Structural Investigations of Metal Nitrate Complexes. Part III.[1] Crystal and Molecular Structures of Two Crystalline Forms of Dinitratobis(α-picoline)copper(II)

By **A. F. Cameron** * and **D. W. Taylor**, Department of Chemistry, University of Glasgow, Glasgow W2
R. H. Nuttall, Department of Chemistry, University of Strathclyde, Glasgow C1

The structures of two crystalline forms of the title compound have been determined by single-crystal *X*-ray analyses. The crystals of both forms are monoclinic, space group $P2_1/c$, with $Z = 4$ in unit cells of dimensions $a = 8{\cdot}31$, $b = 14{\cdot}81$, $c = 14{\cdot}14$ Å, $\beta = 123{\cdot}9°$ [Form (I)] and $a = 8{\cdot}57$, $b = 14{\cdot}39$, $c = 14{\cdot}20$ Å, $\beta = 119{\cdot}5°$ [Form (II)]. Both structures were solved by conventional Patterson and Fourier methods from 1134 [Form (I)] and 1341 [Form (II)] observed data and refined by block-diagonal least-squares calculations to R 0·12 [Form (I)] and 0·09 [Form (II)]. Although both forms of the complexes possess grossly similar monomeric molecular structures, there are detailed differences in molecular geometry which may arise from the different packing within the two types of crystals.

SEVERAL complexes of the type $L_2M(NO_3)_2$ (L = amine, M = Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II}) have been predicted[2] to have structural features similar to those of $(Me_3PO)_2Co(NO_3)_2$.[3] However, recent *X*-ray analyses of $(py)_2Cu(NO_3)_2$[4] and $(py)_2Zn(NO_3)_2$[1] have revealed molecules whose structures are quite unrelated to this species, the copper complex in particular being a centrosymmetric dimer with asymmetric and non-equivalent nitrate groups. To investigate the structural effects of ligands bulkier than pyridine in copper–nitrate complexes, we have determined the crystal structures of two crystalline modifications of $(\alpha\text{-pic})_2Cu(NO_3)_2$[5,6] (α-pic = 2-methylpyridine). Initially we were aware of the existence of only one form of this compound, our attention being drawn to the second form[7] after completing the first X-ray analysis. The existence of the two crystalline modifications represents an almost unique type of polymorphism, since both forms utilise the same space-group symmetry with almost identical unit cells, yet have quite different crystal packing. We

---

[1] Part II, A. F. Cameron, R. H. Nuttall, and D. W. Taylor, *J. Chem. Soc.* (*A*), 1971, 3402.

[2] A. B. P. Lever, *Inorg. Chem.*, 1965, **4**, 1042.

[3] F. A. Cotton and R. H. Soderberg, *J. Amer. Chem. Soc.*, 1963, **85**, 2402.

[4] A. F. Cameron, K. P. Forrest, R. H. Nuttall, and D. W. Taylor, *Chem. Comm.*, 1970, 210; *J. Chem. Soc.* (*A*), 1971, 2492.

[5] A. F. Cameron, R. H. Nuttall, and D. W. Taylor, *Chem. Comm.*, 1970, 865.

[6] A. F. Cameron, R. H. Nuttall, and D. W. Taylor, *Chem. Comm.*, 1971, 253.

[7] B. J. Hathaway, personal communication.

therefore determined the structure of the second modification in order to evaluate the effects of crystal packing on the molecular geometries of such complexes.

EXPERIMENTAL

Preparation of Crystals.—The complex $(\alpha\text{-pic})_2Cu(NO_3)_2$ was prepared according to the method of Lever,[2] and recrystallised from methanol–2,2-dimethoxypropane (1 : 1) containing a little α-picoline. The isolation of two separate crystalline forms is dependent upon the temperature to which the crystallising liquid is heated before cooling: [7] if it is only warmed, crystals of Form (I) result, but, if it is boiled for several minutes, Form (II) crystals are obtained.

Crystal Data.—$C_6H_7CuN_3O_6$, $M = 373{\cdot}6$.

Form (I). Monoclinic, $a = 8{\cdot}31 \pm 0{\cdot}03$, $b = 14{\cdot}81 \pm 0{\cdot}03$, $c = 14{\cdot}14 \pm 0{\cdot}03$ Å, $\beta = 123{\cdot}9 \pm 0{\cdot}2°$, $U = 1444$ Å^3, $D_m = 1{\cdot}70$, $Z = 4$, $D_c = 1{\cdot}72$, $F(000) = 764$. Space group $P2_1/c$ (C^5_{2h}, No. 14). Cu-K_α X-rays, $\lambda = 1{\cdot}5418$ Å; μ(Cu-K_α) = 25·5 cm^{-1}.

Form (II). Monoclinic, $a = 8{\cdot}57 \pm 0{\cdot}03$, $b = 14{\cdot}39 \pm 0{\cdot}03$, $c = 14{\cdot}20 \pm 0{\cdot}03$ Å, $\beta = 119{\cdot}5 = 0{\cdot}2°$, $U = 1524$ Å^3, $D_m = 1{\cdot}63$, $Z = 4$, $D_c = 1{\cdot}63$, $F(000) = 764$. Space group $P2_1/c$ (C^5_{2h}, No. 14). μ(Cu-K_α) = 24·2 cm^{-1}.

