

By means of a small furnace-sample holder kindly loaned by Dr Robert S. Roth of the National Bureau of Standards, samples of both the monoclinic and triclinic forms were heated for varying periods of time ($\frac{1}{2}$ hour to about 16 hours) while the furnace was mounted on an X-ray diffractometer. Patterns could be taken at any temperature. No change from one polymorphic form to another could be detected. Only dehydration occurred, at temperatures as low as 50 °C if the sample was heated 12 or more hours and at 75 °C after 1 hour of heating. A transition in the solid state seems unlikely from a comparison of the two structures. Although the structures have similarities, major shifts in the relative positions of the anions, and in the sodium coordination would have to occur.

The author wishes to thank the following people: Dr H. T. Evans, of the U.S. Geological Survey for running the piezoelectric test; Mr Alvin Van Valkenburg for obtaining the optical data, Mrs Marlene C. Morris, for obtaining the powder data and assisting in refining the cell parameters, Mr Gary Mason for measuring the intensities and Mr Robert Gates for assistance in processing the data, all of the National Bureau of Standards.

Acta Cryst. (1964). **17**, 1145

The Crystal Structure of Bisethylenediaminecopper(II) Nitrate

BY Y. KOMIYAMA* AND E. C. LINGAFELTER

Department of Chemistry, University of Washington, Seattle 5, Washington, U.S.A.

(Received 23 September 1963)

The crystal structure of bisethylenediaminecopper(II) nitrate, $\text{Cu}(\text{C}_2\text{N}_2\text{H}_8)_2(\text{NO}_3)_2$, has been determined from three-dimensional X-ray diffraction data. The dimensions of the monoclinic ($P2_1/c$) cell are $a_0=8.30$, $b_0=10.05$, $c_0=8.07$ Å, $\beta=111^\circ 6'$, $z=2$. The structure was refined by three-dimensional difference syntheses to $R=0.097$.

The copper ion has the usual distorted octahedral coordination with four N atoms at 2.03 Å and two O atoms at 2.59 Å. The ethylenediamine molecule is in the *gauche* configuration, with one C atom 0.39 Å from the CuN_4 plane and the other -0.19 Å

Introduction

As a part of a study of the coordination configuration of Cu^{2+} , we have determined the crystal structure of bisethylenediaminecopper(II) nitrate, $\text{Cu}(\text{C}_2\text{N}_2\text{H}_8)_2(\text{NO}_3)_2$, which was originally prepared and described as a dihydrate by Grossman & Schuck (1906), but later shown to be anhydrous by Johnson & Bryant (1934). A short report of preliminary work on this structure was reported by Watanabe & Atoji (1951). They report

- ### References
- BARNEY, D. L. & GRYDER, J. W. (1955). *J. Amer. Chem. Soc.* **77**, 3195.
 BELL, R. N., AUDRIETH, W. F. & HILL, O. F. (1952). *Ind. Engng Chem.* **44**, 568.
 BERGHUIS, J., HAANAPPEL, IJ. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478.
 BUSING, W. R. & LEVY, H. A. (1959a). *A Crystallographic Least Squares Refinement Program for the IBM 704*. Oak Ridge National Laboratory Report 59-4-37.
 BUSING, W. R. & LEVY, H. A. (1959b). *A Crystallographic Function and Error Program for the IBM 704*. Oak Ridge National Laboratory Report 59-12-3.
 CORBRIDGE, D. E. C. (1960). *Acta Cryst.* **13**, 263.
 CORBRIDGE, D. E. C. & TROMANS, F. R. (1958). *Anal. Chem.* **30**, 1101.
 DAVIES, D. R. & CORBRIDGE, D. E. C. (1958). *Acta Cryst.* **11**, 315.
 GROSS, R. J. (1955). Unpublished Dissertation, The Johns Hopkins University.
 GROSS, R. J., GRYDER, J. W. & DONNAY, G. (1955). *Abstracts of Papers*. 128th Meeting. Amer. Chem. Soc.
 ONDIK, H. M., BLOCK, S. & MACGILLAVRY, C. H. (1961). *Acta Cryst.* **14**, 555.
 STEGER, E. (1958). *Z. anorg. Chem.* **294**, 146.
 STEGER, E. & SIMON, A. (1958). *Z. anorg. Chem.* **294**, 1.
 TOMIE, Y. & STAM, C. H. (1958). *Acta Cryst.* **11**, 126.
 WARSCHAUER, F. (1903). *Z. anorg. Chem.* **36**, 137.

