ Å. From a study of several versions of these R.D. curves, we are convinced that the narrow peaks at 1.68, 2.7, and 3.2 Å. are also spurious. An example of the other versions is the dashed R.D.[III], which was computed from the dashed experimental (V) curve.

An analysis of R.D.[II] showed that of the three suggested models for $Cu(NO_3)_2$ vapor only some form of model II, the bidentate structure, would be acceptable. Further, owing to the large number of atoms making up the molecule, one could not make a complete structure determination from R.D.[II], since it is not based on quantitative intensity data.

D. Correlation of the Intensity Curves

The theoretical intensity curves of the many models (≈ 80) which are compatible with the over-all features of R.D.[II] were calculated from eq. 1 and compared with the experimental composite intensity curve V. In the first model tested, point group symmetry V_h, the atoms of the nitrate groups were maintained coplanar with themselves and with the rest of the molecule. In the V_d models, the nitrate groups were individually maintained copolanar with the Cu atom but their planes were rotated about the N–Cu–N axis to give a tetrahedral configuration of the near oxygens around the central copper atom. In $C_{2h}(a)$, the nitrate groups are rotated in their common plane so as to make two of the four near Cu–O distances shorter than the other two; in $C_{2h}(b)$ the furthest oxygens of the nitrates are dis-

placed symmetrically above and below the common plane of symmetry. Finally, in $C_{2h}(c)$ the furthest N–O's were symmetrically pointing above and below the plane of symmetry of the atoms around the central copper.
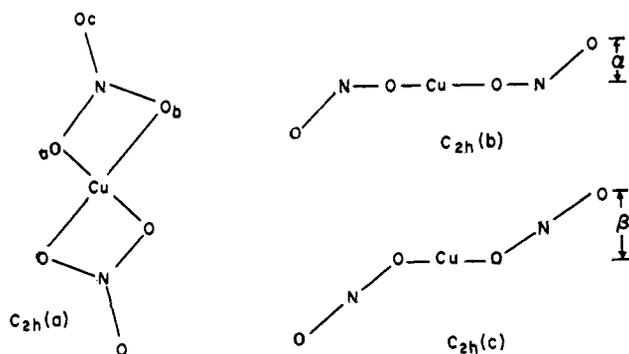
The structural parameters and temperature factors[9] assumed for selected models are listed in Tables II and III with their respective curves plotted in Fig. 2. The $C_{2h}(a)$ models tested were not included since their correlation with the observed intensity curve was very poor. Of the intensity curves shown in Fig. 2, the $C_{2h}(c)$ models may be discarded because of the reversed relative intensity of the third and fourth maxima. The deep fourth minimum, absence of a fifth minimum, and the weak fifth maximum of the $C_{2h}(b)$ models do not agree well with curve V. Comparison of the intensity curve over the region including the third to sixth maxima for the V_h and V_d models shows the latter provides the best fit with the experimental (V) curve. The effect of including temperature factors is shown by the dotted V_h and V_d curves. As expected, the relative intensities of adjacent peaks are not affected.

TABLE II

	CuN	$CuO_{a,b}$	CuO_c	O_aO_b	O_aO_c	$NO_{a,b}$	NO_c			
$V_h(22)$	2.31	2.00	3.55	2.28	2.22	1.32	1.24			
$V_d(22)$	2.31	2.00	3.55	2.28	2.22	1.32	1.24			
$V_d(19)$	2.27	2.00	3.57	2.28	2.24	1.30	1.30			
$V_h(21)$	2.25	2.00	3.49	2.33	2.19	1.32	1.24			
$V_h(3)$	2.21	1.97	3.45	2.33	2.19	1.32	1.24			
$V_h(4)$	2.27	1.97	3.51	2.28	2.22	1.32	1.24			
$V_h(2)$	2.23	1.97	3.53	2.28	2.23	1.30	1.30			
$V_h(15)$	2.28	2.00	3.52	2.30	2.21	1.32	1.24			
$C_{2h}(9)$	2.28	2.00	3.54	2.30	2.24	1.32	1.28	α	=	0.3
$C_{2h}(16)$	2.33	2.00	3.54	2.30	2.33	1.34	1.24	α	=	.3
$C_{2h}(17)$	2.29	2.00	3.53	2.30	2.25	1.34	1.24	β	=	.5
$C_{2b}(13)$	2.22	1.97	3.50	2.28	2.23	1.30	1.30	β	=	.5

TABLE III

TEMPERATURE COEFFICIENTS USED FOR V_h (22)

r_{ij}	L_{ij}	r_{ij}	L_{ij}	r_{ij}	L_{ij}
1.24	0.050	2.31	0.075	5.31	0.090
1.32	.050	3.28	.080	4.62	.090
2.00	.055	3.55	.085	5.86	.100
2.28	.070	4.00	.080	7.10	.100
2.22	.075	4.11	.085		

The correlation of these theoretical intensity curves is not complete as can be noted from the depth of the second and third minima and the positions of ninth and tenth maxima. The latter were measured at scattering angles larger than expected for the models which are otherwise satisfactory. Since this feature is common to all the curves computed, we concluded that the positions of the ninth and tenth halos were displaced