Crystallographic Measurements.—The unit-cell parameters for both crystals were determined from oscillation and Weissenberg photographs taken with Cu-K_α radiation, and from precession photographs taken with Mo-K_α ($\lambda = 0{\cdot}7101$ Å) radiation. The systematic absences ($0k0$ absent when k is odd, $h0l$ when l is odd) uniquely determine the space group as $P2_1/c$ in both cases.

1134 independent reflexions from the reciprocal-lattice nets 0—$6kl$ for Form (I) and 1341 from the nets 0—$7kl$ for Form (II), were recorded on equatorial and equi-inclination Weissenberg photographs by the multiple-film technique and were estimated visually by comparison with a calibrated strip. After correction for Lorentz, polarisation, and rotation factors, the structure amplitudes were placed on an overall scale by comparison with values obtained from the $h0l$ reciprocal-lattice net recorded by precession methods. Unobserved reflexions were not included in the calculations and absorption corrections were not applied.

Structure Determinations.—Both structures were revealed by conventional Patterson and electron-density calculations with initial phasing appropriate to the respective copper atoms. Several cycles of structure-factor and electron-density calculations effected initial refinement which reduced the respective R values to 0·21 [Form (I)] and 0·20 [Form (II)]. During these preliminary calculations an overall isotropic vibration parameter, U_{iso} (0·06 Å) was assigned to the atoms.

Structure Refinements.—The least-squares refinement of positional, anisotropic thermal and scale parameters in each case converged after 10 cycles. For Form (I), the final R was 0·116 and R' $(= \Sigma w\Delta^2/\Sigma wF_o^2)$ was 0·023. For Form (II), the final R was 0·093 and R' was 0·016. Details of both refinements are given in Table 1. After the initial refinement, both sets of data were put on overall absolute scales and in the subsequent cycles these overall scale parameters were refined.

The refinement of anisotropic thermal parameters necessitated the use of the block-diagonal approximation to the normal-equation matrix because of computer-store limitations in both cases.

In all refinement cycles, a weighting scheme of the form:

$$\sqrt{w} = \left\{[1 - \exp(-p_1\{\sin(\theta/\lambda)\}^2]/[1 + p_2|F_o| + p_3|F_o|^2]\right\}^{1/2}$$

was applied to the data. Initially the parameters p were chosen to give unit weights to all reflexions, but they were varied in later cycles as indicated by an [F_0 and (sin θ/λ)] analysis of $\Sigma w\Delta^2$. For Form (I) the final values are: p_1 50, p_2 0·1, and p_3 0·0001; for Form (II): p_1 50, p_2 0·01, and p_3 0·0001.

TABLE 1

Course of refinements

Parameters refined	Form	Cycles	Final R	Final R'
x, y, z, U_{iso} for Cu, N, O, C; layer scale-factors, unit weights, full matrix	(I)	1—3	0·149	0·040
	(II)	1—3	0·135	0·031
x, y, z, U_{iso} for Cu, N, O, C; layer scale-factors, weighting scheme adjusted, full matrix	(I)	4—5	0·146	0·033
	(II)	4—6	0·130	0·026
x, y, z, U_{ij} $(i, j = 1, 2, 3)$ for Cu, N, O, C; overall scale, small adjustments to weighting scheme, block-diagonal approximation to normal equation matrix	(I)	6—10	0·116	0·021
	(II)	7—10	0·093	0·016

TABLE 2

Form (I): fractional co-ordinates (× 10^4)

	x/a	y/b	z/c
Cu(1)	2523·1(34)	6597·6(14)	2804·0(18)
C(1)	2258(21)	4774(10)	3445(12)
C(2)	2249(24)	3834(10)	3431(13)
C(3)	2363(30)	3413(11)	2626(14)
C(4)	2409(27)	3898(10)	1878(16)
C(5)	2473(26)	4817(12)	1964(13)
C(6)	2179(26)	5281(12)	4292(11)
C(7)	2794(27)	8369(12)	3762(15)
C(8)	2873(28)	9301(11)	3786(17)
C(9)	2858(25)	9764(11)	3006(17)
C(10)	2644(31)	9311(11)	2157(18)
C(11)	2515(30)	8385(12)	2120(15)
C(12)	2789(34)	7813(13)	4600(16)
O(1)	301(20)	6606(10)	856(10)
O(2)	−2693(21)	6522(12)	362(13)
O(3)	− 386(23)	6618(9)	2041(11)
O(4)	5343(18)	6528(8)	3947(9)
O(5)	7986(19)	6503(10)	3983(12)
O(6)	5183(21)	6636(8)	2487(11)
N(1)	2415(21)	5248(8)	2745(11)
N(2)	2625(20)	7924(8)	2936(11)
N(3)	− 930(21)	6582(10)	1035(11)
N(4)	6284(22)	6551(10)	3483(13)

At the conclusions of both refinements, difference syntheses and final electron-density distributions were evaluated and revealed no errors in the structures, although peaks identified from the difference syntheses were in positions stereochemically acceptable for hydrogen atoms. These were not included in the analysis.

In all the previous structure-factor calculations, the atomic scattering factors used are those given in ref. 8. Values of F_o and F_c are listed in Supplementary Publication No. SUP 20250 (4 pp., 1 microfiche *). The fractional co-ordinates of all non-hydrogen atoms are given in Table 2

---

* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. will be supplied as full page copies).