the cell to have dimensions $a=8.00$, $b=10.00$, $c=15.53$ Å, $\beta=97^\circ 25'$, $Z=4$ molecules, space group $B2_1/a$. In *Structure Reports* (1951) it is erroneously suggested that this space group symbol is a misprint for $P2_1/a$. However, transformation of their cell to a primitive cell gives $a=8.00$, $b=10.00$, $c=8.27$ Å, $\beta=111^\circ 19'$, in quite satisfactory agreement with our results.

Experimental

Bisethylenediaminecopper(II) nitrate was prepared by the method described by Grossman & Schuck (1906)

* Present address: Department of Chemistry, Yamanashi University, Japan.

and crystallized from water. The violet-colored crystals are six-sided holohedral monoclinic plates on $\{100\}$, bounded by $\{010\}$ and $\{011\}$.

Cell dimensions were calculated from measurements on rotation and Weissenberg photographs, calibrated with NaCl ($a_0 = 5.6387 \text{ \AA}$) using Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The results are $a_0 = 8.302 \pm 0.01$; $b_0 = 10.052 \pm 0.004$; $c_0 = 8.065 \pm 0.01 \text{ \AA}$; $\beta = 111^\circ 6' \pm 12'$. The cell contains two molecules, density calculated: 1.630 g.cm^{-3} ; measured: 1.622 g.cm^{-3} . Systematic absence of $h0l$ for $l \neq 2n$ and of $0k0$ for $k \neq 2n$ indicate the space group to be $P2_1/c$.

Relative intensities were obtained from equi-inclination Weissenberg photographs taken on a Nonius integrating camera with Cu radiation using multiple films and a range of exposure times.

The crystal was a rod of dimensions $0.02 \times 0.09 \times 0.45 \text{ mm}$, rotated about its long dimension, the b axis. The camera integration was carried out in one direction only, and each spot in the linear response range on each film was scanned in the other direction with a Moll-type densitometer feeding into a Leeds & Northrup amplifier and recorder with a logarithmic slide wire. The area under each spot tracing was measured with a planimeter and used directly as relative intensity. The several films for each level were placed on a common scale for that level by correlation of spots appearing on more than one film. The range of relative intensities was 1 to 2000. 565 reflections fell within this range, while 491 others could have been recorded on the films and were therefore listed as 'less-than-1'.

Data were collected for all levels from $h0l$ through $h7l$. Lorentz and polarization factors were applied, but no corrections were made for absorption nor dispersion. The structure factors on the several levels were placed on a common scale by comparison of observed and calculated structure factors at each stage of the refinement of the structure.

Determination of the structure

The presence of two molecules in a unit cell of space group $P2_1/c$ requires the copper ions to occupy one of the sets of twofold positions. They could be placed at 000 and $0\frac{1}{2}\frac{1}{2}$ without loss of generality.

In order to determine the positions of the light atoms, two calculations were made, a three-dimensional Patterson function and the electron-density projection, $\rho(x, z)$, using all phase angles zero due to the special positions of the copper atoms. It was possible to locate all atoms in this manner.

The structure was then refined by three-dimensional difference syntheses. For structure factor calculations, scattering factors were obtained from Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for oxygen, nitrogen, carbon and hydrogen and from Thomas & Umeda (1957) for copper. In calculating the difference syntheses, ΔF was included

for all measured reflections and for those 'less-thans' for which $F_c > F_{\min}$. All calculations were carried out on an IBM 650 computer. The final value of $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.097$. Hydrogen atoms were placed in calculated positions, but not refined. Atomic anisotropic temperature factors of the form

$$\exp [-2\pi^2(a^*h^2U_{11} + b^*k^2U_{22} + c^*l^2U_{33} + 2a^*b^*hkU_{12} + 2a^*c^*hlU_{13} + 2b^*c^*klU_{23})]$$

were applied.

