Table IV. Root-Mean-Square Amplitudes of Vibration (Å) for for $Cs_2LiM(CN)_6$

	Mn	Fe	Co
Li	0.145 (16)	0.167 (12)	0.170 (17)
Cs	0.232 (2)	0.216 (1)	0.205 (1)
M	0.144 (3)	0.131 (2)	0.121 (2)
C(max)[a]	0.216 (6)	0.188 (5)	0.165 (4)
C(min)	0.164 (10)	0.153 (8)	0.145 (8)
N(max)	0.327 (8)	0.272 (6)	0.242 (5)
N(min)	0.166 (10)	0.153 (8)	0.145 (8)

[a] Maximum direction for C and N atoms is perpendicular to the C-N bond while minimum direction is coaxial with the C-N bond.

the Li-N bond lengths in $Cs_2LiM(CN)_6$ are comparable to the combined Li and N atomic radii (2.1 Å) and are constant through the series Mn → Co. The foregoing indicates that the $Cs_2LiM(CN)_6$ crystal structures are held together by strong Li-N bonds while the Cs atoms do little more than occupy space. This is in agreement with the high Li-N and low Cs-N force constants observed for $Cs_2LiCo(CN)_6$.[14]

The Cs atom thermal motion is shown to decrease monotonically in the series Mn → Co as do the mean amplitudes of vibration perpendicular to the C-N bond for both C and N atoms.

The decreases in Cs, C, and N atom thermal motion are to be expected since the structures are becoming more tightly packed (and the Cs atom hole size is reduced) as indicated by the monotonic decreases in the M-C and Cs-N bond lengths.

It should be possible to obtain meaningful potential constants for this series of compounds since lattice perturbations can be included[13] and since isotopic vibrational data can be obtained.[26] It will, no doubt, be useful to correlate the bond lengths obtained in this study with potential constants for the $Cs_2LiM(CN)_6$ complexes.[28]

Registry No. $Cs_2LiMn(CN)_6$, 37164-28-6; $Cs_2LiFe(CN)_6$, 37164-29-7; $Cs_2LiCo(CN)_6$, 23591-91-5.

Acknowledgment. The help of D. Cromer, Los Alamos Scientific Laboratory, is gratefully acknowledged.

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(28) A supplementary structure factor table will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-283.

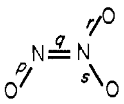
Contribution from the Department of Chemistry,
University of California, Davis, California 95616

Angeli's Salt. Crystal Structure of Sodium Trioxodinitrate(II) Monohydrate, $Na_2N_2O_3 \cdot H_2O$[1]

HAKON HOPE* and MICHAEL R. SEQUEIRA

Received July 10, 1972

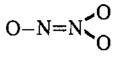
The structure of sodium trioxodinitrate(II) monohydrate, $Na_2N_2O_3 \cdot H_2O$, has been determined by X-ray diffraction methods. The salt crystallizes in the orthorhombic system, space group *Pbcm*, $a = 6.359$ (2), $b = 9.765$ (4), $c = 6.677$ (9) Å. The unit cell contains four formula units. The structure was solved by direct methods and refined by full-matrix least squares to an R index of 0.032. The anion is planar with the structure



Bond distances and angles are as follows: $p = 1.347$ (4), $q = 1.264$ (5), $r = 1.310$ (4), $s = 1.322$ (4) Å; $(pq) = 112.9$ (3), $(qr) = 118.4$ (3), $(qs) = 122.5$ (3)°. The water of hydration is hydrogen bonded to O(s) with O···O = 2.784 (3) Å. The shortest Na–O contact distance is 2.35 Å.

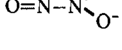
Introduction

Angeli's salt, $Na_2N_2O_3$, was first described by Angeli[2] in 1896. He proposed the structure



$$\left[O{-}N{=}N\begin{smallmatrix}O\\O\end{smallmatrix}\right]^{2-}$$

for the anion. Over the years other atomic arrangements have been suggested, and considerable effort has been expended on this problem.[3-6] Based on the uv spectrum of solutions of the salt Addison, *et al.*,[3] have concluded that the anion contains an N=N double bond. Hendrickson, *et al.*, in an X-ray photoelectron spectroscopic study[6] determined the presence of two chemically nonequivalent N atoms, and presented the formula



$$O{=}N{-}N\begin{smallmatrix}O^-\\O^-\end{smallmatrix}$$

as the most probable.

It seemed to us that an X-ray study would represent the best approach to this structural problem. We now report our results for the monohydrate of Angeli's salt, $Na_2N_2O_3 \cdot H_2O$.

Experimental Section

Angeli's salt was prepared according to the procedure of Addison,

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(1) Abstracted from the M.S. thesis of M. R. Sequeira, University of California, Davis, Calif., 1971.