[8] 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

[Form (I)] and Table 4 [Form (II)] and the respective anisotropic thermal parameters are included in Tables 3 [Form (I)] and 5 [Form (II)]. These are the values of U_{ij} in the expression:

$$\exp\left[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{31}lhc^*a^* + 2U_{12}hka^*b^*)\right]$$

TABLE 3

Form (I): (*a*) anisotropic temperature factors (Å² × 10³)

	U_{11}	U_{22}	U_{33}	$2U_{32}$	$2U_{31}$	$2U_{12}$
Cu(1)	41	32	43	0	52	1
C(1)	13	29	35	−16	33	5
C(2)	23	24	37	5	22	−9
C(3)	62	33	47	−7	72	−17
C(4)	42	19	68	−20	79	−12
C(5)	34	44	39	−15	48	19
C(6)	49	57	16	−15	29	−21
C(7)	40	37	45	6	50	1
C(8)	40	28	68	−19	52	−5
C(9)	18	31	85	−2	77	−9
C(10)	65	33	68	6	85	−7
C(11)	60	46	34	7	65	−4
C(12)	75	47	50	13	84	26
O(1)	46	71	44	16	50	1
O(2)	30	94	71	19	33	2
O(3)	89	36	66	−8	97	5
O(4)	52	41	27	4	49	6
O(5)	32	61	73	20	56	21
O(6)	66	38	61	−7	91	−16
N(1)	40	19	38	−8	54	−10
N(2)	34	25	40	−6	58	4
N(3)	39	34	36	14	31	7
N(4)	30	54	49	4	56	−5

(*b*) Mean estimated standard deviations (Å² × 10³)

	U_{11}	U_{22}	U_{33}	$2U_{32}$	$2U_{31}$	$2U_{12}$
Cu	1	1	1	2	2	3
C	11	9	10	16	19	18
O	8	7	7	11	12	13
N	9	7	7	12	14	14

TABLE 4

Form (II): fractional co-ordinates (× 10⁴)

	x/*a*	*y*/*b*	*z*/*c*
Cu(1)	2659·8(22)	1759·5(10)	2319·6(14)
C(1)	6225(18)	2636(9)	3095(10)
C(2)	8017(19)	2660(10)	3557(12)
C(3)	9004(19)	1857(11)	3935(12)
C(4)	8118(20)	1035(10)	3827(14)
C(5)	6241(20)	1046(9)	3373(12)
C(6)	5110(21)	3495(8)	2672(14)
C(7)	−766(17)	2732(8)	1499(10)
C(8)	−2613(19)	2813(10)	968(11)
C(9)	−3711(19)	2031(11)	636(12)
C(10)	−2862(20)	1201(11)	801(13)
C(11)	−1072(20)	1129(9)	1310(13)
C(12)	421(21)	3547(9)	1861(14)
O(1)	2463(17)	478(7)	1059(10)
O(2)	2090(16)	1073(8)	−456(9)
O(3)	2415(12)	1955(6)	870(7)
O(4)	2959(13)	1678(6)	3809(9)
O(5)	2935(16)	603(9)	4845(10)
O(6)	2695(15)	256(7)	3271(9)
N(1)	5327(13)	1835(7)	2991(8)
N(2)	3(14)	1889(6)	1664(8)
N(3)	2344(15)	1142(7)	0460(9)
N(4)	2863(16)	807(8)	3995(9)

The atomic numbering schemes for Forms (I) and (II) are shown in Figures 1 and 2. Figures 3 and 4 show the packing arrangements for the two forms.

Table 6 lists bonded distances, valence angles, intramolecular, and intermolecular distances for both modifications. The estimated standard deviations recorded in Tables 2—6 were derived from the inverse of the least-squares normal-equation matrix, and are probably best regarded as minimum values. A number of planes were calculated for portions of the molecular frameworks and details of these are given in Tables 7 [Form (I)] and 8 [Form (II)].

TABLE 5

Form (II): (*a*) anisotropic temperature factors (Å² × 10³)

	U_{11}	U_{22}	U_{33}	$2U_{32}$	$2U_{31}$	$2U_{12}$
Cu(1)	37	25	47	2	49	−1
C(1)	41	32	35	5	42	−10
C(2)	39	62	59	−31	73	−44
C(3)	38	66	45	−15	52	−13
C(4)	33	47	76	1	61	24
C(5)	52	28	59	13	74	29
C(6)	53	17	86	18	47	−11
C(7)	40	23	44	−7	59	13
C(8)	48	42	42	−2	54	11
C(9)	32	71	46	1	40	2
C(10)	37	52	69	9	59	−13
C(11)	46	21	76	5	76	−4
C(12)	50	26	87	−9	79	14
O(1)	86	39	74	25	91	7
O(2)	79	65	48	−22	86	−34
O(3)	44	38	44	8	56	6
O(4)	44	40	41	10	40	7
O(5)	81	76	73	72	90	39
O(6)	66	40	69	24	81	−19
N(1)	32	26	38	6	47	−2
N(2)	30	28	37	8	43	8
N(3)	43	38	42		56	3
N(4)	39	52	47	50	55	7

(*b*) Mean estimated standard deviations (Å² × 10³)