The final atomic positions and their estimated standard deviations (Cruickshank, 1949) are given in Table 1 and the temperature factor parameters in Table 2. Table 3 gives the comparison of observed and calculated structure factors.

Table 1. Final coordinates and standard deviations

Atom	x/a	y/b	z/c
Cu	0.0000	0.0000	0.0000
C(1)	0.3271	0.1318	0.1770
C(2)	0.3601	-0.0195	0.2007
N(1)	0.1639	0.1567	0.0245
N(2)	0.2000	-0.0904	0.1865
N(3)	0.1687	0.5571	0.1658
O(1)	0.2282	0.6279	0.0743
O(2)	0.2023	0.4338	0.1817
O(3)	0.0960	0.6117	0.2608
$\sigma(C)$	0.012	0.009	0.012
$\sigma(N)$	0.009	0.007	0.009
$\sigma(O)$	0.008	0.006	0.008

Table 2. Final temperature factor parameters

Atom	$(\times 100)$					
	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	5.37	4.50	5.72	0.06	2.41	-0.08
C(1)	6.73	6.46	7.14	0.09	2.36	-0.01
C(2)	6.46	6.59	7.27	0.09	2.33	0.00
N(1)	5.56	5.19	5.60	0.06	2.14	0.03
N(2)	5.36	5.26	5.33	0.05	2.03	0.01
N(3)	5.41	5.19	5.40	0.08	1.99	0.04
O(1)	6.50	5.83	6.23	0.08	2.52	0.05
O(2)	6.57	6.08	6.59	0.09	2.57	0.01
O(3)	6.45	6.08	6.23	0.04	2.56	0.00

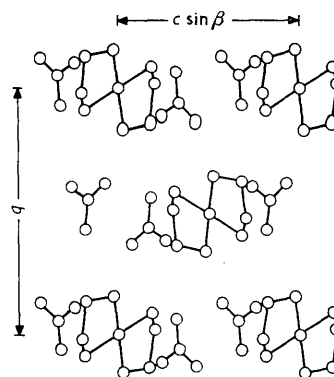


Fig. 1. Projection of structure along $[100]$.

Table 3. Calculated and observed structure factors
Columns are $h, F_o \times 10, F_c \times 10$. Unobserved marked by *