(2) A. Angeli, *Gazz. Chim. Ital.*, 26, 7 (1896).

(3) (a) C. C. Addison, G. A. Gamlen, and R. Thompson, *J. Chem. Soc.*, 338 (1952); (b) H. R. Hunt, Jr., J. R. Cox, and J. D. Ray, *Inorg. Chem.*, 1, 938 (1962).

(4) P. E. Sturrock, J. D. Ray, J. McDowell, and H. R. Hunt, Jr., *Inorg. Chem.*, 2, 649 (1963).

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

(6) D. Hendrickson, J. M. Hollander, and W. L. Jolly, *Inorg. Chem.*, 8, 2642 (1969).

Table I. Final Positional Parameters[a]

Atom	x	y	z
Na1	0	0	0
Na2	0.3382 (2)	0.25	0
O3	0.7356 (5)	0.5621 (3)	0.25
O4	0.6082 (5)	0.3451 (3)	0.25
N5	0.5735 (5)	0.4773 (3)	0.25
N6	0.3903 (6)	0.5274 (3)	0.25
O7	0.2386 (5)	0.4312 (3)	0.25
O8	0.9267 (5)	0.25	0
H	0.8627 (48)	0.2718 (41)	0.1015 (43)

[a] Estimated standard deviations in parentheses here and in Table II apply to the least significant digits.

Table II. Final Temperature Parameters (Å^2)[a]

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Na1	2.00 (6)	2.65 (6)	2.85 (7)	−0.80 (5)	0.00 (8)	0.19 (9)
Na2	2.45 (7)	1.65 (5)	2.58 (7)	0	0	−0.15 (8)
O3	1.46 (12)	1.75 (13)	3.18 (20)	−0.51 (11)	0	0
O4	1.99 (12)	1.08 (10)	4.53 (17)	0.35 (10)	0	0
N5	1.69 (16)	1.21 (15)	2.27 (19)	0.07 (12)	0	0
N6	1.36 (14)	1.50 (15)	2.96 (21)	0.44 (13)	0	0
O7	1.31 (13)	2.07 (13)	3.00 (20)	−0.26 (12)	0	0
O8	2.70 (13)	2.97 (13)	3.12 (15)	0	0	−0.71 (19)
H	6 (1)					

[a] Anisotropic temperature factor: $\exp(-{}^1/_4 h^2a^{*2}B_{11} - \cdots - {}^1/_2 klb^*c^*B_{23})$; isotropic: $\exp(-B(\sin^2\theta)/\lambda^2)$.

et al.,[3] which essentially follows the original approach of Angeli.[2]

The salt is very soluble in water, and when excess aqueous ethanol or water is added to the solid without agitation, a sharply bounded two-layer system results. We prepared suitable crystals of $Na_2N_2O_3 \cdot H_2O$ by carefully replacing the top layer with ethanol and letting the system stand for a few days. Because oxidation to $NaNO_2$ occurs quite readily, it is important to keep exposure to air at a minimum. The crystallization method is similar to that used by Addison, *et al.*,[3] but because they dried their product they did not note the formation of the monohydrate.[7]

The clear, colorless crystals are of prismatic, rectangular habit. Oscillation and Weissenberg photographs indicated orthorhombic symmetry. The systematic absences ($0kl$, $k = 2n + 1$; $h0l$, $l = 2n + 1$) are consistent with the space groups $Pbcm$ and $Pbc2_1$. Statistical indications, as well as the shape of the Patterson function pointed to $Pbcm$ as the correct one; this choice was later confirmed by the successful refinement of the structure.

Cell dimensions were obtained by a least-squares fit to 11 sets of 2θ, χ, ω angles measured on a Picker four-circle diffractometer with Mo Kα radiation. They are $a = 6.359$ (2), $b = 9.765$ (4), and $c = 6.667$ (9) Å. The density calculated for four units of $Na_2N_2O_3 \cdot H_2O$ per unit cell is 2.24 g cm^{-3} and that observed by flotation is 2.26 g cm^{-3}.

The crystal used for the exploratory photographs underwent a gradual oxidation to $NaNO_2$, as evidenced by the diffraction pattern. Therefore, the specimen (approximate dimensions 0.2 × 0.3 × 0.4 mm^3) used to collect the intensity data was sealed inside a capillary tube which had been flushed with nitrogen. Intensity data (Mo Kα) were collected with a Picker automatic diffractometer equipped with an incident-beam graphite monochromator and a pulse height analyzer. Coincidence losses were limited by the attenuator mechanism which was set to keep counting rates below 9500 cps. A total of 485 unique reflections below $2\theta = 52°$ were scanned with the θ-2θ method at a scan speed (2θ) of 1° min^{-1} and a range defined by $[(2\theta(\alpha_1) - 1°] - [(2\theta(\alpha_2) + 1°]$. Stationary background counts were taken for 40 sec at each end of the scan. Two monitor reflections measured after about every 70 reflections showed no systematic variation. Lorentz and polarization corrections were applied to the net intensities. The polarization factor is that given by Hope.[8]