	U_{11}	U_{22}	U_{33}	$2U_{32}$	$2U_{31}$	$2U_{12}$
Cu	1	1	1	2	1	2
C	8	8	9	12	14	12
O	8	6	7	10	12	10
N	7	6	6	10	10	9

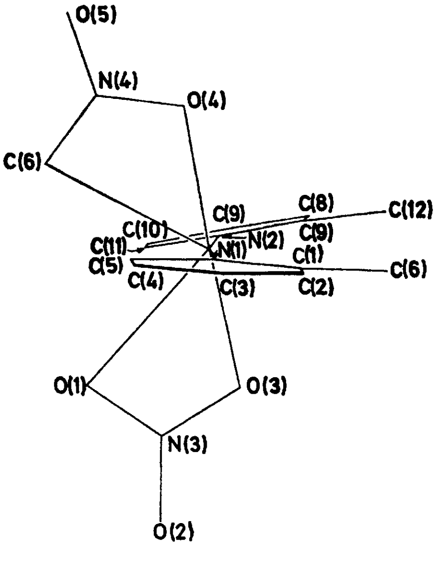

FIGURE 1 A view of Form (I) along *b* showing the atomic numbering

DISCUSSION

The two *X*-ray analyses reveal that both crystalline forms of (α-pic)$_2$Cu(NO$_3$)$_2$ contain very similar, but not identical, molecular configurations which are based on a

TABLE 6

Interatomic distances (Å) and angles (°) for both forms with estimated standard deviations in parentheses

(*a*) Interatomic distances

	Form (I)	Form (II)
Cu–O(1)	2·307(13)	2·517(8)
Cu–O(3)	2·026(16)	1·983(10)
Cu–O(4)	1·971(13)	2·005(10)
Cu–O(6)	2·489(14)	2·551(7)
Cu–N(1)	2·000(12)	2·000(10)
Cu–N(2)	1·970(12)	1·999(10)
C(1)–N(1)	1·28(2)	1·35(2)
C(1)–C(2)	1·39(2)	1·34(2)
C(1)–C(6)	1·44(2)	1·49(2)
C(2)–C(3)	1·35(2)	1·38(2)
C(3)–C(4)	1·30(2)	1·37(2)
C(4)–C(5)	1·36(2)	1·41(2)
C(5)–N(1)	1·30(2)	1·33(2)
C(7)–N(2)	1·28(2)	1·35(2)
C(7)–C(8)	1·38(2)	1·38(2)
C(7)–C(12)	1·44(2)	1·47(2)
C(8)–C(9)	1·30(3)	1·39(2)
C(9)–C(10)	1·30(3)	1·36(2)
C(10)–C(11)	1·37(2)	1·34(2)
C(11)–N(2)	1·32(2)	1·36(2)
N(3)–O(1)	1·23(2)	1·25(2)
N(3)–O(2)	1·20(2)	1·21(2)
N(3)–O(3)	1·23(2)	1·29(2)
N(4)–O(4)	1·27(2)	1·29(2)
N(4)–O(5)	1·20(2)	1·21(2)
N(4)–O(6)	1·20(2)	1·24(2)

(*b*) Interbond angles

	Form (I)	Form (II)
O(1)–Cu–O(3)	56·0(5)	55·3(4)
O(1)–Cu–O(4)	140·6(5)	129·5(4)
O(1)–Cu–O(6)	89·1(5)	74·8(4)
O(1)–Cu–N(1)	88·2(5)	92·3(4)
O(1)–Cu–N(2)	94·1(5)	94·3(4)
O(3)–Cu–O(4)	163·2(5)	175·1(4)
O(3)–Cu–O(6)	145·1(5)	130·0(4)
O(3)–Cu–N(1)	88·9(6)	90·0(5)
O(3)–Cu–N(2)	90·6(6)	89·4(5)
O(4)–Cu–O(6)	51·7(4)	54·9(4)
O(4)–Cu–N(1)	89·3(5)	88·7(5)
O(4)–Cu–N(2)	90·3(5)	91·2(5)
O(6)–Cu–N(1)	92·2(5)	95·3(4)
O(6)–Cu–N(2)	89·9(5)	91·6(4)
N(1)–Cu–N(2)	176·9(5)	171·5(4)
C(2)–C(1)–C(6)	121·9(14)	121·8(13)
C(2)–C(1)–N(1)	122·7(14)	121·9(12)
C(6)–C(1)–N(1)	115·4(14)	116·3(12)
C(1)–C(2)–C(3)	118·1(15)	120·4(14)
C(2)–C(3)–C(4)	118·8(16)	118·7(14)
C(3)–C(4)–C(5)	119·9(16)	119·0(13)
C(4)–C(5)–N(1)	123·2(15)	120·4(12)
Cu–N(1)–C(1)	122·5(10)	123·6(8)
Cu–N(1)–C(5)	120·4(11)	116·9(9)
C(1)–N(1)–C(5)	117·2(13)	119·5(11)
C(8)–C(7)–C(12)	125·0(17)	122·2(12)
C(8)–C(7)–N(2)	121·1(17)	120·1(11)
C(12)–C(7)–N(2)	113·9(16)	117·6(11)
C(7)–C(8)–C(9)	122·3(19)	121·3(13)
C(8)–C(9)–C(10)	116·2(17)	116·0(13)
C(9)–C(10)–C(11)	122·4(18)	122·3(14)
C(10)–C(11)–N(2)	120·2(16)	121·8(12)
Cu–N(2)–C(7)	125·3(11)	120·8(8)
Cu–N(2)–C(11)	116·9(11)	120·5(9)
C(7)–N(2)–C(11)	117·8(15)	118·5(11)
Cu–O(1)–N(3)	87·5(10)	83·0(8)
Cu–O(3)–N(3)	100·1(11)	107·2(8)
Cu–O(4)–N(4)	111·7(10)	106·5(9)
Cu–O(6)–N(4)	87·6(10)	81·9(8)
O(1)–N(3)–O(2)	129·6(16)	125·3(12)
O(1)–N(3)–O(3)	116·1(15)	114·5(13)
O(2)–N(3)–O(3)	116·3(16)	120·1(12)
O(4)–N(4)–O(5)	124·7(15)	117·4(13)
O(4)–N(4)–O(6)	109·0(14)	116·7(14)
O(5)–N(4)–O(6)	129·3(16)	125·9(13)