H ₂ ,0,C	91 154 200 427 439 486 498	93 144 174 439 468 486 500	H ₂ ,2,2	60 82 103 125 146 167 188 209 230 251 272 293 314 335 356 377 398 419 440 461 482 503 524 545 566 587 608 629 650 671 692 713 734 755 776 797 818 839 860 881 902 923 944 965 986 1007	H ₃ ,1,1	266 287 308 329 350 371 392 413 434 455 476 497 518 539 560 581 602 623 644 665 686 707 728 749 770 791 812 833 854 875 896 917 938 959 980 1001 1022 1043 1064 1085 1106 1127 1148 1169 1190 1211 1232 1253 1274 1295 1316 1337 1358 1379 1400 1421 1442 1463 1484 1505 1526 1547 1568 1589 1610 1631 1652 1673 1694 1715 1736 1757 1778 1799 1820 1841 1862 1883 1904 1925 1946 1967 1988 2009 2030 2051 2072 2093 2114 2135 2156 2177 2198 2219 2240 2261 2282 2303 2324 2345 2366 2387 2408 2429 2450 2471 2492 2513 2534 2555 2576 2597 2618 2639 2660 2681 2702 2723 2744 2765 2786 2807 2828 2849 2870 2891 2912 2933 2954 2975 2996 3017 3038 3059 3080 3101 3122 3143 3164 3185 3206 3227 3248 3269 3290 3311 3332 3353 3374 3395 3416 3437 3458 3479 3500 3521 3542 3563 3584 3605 3626 3647 3668 3689 3710 3731 3752 3773 3794 3815 3836 3857 3878 3899 3920 3941 3962 3983 4004 4025 4046 4067 4088 4109 4130 4151 4172 4193 4214 4235 4256 4277 4298 4319 4340 4361 4382 4403 4424 4445 4466 4487 4508 4529 4550 4571 4592 4613 4634 4655 4676 4697 4718 4739 4760 4781 4802 4823 4844 4865 4886 4907 4928 4949 4970 4991 5012 5033 5054 5075 5096 5117 5138 5159 5180 5201 5222 5243 5264 5285 5306 5327 5348 5369 5390 5411 5432 5453 5474 5495 5516 5537 5558 5579 5600 5621 5642 5663 5684 5705 5726 5747 5768 5789 5810 5831 5852 5873 5894 5915 5936 5957 5978 5999 6020 6041 6062 6083 6104 6125 6146 6167 6188 6209 6230 6251 6272 6293 6314 6335 6356 6377 6398 6419 6440 6461 6482 6503 6524 6545 6566 6587 6608 6629 6650 6671 6692 6713 6734 6755 6776 6797 6818 6839 6860 6881 6902 6923 6944 6965 6986 7007 7028 7049 7070 7091 7112 7133 7154 7175 7196 7217 7238 7259 7280 7301 7322 7343 7364 7385 7406 7427 7448 7469 7490 7511 7532 7553 7574 7595 7616 7637 7658 7679 7700 7721 7742 7763 7784 7805 7826 7847 7868 7889 7910 7931 7952 7973 7994 8015 8036 8057 8078 8099 8120 8141 8162 8183 8204 8225 8246 8267 8288 8309 8330 8351 8372 8393 8414 8435 8456 8477 8498 8519 8540 8561 8582 8603 8624 8645 8666 8687 8708 8729 8750 8771 8792 8813 8834 8855 8876 8897 8918 8939 8960 8981 9002 9023 9044 9065 9086 9107 9128 9149 9170 9191 9212 9233 9254 9275 9296 9317 9338 9359 9380 9401 9422 9443 9464 9485 9506 9527 9548 9569 9590 9611 9632 9653 9674 9695 9716 9737 9758 9779 9800 9821 9842 9863 9884 9905 9926 9947 9968 9989 10010 10031 10052 10073 10094 10115 10136 10157 10178 10199 10220 10241 10262 10283 10304 10325 10346 10367 10388 10409 10430 10451 10472 10493 10514 10535 10556 10577 10598 10619 10640 10661 10682 10703 10724 10745 10766 10787 10808 10829 10850 10871 10892 10913 10934 10955 10976 10997 11018 11039 11060 11081 11102 11123 11144 11165 11186 11207 11228 11249 11270 11291 11312 11333 11354 11375 11396 11417 11438 11459 11480 11501 11522 11543 11564 11585 11606 11627 11648 11669 11690 11711 11732 11753 11774 11795 11816 11837 11858 11879 11900 11921 11942 11963 11984 12005 12026 12047 12068 12089 12110 12131 12152 12173 12194 12215 12236 12257 12278 12299 12320 12341 12362 12383 12404 12425 12446 12467 12488 12509 12530 12551 12572 12593 12614 12635 12656 12677 12698 12719 12740 12761 12782 12803 12824 12845 12866 12887 12908 12929 12950 12971 12992 13013 13034 13055 13076 13097 13118 13139 