(9) A temperature damping term of the form $\exp(-\pi^2 L_{ij} \, q^2/200)$ was used in eq. 1, with the coefficients L_{ij}, for the respective r_{ij} distances, given in Table III.
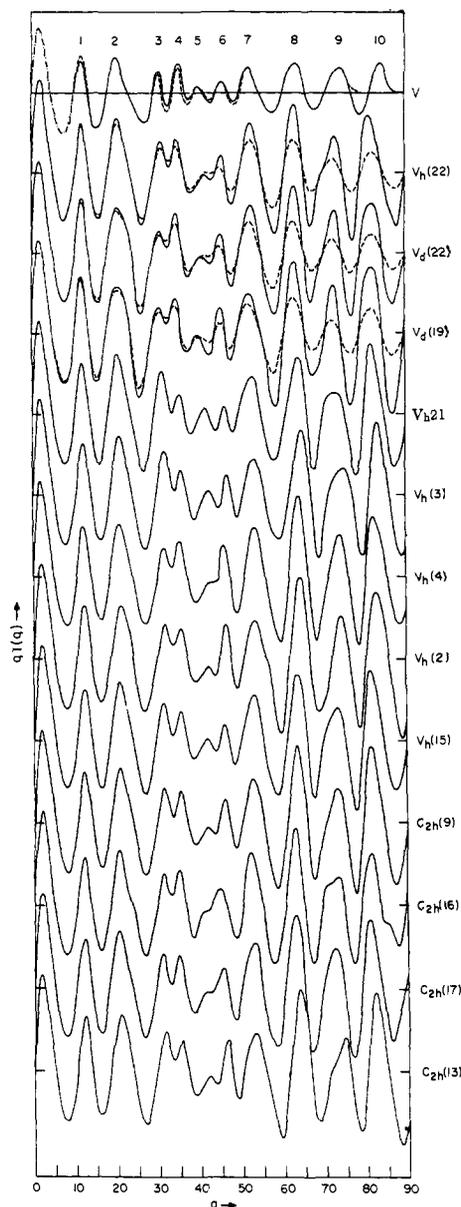

Fig. 2.—Intensity curves. For the dashed intensity curve V, the background between the third and sixth maxima was arbitrarily changed relative to the solid curve V. The dashed V_h and V_d curves are the models with the temperature damping term included and designated $V_h(22T)$, $V_d(22T)$, and $V_d(19T)$.

by an extraneous background of undetermined origin. The photographic plates, from which the ninth and tenth halos were measured, required an exposure of 8 min. and some charge accumulation may have occurred, and the patterns were distorted.

With the shortcomings of visual data in mind, we conclude that the molecular structure of gaseous copper nitrate is of the bidentate form. The central copper atom has four nearest oxygen atoms at 2.00 ± 0.02 Å., and two Cu–N distances of 2.30 ± 0.03 Å. In the nitrate groups the $\langle N-O \rangle_{av} = 1.30 \pm 0.04$, $\angle O_a NO_b = 120 \pm 2°$, and $\angle O_a CuO_b \approx 70°$. The errors shown are mean deviations. The orientation of the nitrate groups relative to each other cannot be established without more accurate intensity data.

E. Discussion

In the molecular structure described above, the N–O separation of 1.30 Å. is in better agreement with distances found in covalent compounds such as CH_3-

ONO_2[10] (mean N–O = 1.28 Å), $FONO_2$[11] (mean N–O = 1.32 Å), and $HONO_2$[12] (mean N–O = 1.272 Å.) than with those reported for ionic nitrate groups such as $NaNO_3$[13] (N–O = 1.218 Å.). It is unlikely that all the N–O distances are equal, but owing to the complexity of the structure a more detailed assignment is not possible at present. That the N–O bonds are of the covalent type is in agreement with the reported infrared spectrum.[4] The possible distortion of the nitrate groups from a coplanar configuration (as in the C_{2h}(b) models) suggests that the unassigned infrared band[4] at about 1088 cm.$^{-1}$ is the "symmetric" N–O stretching frequency (ν_1) "forbidden" for the point group D_{3h}.

The near copper–oxygen distances reported for a number of different compounds,[14–31] where the oxygen atoms have a square-planar or some form of octahedral configuration around the central copper atom, range from 1.90 to 2.00 Å. with most of the values closer to the larger distance. This suggests by analogy that for

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$Cu(NO_3)_2$ an electronic configuration in which the copper atom has square-planar orbitals (V_h model) is to be preferred.

In crystalline state[5] copper(II) nitrate was found to consist of parallel chains of NO_3 groups bridged by copper atoms
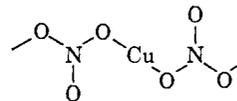
with Cu–O = 1.9 Å. Each of the copper atoms in turn is surrounded by a puckered ring of six oxygen atoms from three nitrate ions distributed in a plane perpendicular to the axes of the (Cu–O–N–O) chains, with Cu–O distances of 2.5 Å. One may visualize the sublimation process for each $Cu(NO_3)_2$ molecule as the breaking of one strong Cu–O (1.9 Å.) bond in the chain and as many as six weaker Cu–O (2.5 Å.) bonds between the neighboring nitrate groups to produce a highly unsymmetric $Cu(NO_3)_2$ with one 1.9 Å, two 2.5 Å., and one 3 Å. near Cu–O distances. The net energy required for the separation of this monomeric molecule from the solid and its rearrangement results in the relatively low heat of vaporization (ΔH = 15.6 kcal./mole).[2] The instability of gaseous $Cu(NO_3)_2$ toward pyrolysis is perhaps due to the distortion of the square configuration, and the strain in the O–Cu–O bond angle (70°).[32]

(32) Note Added in Proof.—The further refinement of the crystal structure of anhydrous $Cu(NO_3)_2$ was reported by S. C. Wallwork at the Sixth General Assembly and International Congress of the International Union of Crystallography, Rome, Italy, 4.45, Sept., 1963. The analysis indicates a more normal distorted octahedral (4 + 2) coordination for each copper atom.