TABLE 6 (*Continued*)

(*c*) Intramolecular non-bonded distances

	Form (I)	Form (II)		Form (I)	Form (II)
Cu ··· C(1)	2·90	2·97	O(3) ··· C(6)	3·32	3·31
Cu ··· C(5)	2·88	2·86	O(3) ··· N(1)	2·82	2·82
Cu ··· C(6)	3·00	3·14	O(3) ··· N(2)	2·84	2·80
Cu ··· C(7)	2·90	2·93	O(4) ··· C(5)	3·54	3·29
Cu ··· C(11)	2·82	2·93	O(4) ··· O(5)	2·17	2·14
Cu ··· C(12)	3·02	3·08	O(4) ··· O(6)	2·00	2·15
Cu ··· N(3)	2·55	2·67	O(4) ··· N(1)	2·79	2·80
Cu ··· N(4)	2·71	2·68	O(4) ··· N(2)	2·79	2·86
O(1) ··· C(5)	3·10	3·39	O(5) ··· O(6)	2·11	2·19
O(1) ··· C(11)	3·13	3·35	O(6) ··· C(5)	3·32	3·21
O(1) ··· O(2)	2·18	2·19	O(6) ··· C(11)	3·25	3·28
O(1) ··· O(3)	2·05	2·14	O(6) ··· N(1)	3·25	3·38
O(1) ··· O(6)	3·37	3·08	O(6) ··· N(2)	3·17	3·29
O(1) ··· N(1)	3·00	3·28	N(1) ··· N(3)	3·16	3·39
O(1) ··· N(2)	3·14	3·33	N(1) ··· N(4)	3·38	3·41
O(2) ··· O(3)	2·06	2·17	N(2) ··· N(3)	3·32	3·38
O(3) ··· C(1)	3·37	3·45	N(2) ··· N(4)	3·37	3·38

(*d*) Intermolecular distances in Form (I)

O(1) ··· C(4^{I})	3·30	O(3) ··· C(3^{VI})	3·29
O(1) ··· C(12^{II})	3·50	O(3) ··· C(9^{V})	3·41
O(1) ··· O(5^{III})	3·59	O(4) ··· C(2^{VII})	3·12
O(2) ··· C(4^{II})	3·37	O(4) ··· C(6^{VII})	3·45
O(2) ··· C(7^{IV})	3·12	O(5) ··· C(3^{VIII})	3·54
O(2) ··· C(8^{IV})	3·30	O(5) ··· C(9^{IX})	3·57
O(2) ··· C(8^{V})	3·54	O(5) ··· C(10^{IX})	3·53
O(2) ··· C(9^{V})	3·53	O(6) ··· C(3^{IX})	3·59
O(2) ··· C(12^{IV})	3·42	O(6) ··· C(9^{IX})	3·47
O(2) ··· O(4^{IV})	3·37	O(6) ··· C(12^{II})	3·50
O(2) ··· N(2^{V})	3·56	N(3) ··· C(4^{I})	3·65
O(3) ··· C(2^{VI})	3·53	N(4) ··· C(3^{IX})	3·65

Roman numerals as superscripts refer to the following equivalent positions relative to the reference molecule at x, y, z:

I $-x, 1-y, -z$
II $x, \frac{3}{2}-y, -\frac{1}{2}+z$
III $-x, \frac{3}{2}-y, -\frac{1}{2}+z$
IV $-1+x, \frac{3}{2}-y, -\frac{1}{2}+z$
V $-x, -\frac{1}{2}+y, \frac{1}{2}-z$
VI $-x, \frac{1}{2}+y, \frac{1}{2}-z$
VII $1-x, 1-y, 1-z$
VIII $1-x, \frac{1}{2}+y, \frac{1}{2}-z$
IX $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$

(*e*) Intermolecular distances in Form (II)