13160 13181 13202 13223 13244 13265 13286 13307 13328 13349 13370 13391 13412 13433 13454 13475 13496 13517 13538 13559 13580 13601 13622 13643 13664 13685 13706 13727 13748 13769 13790 13811 13832 13853 13874 13895 13916 13937 13958 13979 13999 14020 14041 14062 14083 14104 14125 14146 14167 14188 14209 14230 14251 14272 14293 14314 14335 14356 14377 14398 14419 14440 14461 14482 14503 14524 14545 14566 14587 14608 14629 14650 14671 14692 14713 14734 14755 14776 14797 14818 14839 14860 14881 14902 14923 14944 14965 14986 15007 15028 15049 15070 15091 15112 15133 15154 15175 15196 15217 15238 15259 15280 15301 15322 15343 15364 15385 15406 15427 15448 15469 15490 15511 15532 15553 15574 15595 15616 15637 15658 15679 15700 15721 15742 15763 15784 15805 15826 15847 15868 15889 15910 15931 15952 15973 15994 16015 16036 16057 16078 16099 16120 16141 16162 16183 16204 16225 16246 16267 16288 16309 16330 16351 16372 16393 16414 16435 16456 16477 16498 16519 16540 16561 16582 16603 16624 16645 16666 16687 16708 16729 16750 16771 16792 16813 16834 16855 16876 16897 16918 16939 16960 16981 17002 17023 17044 17065 17086 17107 17128 17149 17170 17191 17212 17233 17254 17275 17296 17317 17338 17359 17380 17401 17422 17443 17464 17485 17506 17527 17548 17569 17590 17611 17632 17653 17674 17695 17716 17737 17758 17779 17800 17821 17842 17863 17884 17905 17926 17947 17968 17989 18010 18031 18052 18073 18094 18115 18136 18157 18178 18199 18220 18241 18262 18283 18304 18325 18346 18367 18388 18409 18430 18451 18472 18493 18514 18535 18556 18577 18598 18619 18640 18661 18682 18703 18724 18745 18766 18787 18808 18829 18850 18871 18892 18913 18934 18955 18976 18997 19018 19039 19060 19081 19102 19123 19144 19165 19186 19207 19228 19249 19270 19291 19312 19333 19354 19375 19396 19417 19438 19459 19480 19501 19522 19543 19564 19585 19606 19627 19648 19669 19690 19711 19732 19753 19774 19795 19816 19837 19858 19879 19900 19921 19942 19963 19984 20005 20026 20047 20068 20089 20110 20131 20152 20173 20194 20215 20236 20257 20278 20299 20320 20341 20362 20383 20404 20425 20446 20467 20488 20509 20530 20551 20572 20593 20614 20635 20656 20677 20698 20719 20740 20761 20782 20803 20824 20845 20866 20887 20908 20929 20950 20971 20992 21013 21034 21055 21076 21097 21118 21139 21160 21181 21202 21223 21244 21265 21286 21307 21328 21349 21370 21391 21412 21433 21454 21475 21496 21517 21538 21559 21580 21601 21622 21643 21664 21685 21706 21727 21748 21769 21790 21811 21832 21853 21874 21895 21916 21937 21958 21979 21999 22020 22041 22062 22083 22104 22125 22146 22167 22188 22209 22230 22251 22272 22293 22314 22335 22356 22377 22398 22419 22440 22461 22482 22503 22524 22545 22566 22587 22608 22629 22650 22671 22692 22713 22734 22755 22776 22797 22818 22839 22860 22881 22902 22923 22944 22965 22986 23007 23028 23049 23070 23091 23112 23133 23154 23175 23196 23217 23238 23259 23280 23301 23322 23343 23364 23385 23406 23427 23448 23469 23490 23511 23532 23553 23574 23595 23616 23637 23658 23679 23700 23721 23742 23763 23784 23805 23826 23847 23868 23889 23910 23931 23952 23973 23994 24015 24036 24057 24078 24099 24120 24141 24162 24183 24204 24225 24246 24267 24288 24309 24330 24351 24372 24393 24414 24435 24456 24477 24498 24519 24540 24561 24582 24603 24624 24645 24666 24687 24708 24729 24750 24771 24792 24813 24834 24855 24876 24897 24918 24939 24960 24981 25002 25023 25044 25065 25086 25107 25128 25149 25170 25191 25212 25233 