Each recorded number of counts, N, was assigned a standard deviation $\sigma(N) = (N + (0.004N)^2)^{1/2}$; the factor 0.004 reproduces the observed variance in the monitor reflections. Standard deviations for net intensities and structure factors were obtained by conventional methods. Reflections for which I_{net} was less than $2\sigma(I_{\text{net}})$ were considered as "unobserved," resulting in 352 reflections being recorded as "observed." With a linear absorption coefficient $\mu = 4.2$ cm^{-1} the maximum variation in the transmission factor was about 5% and no absorption correction was applied.

Structure Determination and Refinement

A sharpened Patterson function clearly indicated that most of the scattering material is located in planes perpendicular to c, $c/4$ apart; inspection of the observed structure factors, which are systematically small for odd l, also leads to the same conclusion. The full interpretation of the Patterson function did not appear straightforward, and we decided to solve the structure by direct methods.

Statistical indications obtained in conjunction with the calculation of normalized structure factors[9] (E's) pointed to the centrosymmetric space group as the most probable. We initially intended to use only E's above 1.5 for input to Long's sign determination program,[10] but since this would have given a set containing no odd l index, we added odd-l E's above 0.98 in order to permit the program to select origin-determining indices of proper parity.

A total of 107 signs were determined. The highest consistency index[10] was obtained for two different sign sets. One of these resulted in an E map which unambiguously showed the positions of all atoms other than hydrogen.

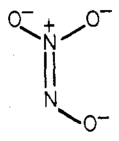
The structure was refined by full-matrix least-squares methods.[11] The R index from the coordinates from the E map ($B = 3$ Å^2) was 0.26. After three cycles of refinement with isotropic temperature factors R was 0.06. At this point the position of the unique H atom was found in a difference Fourier map. In the final stage of the refinement all variable parameters were refined, including anisotropic temperature parameters for Na, O, and N and isotropic B for H. The final R index is 0.032.

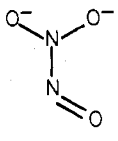
Because of symmetry requirements a number of the positional and thermal parameters are fixed. They are identified in Tables I and II by their absent estimated standard deviations. Table I lists the final positional parameters, Table II gives the final thermal parameters, and Table III[12] gives the calculated and observed structure factors.

Description and Discussion

The anion, situated on a mirror plane, is required to be planar. The two sodium ions occupy positions at a center of symmetry and on a twofold axis, respectively. The water of hydration is also located on a twofold axis, leaving the crystallographically unique hydrogen as the only atom in a general position.

Bond distances and angles are given in Figure 1. Among the resonance structures I-IV, we find that I most closely corresponds to the observed geometry, but the contributions II, III, and IV are also significant. The N=N distance is close to


I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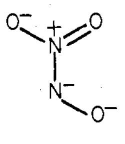
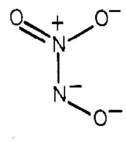

III


IV

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[7] At this stage we were not aware of a paper (J. Veprek-Siska, V. Pliska, F. Smirous, and F. Vesely, *Collect. Czech. Chem. Commun.*, **24**, 687 (1959)) describing the crystallization of both the anhydrous salt and the monohydrate.

[8] H. Hope, *Acta Crystallogr., Sect. A*, **27**, 392 (1971).

[9] I. L. Karle, K. S. Dragonette, and S. A. Brenner, *Acta Crystallogr.*, **19**, 713 (1965).

[10] R. E. Long, Ph.D. Dissertation, University of California, Los Angeles, Calif., 1965.

[11] Most of the computer programs used in this study have been identified elsewhere: H. Hope and A. T. Christensen, *Acta Crystallogr., Sect. B*, **24**, 375 (1968). The form factors are as follows: for N and O, H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964); for Na$^+$, "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962; for H, R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965). The R index is $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. Only "observed" reflections were used in the refinement. The weights for $(\Delta F)^2$ were proportional to $1/\sigma^2(F)$.

[12] Table III will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-286.

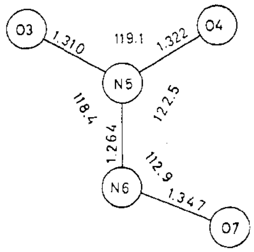

Figure 1. Distances and angles. Esd's are about 0.005 Å and 0.3°, respectively.