O(1) ··· C(6^{I})	3·47	O(4) ··· C(8^{VII})	3·59
O(2) ··· C(2^{II})	3·56	O(4) ··· C(9^{VII})	3·32
O(2) ··· C(9^{III})	3·43	O(4) ··· C(12^{VIII})	3·59
O(2) ··· C(10^{IV})	3·42	O(5) ··· C(3^{VI})	3·46
O(2) ··· C(11^{IV})	3·35	O(5) ··· C(4^{IX})	3·41
O(2) ··· C(12^{V})	3·39	O(5) ··· C(5^{IX})	3·28
O(2) ··· O(4^{V})	3·59	O(5) ··· O(6^{IX})	3·61
O(3) ··· C(2^{II})	3·62	O(6) ··· C(12^{X})	3·54
O(3) ··· C(3^{II})	3·33	O(6) ··· O(5^{IX})	3·61
O(3) ··· C(9^{V})	3·50	N(3) ··· C(9^{V})	3·51
O(4) ··· C(3^{VI})	3·49	N(4) ··· C(3^{VI})	3·60

Roman numerals as superscripts refer to the following equivalent positions relative to the reference molecule at x, y, z:

I $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$
II $-1+x, \frac{1}{2}-y, -\frac{1}{2}+z$
III $1+x, y, z$
IV $-x, -y, -z$
V $x, \frac{1}{2}-y, -\frac{1}{2}+z$
VI $-1+x, y, z$
VII $1+x, \frac{1}{2}-y, \frac{1}{2}+z$
VIII $x, \frac{1}{2}-y, \frac{1}{2}+z$
IX $1-x, -y, 1-z$
X $x, \frac{1}{2}-y, -\frac{1}{2}+z$

monomeric, six-co-ordinate structure in which the nitrate groups are asymmetrically bidentate with respect to the copper atom (Figures 1 and 2). One distinction between the two molecules is found in the respective non-equivalence and equivalence of the nitrate groups in Forms (I) and (II). The non-equivalence of the nitrate groups in Form (I) [Cu–O(1) 2·307(13), Cu–O(3) 2·026(16), Cu–O(4) 1·971(13), and Cu–O(6) 2·557(7) Å) parallels the situation which exists in the dimeric molecule of $[(py)_2Cu(NO_3)_2,0{\cdot}5(py)]_2$.[4] This similarity is

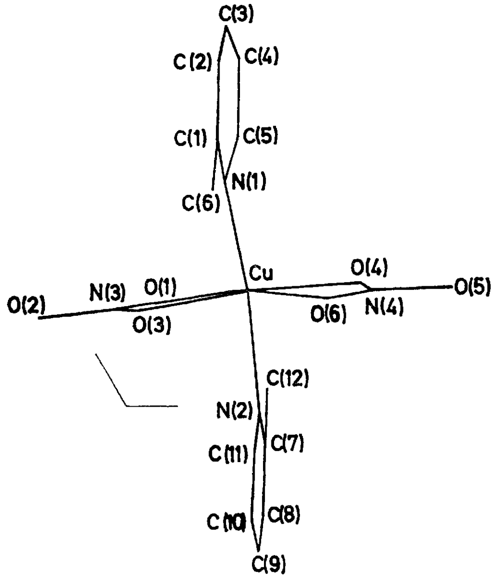

FIGURE 2 A view of Form (II) along *b* showing the atomic numbering

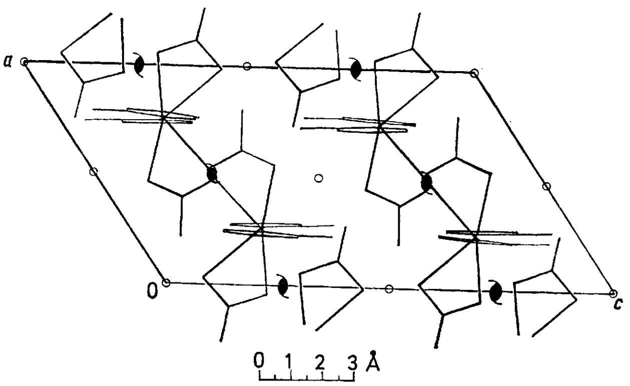

FIGURE 3 The molecular packing of Form (I) viewed along the *b* axis

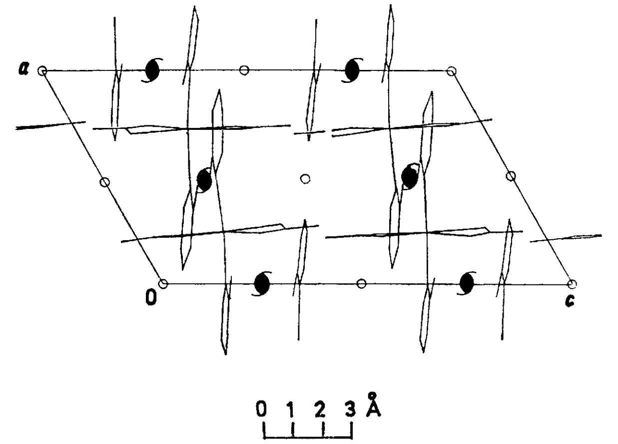

FIGURE 4 The molecular packing of Form (II) viewed along the *b* axis

TABLE 7

Equations of least-squares planes for Form (I), where X', Y', and Z' are co-ordinates in Å, and in square brackets distances (Å) of atoms from the planes

Plane (1):

O(1)—(3), N(3) $-0{\cdot}0684X' + 0{\cdot}9973Y' - 0{\cdot}0257Z' = 9{\cdot}7154$

[O(1) −0·001, O(2) −0·001, O(3) −0·001, N(3) 0·002, Cu −0·061]