25254 25275 25296 25317 25338 25359 25380 25401 25422 25443 25464 25485 25506 25527 25548 25569 25590 25611 25632 25653 25674 25695 25716 25737 25758 25779 25800 25821 25842 25863 25884 25905 25926 25947 25968 25989 26010 26031 26052 26073 26094 26115 26136 26157 26178 26199 26220 26241 26262 26283 26304 26325 26346 26367 26388 26409 26430 26451 26472 26493 26514 26535 26556 26577 26598 26619 26640 26661 26682 26703 26724 26745 26766 26787 26808 26829 26850 26871 26892 26913 26934 26955 26976 26997 27018 27039 27060 27081 27102 27123 27144 27165 27186 27207 27228 27249 27270 27291 27312 27333 27354 27375 27396 27417 27438 27459 27480 27501 27522 27543 27564 27585 27606 27627 27648 27669 27690 27711 27732 27753 27774 27795 27816 27837 27858 27879 27900 27921 27942 27963 27984 28005 28026 28047 28068 28089 28110 28131 28152 28173 28194 28215 28236 28257 28278 28299 28320 28341 28362 28383 28404 28425 28446 28467 28488 28509 28530 28551 28572 28593 28614 28635 28656 28677 28698 28719 28740 28761 28782 28803 28824 28845 28866 28887 28908 28929 28950 28971 28992 29013 29034 29055 29076 29097 29118 29139 29160 29181 29202 29223 29244 29265 29286 29307 29328 29349 29370 29391 29412 29433 29454 29475 29496 29517 29538 29559 29580 29601 29622 29643 29664 29685 29706 29727 29748 29769 29790 29811 29832 29853 29874 29895 29916 29937 29958 29979 30000	H ₃ ,2,1	266 287 308 329 350 371 392 413 434 455 476 497 518 539 560 581 602 623 644 665 686 707 728 749 770 791 812 833 854 875 896 917 938 959 980 1001 1022 1043 1064 1085 1106 1127 1148 1169 1190 1211 1232 1253 1274 1295 1316 1337 1358 1379 1400 1421 1442 1463 1484 1505 1526 1547 1568 1589 1610 1631 1652 1673 1694 1715 1736 1757 1778 1799 1820 1841 1862 1883 1904 1925 1946 1967 1988 2009 2030 2051 2072 2093 2114 2135 2156 2177 2198 2219 2240 2261 2282 2303 2324 2345 2366 2387 2408 2429 2450 2471 2492 2513 2534 2555 2576 2597 2618 2639 2660 2681 2702 2723 2744 2765 2786 2807 2828 2849 2870 2891 2912 2933 2954 2975 2996 3017 3038 3059 3080 3101 3122 3143 3164 3185 3206 3227 3248 3269 3290 3311 3332 3353 3374 3395 3416 3437 3458 3479 3500 3521 3542 3563 3584 3605 3626 3647 3668 3689 3710 3731 3752 3773 3794 3815 3836 3857 3878 3899 3920 3941 3962 3983 4004 4025 4046 4067 4088 4109 4130 4151 4172 4193 4214 4235 4256 4277 4298 4319 4340 4361 4382 4403 4424 4445 4466 4487 4508 4529 4550 4571 4592 4613 4634 4655 4676 4697 4718 4739 4760 4781 4802 4823 4844 4865 4886 4907 4928 4949 4970 4991 5012 5033 5054 5075 5096 5117 5138 5159 5180 5201 5222 5243 5264 5285 5306 5327 5348 5369 5390 5411 5432 5453 5474 5495 5516 5537 5558 5579 5599 5620 5641 5662 5683 5704 5725 5746 5767 5788 5809 5830 5851 5872 5893 5914 5935 5956 5977 5998 6019 6040 6061 6082 6103 6124 6145 6166 6187 6208 6229 6250 6271 6292 6313 6334 6355 6376 6397 6418 6439 6460 6481 6502 6523 6544 6565 6586 6607 6628 6649 6670 6691 6712 6733 6754 6775 6796 6817 6838 6859 6880 6901 6922 6943 6964 6985 7006 7027 7048 7069 7090 7111 7132 7153 7174 7195 7216 7237 7258 7279 7300 7321 7342 7363 7384 7405 7426 7447 7468 7489 7510 7531 7552 7573 7594 7615 7636 7657 7678 7699 7720 7741 7762 7783 7804 7825 7846 7867 7888 7909 7930 7951 7972 7993 8014 8035 8056 8077 8098 8119 8140 8161 8182 8203 8224 8245 8266 8287 8308 8329 8350 8371 8392 8413 8434 8455 8476 8497 8518 8539 8560 8581 8602 8623 8644 8665 868
---------------------	--	--	---------------------	---	---------------------	--	---------------------	--