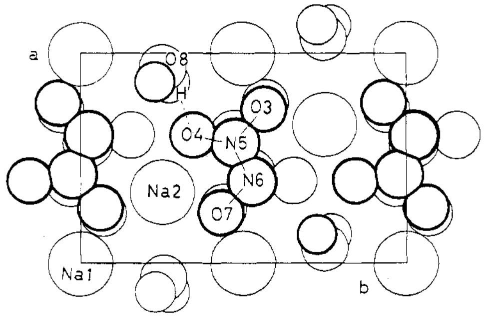

Figure 2. Packing diagram showing the structure projected along *c*.

that found in azobenzenes.[13] The N-O distances are all quite long compared to those in the nitrate[14] and nitrite[15] ions (~1.24 Å), whereas the situation observed in potassium *syn*-methyldiazotate[16] appears to correspond more closely to that found in the present case. This would indicate a high degree of charge localization on the oxygen atoms in Angeli's salt.

The angle N5-N6-O7 (112.9°) is nearly the same as that found in azobenzenes[13] or in azoxy compounds,[17] also testifying to a similarity in electronic structure.

The interesting question of the position of the protons in the free acid cannot be unambiguously answered on the basis of our results. However, the geometry around N6 indicates a preference for an N-O single bond, and it seems reasonable to assume that O7 is the site of one proton. We also see no reason why there would be an absolute preference of one of the remaining oxygen atoms over the other, so that we envision a case of tautomerism involving these two atoms.

The O4· · ·H-O8 hydrogen bond (2.784 Å) indicates a rather weak bond.

The Na^+ ions at centers of symmetry have six oxygen contacts ranging from 2.35 (O7′) to 2.49 Å (H_2O), averaging 2.42 Å. The Na^+ ions on the twofold axis have seven oxygen contacts in the range 2.51 (O7)-2.62 Å (H_2O), for an average of 2.55 Å. We note that the presumably most negative oxygen atom, O7, also is the one which makes the shortest Na-O contacts. The difference in average Na-O distance for six- and seven-coordination corresponds to earlier observations.[18]

Registry No. $Na_2N_2O_3{\cdot}H_2O$, 37035-81-7.

Acknowledgment. The authors are pleased to acknowledge the financial support of this study by the National Science Foundation.

(13) H. Hope and D. Victor, *Acta Crystallogr., Sect. B*, **25**, 1849 (1969), and references cited therein.

(14) P. Cherin, W. C. Hamilton, and B. Post, *Acta Crystallogr.*, **23**, 455 (1967).

(15) M. J. Kay and B. C. Frazer, *Acta Crystallogr.*, **14**, 56 (1961).

(16) R. Huber, R. Langer, and W. Hoppe, *Acta Crystallogr.*, **18**, 467 (1965).

(17) N. R. Krigbaum, Y. Chatani, and P. G. Barber, *Acta Crystallogr., Sect. B*, **26**, 97 (1970).

(18) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, Table 4.1.1.

Contribution from the Department of Chemistry,
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Crystal and Molecular Structure of 5,6-μ-Diphenylphosphino-decaborane(14)[1]

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Received August 2, 1972

The compound 5,6-μ-diphenylphosphino-decaborane(14), $B_{10}H_{13}P(C_6H_5)_2$, crystallizes in the orthorhombic space group $P2_12_12_1$ with $a = 7.39$ (1), $b = 12.59$ (1), $c = 20.02$ (2) Å, $Z = 4$, $\rho_{\text{calcd}} = 1.093$ g/cm^3, and $\rho_{\text{exptl}} = 1.09$ (1) g/cm^3. The structure of the molecule was determined using the heavy-atom technique and refined by the full-matrix least-squares method to a conventional R factor of 10.2% for 833 independent observed photographic data. The phosphorus atom of the diphenylphosphino group occupies a bridging position between B5 and B6 of a distorted B_{10} icosahedral fragment, confirming for the first time the substitution of a nonmetallic atom in a bridge hydrogen position in the decaborane(14) molecule.

Introduction

Several years ago the diphenylphosphino derivative of decaborane(14), formulated $B_{10}H_{13}P(C_6H_5)_2$, was prepared independently in two laboratories. Muetterties and Aftandilian obtained $B_{10}H_{13}P(C_6H_5)_2$ from the reaction of the decaboranyl Grignard reagent with diphenylchlorophosphine[2]

$$B_{10}H_{13}MgI + (C_6H_5)_2PCl \rightarrow B_{10}H_{13}P(C_6H_5)_2 + NaCl$$

while Schroeder prepared the compound by treating sodium

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(1) Presented in part at the International Meeting on Boron Compounds, Liblice, Czechoslovakia, June 21-25, 1971.

(2) (a) E. L. Muetterties and V. D. Aftandilian, *Inorg. Chem.*, **1**, 731 (1962); (b) V. D. Aftandilian, U. S. Patent 3,013,041 (1961); (c) E. L. Muetterties, U. S. Patent 3,118,932 (1964).