Plane (2):

O(4)—(6), N(4) $-0{\cdot}0705X - 0{\cdot}9947Y' - 0{\cdot}0747Z' = -10{\cdot}1100$

[O(4) −0·001, O(5) −0·001, O(6) −0·001, N(4) 0·003, Cu 0·059]

Plane (3):

O(1)—(6), N(3), N(4) $-0{\cdot}0072X' - 0{\cdot}9997Y' - 0{\cdot}0242Z' = -9{\cdot}7858$

[O(1) −0·021, O(2) 0·101, O(3) −0·085, O(4) 0·017, O(5) 0·073, O(6) −0·091, N(3) −0·001, N(4) 0·007, Cu −0·062]

Plane (4):

C(1)—(6), N(1) $-0{\cdot}9981X' + 0{\cdot}0160Y' - 0{\cdot}0593Z' = -1{\cdot}6813$

[C(1) 0·015, C(2) −0·004, C(3) −0·019, C(4) 0·026, C(5) −0·003 C(6) 0·006, N(1) −0·021, Cu −0·065]

Plane (5):

C(7)—(12), N(2) $0{\cdot}9956X' - 0{\cdot}0608Y' - 0{\cdot}0712Z' = 0{\cdot}8586$

[C(7) 0·017, C(8) −0·011, C(9) 0·016, C(10) −0·011, C(11) −0·016, C(12) −0·016, N(2) 0·022, Cu 0·081]

Plane (6):

O(3), O(4), N(1), N(2) $0{\cdot}0104X' + 0{\cdot}0431Y' - 0{\cdot}9990Z' = -2{\cdot}5255$

[O(3) −0·117, O(4) −0·120, N(1) 0·119, N(2) 0·118, Cu 0·172, C(6) −2·174, C(12) −2·162, O(1) 1·879, O(6) 1·872]

Dihedral angles (°) between planes

(1)–(2)	10	(2)–(4)	87
(1)–(4)	85	(2)–(5)	90
(1)–(5)	83	(4)–(5)	8

striking when the crystal packing of Form (I) is considered (Figure 3). It is apparent that centrosymmetrically related molecules of this Form are aligned throughout the crystal such that a relatively small reduction in intermolecular separation could produce dimerisation similar to that found in $[(py)_2Cu(NO_3)_2,0{\cdot}5(py)]_2$, were it not for the blocking action of the *cis*-α-methyl groups. In Form (II) the significant spatial relationship to the bis(pyridine) complex does not pertain, and the nitrate groups are not only equivalent [Cu–O(1) 2·517(8), Cu–O(3) 1·983(10), Cu–O(4) 2·005(10), and Cu–O(6) 2·551(7) Å), but show asymmetry of the same order as that found in $Cu(NO_3)_2,2{\cdot}5H_2O$ [9] and in $Cu(NO_3)_2(C_2H_4N_2)$.[10]

It was previously expected [2,11,12] that the structures of complexes of the type $L_2M(NO_3)_2$ (L = amine, M = Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II}) would bear a close resemblance to that of $(Me_3PO)_2Co(NO_3)_2$ [3] which has symmetrically bidentate nitrate groups in a quasitetrahedral arrangement. However, as yet there are no reported copper(II)-nitrate complexes whose structures conform to this. Comparison of the molecular structures of the two forms of $(\alpha\text{-pic})_2Cu(NO_3)_2$ with those of

---

[9] B. Morosin, *Acta Cryst.*, 1970, *B*, **26**, 1203.

[10] A. Santoro, A. D. Mighell, and C. W. Reimann, *Acta Cryst.*, 1970, *B*, **26**, 979.

[11] R. H. Nuttall and D. W. Taylor, *Chem. Comm.*, 1968, 1417.

[12] A. F. Cameron, R. H. Nuttall, and D. W. Taylor, *J. Chem. Soc.* (*A*), 1971, 3103.

$[(py)_2Cu(NO_3)_2,0{\cdot}5(py)]_2$ [4] and $Cu(NO_3)_2,2{\cdot}5H_2O$,[9] reveals that all four complexes are based on a short-bonded, square-planar arrangement, with two long-bonded oxygens of the nitrate groups lying below this plane in a *cis*-fashion. This is in contrast to $Cu(NO_3)_2(C_4H_4N_2)$ in which the long-bonded oxygens of the nitrate groups are *trans*.[10] Above the square-plane in both the pyridine and hydrate complexes, there are longer Cu–O bonds which bridge the two monomeric units to effect polymerisation. However, in both forms of $(\alpha\text{-pic})_2Cu(NO_3)_2$, this position is blocked by the presence of the *cis*-α-methyl groups. The *cis*-relationship of the α-methyl groups is also found in $(\alpha\text{-pic})_2CuCl_2$,[13] although in this case the smaller steric requirements of chlorine atoms in comparison with nitrate groups, allow a dimerising bond on the opposite side of the square-plane from the methyl groups.