Discussion

The arrangement of the atoms is illustrated in Fig. 1, which depicts the projection along [100]. Bond distances and angles and their standard deviations are given in Table 4.

Table 4. Bond distances and angles

Cu-N(1)	2.044 Å (0.013) Å	N(1)-Cu-N(2)	86.2°
Cu-N(2)	2.012 (0.013)	Cu-N(1)-C(1)	109.1
Cu-O(3')	2.593 (0.012)		
N(1)-C(1)	1.487 (0.025)	Cu-N(2)-C(2)	108.5
N(2)-C(2)	1.476 (0.025)	N(1)-C(1)-C(2)	109.6
C(1)-C(2)	1.545 (0.027)	N(2)-C(2)-C(1)	110.6
N(3)-O(1)	1.248 (0.020)	O(1)-N(3)-O(2)	119.9
N(3)-O(2)	1.267 (0.020)	O(2)-N(3)-O(3)	120.1
N(3)-O(3)	1.259 (0.020)	O(1)-N(3)-O(3)	119.3
N(2)-H...O(1')	3.007 [O(1') at $x, -1+y, z$]		
N(1)-H...O(2')	3.029 [O(2') at $x, \frac{1}{2}-y, -\frac{1}{2}+z$]		
N(1)-H...O(2)	3.035		
N(2)-H...O(1')	3.075 [O(1') at $x, \frac{1}{2}-y, \frac{1}{2}+z$]		

The copper ion is surrounded by a tetragonally distorted octahedron, with four nitrogen atoms, from the two ethylenediamine molecules, at 2.03 Å and two oxygen atoms, from the nitrate ions, at 2.59 Å. The bond angles in the coordination polyhedron deviate only slightly from 90°. The intrachelate N-Cu-N angle is 86.2°, and the angle between the Cu-O bond and the CuN₄ plane is 87.0°. These values may be compared with corresponding values from other copper compounds. Copper-amine nitrogen 'short' distances: 1.99, 2.02 Å in Cu(en)₂(SCN)₂ (Brown & Lingafelter, 1964); 1.98, 1.99 Å in [Cu(en)₂(H₂O)Cl]Cl and 1.97, 1.98 Å in [Cu(en)₂(H₂O)Br]Br (Mazzi, 1953); 1.99 Å in Cu(C₅H₈O₂N)₂·2H₂O (Mathieson & Welsh, 1952); 2.04, 2.06 Å in Cu(NH₃)₄SO₄·H₂O (Mazzi, 1955); and 2.05 Å in NH₄Cu(NH₃)₄(ClO₄)₂·NH₃ (Bukovska & Porai-Koshits, 1960). Copper-oxygen 'long' distances: 2.68 Å in [Cu(en)₂(H₂O)Cl]Cl and 2.78 Å in [Cu(en)₂(H₂O)Br]Br (Mazzi, 1953); 2.53 Å in bis-(salicylaldehydeisopropylenediimine) copper monohydrate (Waters, Hall & Llewellyn, 1958); 2.89 Å in copper(II) salicylate tetrahydrate (Hanic, 1958).