TABLE 8

Equations of least-squares planes for Form (II) where X', Y', and Z' are co-ordinates in Å, and in square brackets distances of atoms from the planes

Plane (1):	O(1)—(3), N(3)	$0{\cdot}9905X' + 0{\cdot}0007Y' - 0{\cdot}1377Z' = 1{\cdot}7617$
		[O(1) −0·006, O(2) −0·005, O(3) −0·005, N(3) 0·017, Cu −0·094]
Plane (2):	O(4)—(6), N(4)	$0{\cdot}9935X' - 0{\cdot}0846Y' - 0{\cdot}0768Z' = 1{\cdot}6718$
		[O(4) −0·003, O(5) −0·003, O(6) −0·003, N(4) 0·009, Cu −0·082]
Plane (3):	O(1)—(6), N(3), N(4), Cu	$0{\cdot}9951X' - 0{\cdot}0439Y' - 0{\cdot}0887Z' = 1{\cdot}6758$
		[O(1) 0·081, O(2) −0·057, O(3) −0·026, O(4) 0·045, O(5) −0·036, O(6) −0·031, N(3) 0·021, N(4) 0·002, Cu −0·006]
Plane (4):	C(1)—(6), N(1)	$-0{\cdot}0785X' - 0{\cdot}1572Y' - 0{\cdot}9844Z' = -2{\cdot}7043$
		[C(1) 0·003, C(2) −0·009, C(3) −0·003, C(4) 0·018, C(5) −0·020, C(6) 0·002, N(1) 0·009, Cu 0·013]
Plane (5):	C(7)—(12), N(2)	$-0{\cdot}0317X' + 0{\cdot}0561Y' - 0{\cdot}9979Z' = -2{\cdot}1937$
		[C(7) −0·014, C(8) 0·011, C(9) −0·018, C(10) 0·018, C(11) 0·002, C(12) 0·011, N(2) −0·010, Cu 0·106]
Plane (6):	O(3), O(4), N(1), N(2)	$-0{\cdot}0284X' - 0{\cdot}9948Y' - 0{\cdot}0978Z' = -2{\cdot}9029$
		[O(3) 0·032, O(4) 0·032, N(1) −0·032, N(2) −0·032, Cu 0·115, C(6) −2·368, C(12) −2·425, O(1) 2·121, O(6) 2·136]

Dihedral angles (°) between planes

(1)–(2)	6	(2)–(4)	89
(1)–(4)	87	(2)–(5)	88
(1)–(5)	84	(4)–(5)	13

The nitrate groups in both forms of the complex show polarisation effects as a result of copper–oxygen co-ordination. This is most clearly evident in the dimensions of Form (II), where the terminal N–O bonds [N(3)–O(2) 1·21(2) and N(4)–O(6) 1·21(2) Å] are just significantly shorter than the N–O bonds associated with the strongest Cu–O interactions [N(3)–O(3) 1·29(2) and N(4)–O(4) 1·29(2) Å]. Moreover, the O–N–O valency angles differ from the ideal value of 120° in the expected manner, with the largest angle opposite the shortest copper–oxygen bond. The Cu–O–N angles are also decreased from the value of 110° [14] obtained for normal unidentate co-ordination, and this reflects the strength of the longer copper–oxygen bonds. All the nitrate groups in both molecules are virtually planar (Tables 7 and 8).

Although the packing arrangements of the two crystalline forms are quite different, there is one feature common to both. In Form (I), the nitrate groups are all approximately aligned in the *ac* plane, and the α-picoline groups are approximately in the *bc* plane, whereas in Form (II), the approximate alignment of the nitrate groups corresponds to the *bc*- and the α-picolines approximately in the *ab*-planes. This may be alternatively stated by considering the local equatorial x and y, and axial z directions, which correspond to the a, b, and c directions respectively in Form (I), but to the a, c, and b directions in Form (II). One possible reason why the molecule may pack in two different ways in almost identical unit cells, is that, in addition to being compact, it has virtually identical dimensions in the two directions of the equatorial plane defined by the extent of the α-picoline and nitrate moieties from the central copper atom. It is therefore relatively easy to envisage the nitrate and α-picoline groups adopting alternative positions, especially when the overall alignment of delocalised planes throughout the crystal is maintained by such a change. In addition, it may be noted that the b and c edges of the two unit cells are all very similar, and it is these lengths which define the localised z-axes in the two crystalline forms.

Although it is difficult to estimate exactly the relative efficiencies of the crystal packing in the two modifications, both forms have exactly the same number of intermolecular contacts <3·5 Å. There are differences, however, between the structures of the two molecules, in particular the non-equivalence of the nitrate groups in Form (I), which may be related to detailed differences in molecular packing. In Form (I), O(2) closely approaches both O(4) and C(7) [O(2) · · · O(4) 3·37 and O(2) · · · C(7) 3·12 Å], and O(4) is close to C(2) [O(4) · · · C(2)]. In Form (II), however, there are no O · · · O contacts <3·59 Å, and no O · · · C contacts <3·32 Å. Since it is in the detailed nitrate co-ordination that the molecules most markedly differ, it is reasonable to assume that the crystal-packing in Form (I) has influenced the molecular geometry to a significant extent.

The computations were performed on the Glasgow University KDF9 computer using programs developed by the Glasgow group. We thank Professor B. J. Hathaway for crystals of Form (II).

[1/1246 *Received, July* 21*st*, 1971]

---

[13] V. F. Duckworth and N. C. Stephenson, *Acta Cryst.*, 1969, *B*, **25**, 1795.

[14] C. D. Garner, J. Hilton, and S. C. Wallwork, paper delivered to 8th Internat. Congress Crystallography, 1969.