The asymmetry of the ethylenediamine molecule with respect to the CuN₄ coordination plane is quite similar to that found in Cu(en)₂(SCN)₂ (Brown & Lingafelter, 1964), Cu(en)₂Hg(SCN)₄ (Scouloudi, 1953) and [Cu(en)₂(H₂O)Cl]Cl (Mazzi, 1953). The ethylenediamine molecule is in the *gauche* configuration with one carbon atom 0.39 Å above the coordination plane and the other 0.19 Å below the plane.

The bond distances in the ethylenediamine molecule appear to be normal and may be compared with values from other molecules: C-C, 1.50 Å and C-N, 1.50 Å in Ni(en)₃(NO₃)₂ (Swink & Atoji, 1960); C-C, 1.50 Å and C-N, 1.46 and 1.50 Å in Ni(en)₂(SCN)₂ (Brown

& Lingafelter, 1963); C-C, 1.56 Å and C-N, 1.46 and 1.49 Å in Cu(en)₂(SCN)₂ (Brown & Lingafelter, 1964); C-C, 1.51 Å and C-N, 1.50 Å in [Cu(en)₂(H₂O)Cl]Cl (Mazzi, 1953).

The deviation of the nitrate ion from planarity is slight (the nitrogen atom is 0.062 Å from the oxygen plane) but significant ($\sigma_N \sim 0.009$ Å). The N-O distances are not significantly different from one another and the mean value 1.258 Å may be compared to the values reported in other nitrates: 1.243 Å in N₂O₅ (Grison, Eriks & deVries, 1950), 1.24 Å in (C₂H₅N₃)NO₃ (Curtis & Pasternak, 1955), 1.21 Å in Ni(en)₃(NO₃)₂ (Swink & Atoji, 1960).

Considering the crystal to be formed from Cu(en)₂²⁺ and NO₃⁻ ions, these ions are bound together in sheets parallel to (100) by the coordination of O(3) to Cu and by a network of NH...O hydrogen bonds of lengths 3.01 to 3.08 Å. This arrangement leads to the thinness of the crystals on {100} and to the easy cleavage parallel to (100).

This investigation was supported in part by the U.S. Public Health Service under Research Grant A-2241.

References

- BERGHUIS, J., HAANAPPEL, IJ. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478.
- BROWN, B. W. & LINGAFELTER, E. C. (1963). *Acta Cryst.* **16**, 753.
- BROWN, B. W. & LINGAFELTER, E. C. (1964). *Acta Cryst.* **17**, 254.
- BUKOVSKA, M. & PORAI-KOSHITS, M. A. (1960). *Soviet Phys.-Cryst.* **5**, 130.
- CRICKSHANK, D. W. J. (1949). *Acta Cryst.* **2**, 65.
- CURTIS, R. M. & PASTERNAK, R. A. (1955). *Acta Cryst.* **8**, 675.
- GRISON, E., ERIKS, K. & DEVRIES, J. L. (1950). *Acta Cryst.* **3**, 290.
- GROSSMAN, H. & SCHUCK, B. (1906). *Z. anorg. Chem.* **50**, 1.
- HANIC, F. (1958). *Angew. Chem.* **70**, 320.
- JOHNSON, C. H. & BRYANT, S. A. (1934). *J. Chem. Soc.* p. 1783.
- MATHIESON, A. & WELSH, H. K. (1952). *Acta Cryst.* **5**, 599.
- MAZZI, F. (1953). *R. C. Soc. Mineral. Ital.* **9**, 148.
- MAZZI, F. (1955). *Acta Cryst.* **8**, 137.
- SCOULOUDI, H. (1953). *Acta Cryst.* **6**, 651.
- Structure Reports* (1951). **15**, 405.
- SWINK, L. N. & ATOJI, M. (1960). *Acta Cryst.* **13**, 639.
- THOMAS, L. H. & UMEDA, K. (1957). *J. Chem. Phys.* **26**, 392.
- WATANABE, T. & ATOJI, M. (1951). *Science (Japan)*, **21**, 301.
- WATERS, T. N., HALL, D. & LLEWELLYN, F. J. (1958). *Chem. & Ind.* p. 1203.