Structural Characterization of Metal Complexes of 2,6-Diacetylpyridinebis(imines). Crystal and Molecular Structure of Dinitrato{2,6-bis[1-(phenylimino)ethyl]pyridine}copper(II)

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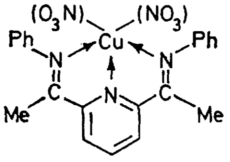
Crystals of the title compound are monoclinic, space group $P2_1/c$ with a = 11.1956(12), b = 14.3477(12), c = 16.2180(15) Å, β = 123.36(1)°, and Z = 4. All atoms were located from a single-crystal *X*-ray analysis based on counter data. The structure was refined to a final R of 0.037 for 2 485 observed reflexions. The complex contains a planar terdentate *NNN*-donor-set [Cu–N(central) 1.913(3), mean Cu–N(term) 2.041(6) Å], and both unidentate [Cu–O 2.213(4) Å] and asymmetric bidentate [Cu–O 1.968(3), 2.533(5) Å] nitrato-groups. The copper atom co-ordination is distorted from regular octahedral by a manifestation of the static Jahn–Teller effect and by the bite of the terdentate ligand.

TERDENTATE *NNN*-donor-ligands are readily obtained from 2,6-diacetylpyridine and substituted anilines by Schiff-base condensation.[1] We have recently reported the synthesis of certain divalent metal nitrate complexes {[LM(NO$_3$)$_2$], M = N$^{\text{II}}$, Cu$^{\text{II}}$, or Zn$^{\text{II}}$; L = $C_{21}H_{19}N_3$} which contain the 2,6-diacetylpyridinebis(anil) derivative as a terdentate *NNN*-donor-ligand (L).[2] One of these, [LNi(NO$_3$)$_2$], has been shown to contain both uni- and near-symmetrically bi-dentate nitrato-groups and the nickel atom is clearly six-co-ordinate.[2] The series of closely related complexes [(py)$_3$M(NO$_3$)$_2$] (M = Co$^{\text{II}}$, Cu$^{\text{II}}$, or Zn$^{\text{II}}$) [3] have bidentate nitrato-groups with distinct but differing degrees of asymmetry in the nitrato-metal bonding. Manifestation of the static Jahn–Teller effect in [LCu(NO$_3$)$_2$] and comparison with the analogous trispyridine series leads to a prediction of marked asymmetry in the bidentate nitrato-bonding of this compound, which we confirm *via* this single-crystal *X*-ray analysis of [LCu(NO$_3$)$_2$], (I).



(I)

EXPERIMENTAL

The complex was prepared as reported in ref. 2. Dark green prismatic crystals suitable for *X*-ray analysis were obtained by slow evaporation from ethanol–nitromethane. Preliminary cell data were obtained from precession and Weissenberg photographs; accurate unit-cell data were obtained from a least-squares refinement of diffractometer setting angles of 12 reflexions.

Crystal Data.—$C_{21}H_{19}CuN_5O_6$, M = 501.0, Monoclinic, a = 11.1956(12), b = 14.3477(12), c = 16.2180(15) Å, β = 123.36(1)°, U = 2 175.9 Å^3, D_c = 1.53, Z = 4. $F(000)$ = 1 028. Space group $P2_1/c$ (C^5_{2h}, No. 14) from systematic absences. Mo-K_α *X*-rays, λ = 0.710 69 Å; μ(Mo-K_α) = 11.0 cm^{-1}.

Crystallographic Measurements.—Data were collected from a crystal of dimensions 0.28 × 0.25 × 0.27 mm with a Hilger and Watts Y 290 computer-controlled diffractometer by use of graphite monochromatized Mo-K_α radiation. A θ—2θ scanning technique was used to collect a unique data set to a maximum θ of 25°; a rate of 60 steps of 0.01° with a 1 s count at each step was used. Background measurements of 15 s were made at the beginning and end of each scan with the counter stationary. The intensity of two standard reflexions, measured at 100 reflexion intervals, was reduced slightly (*ca.* 1%) during data collection and this was corrected for by application of linear scale factors. A total of 4 016 intensity maxima were collected and corrected for Lorentz and polarization effects; absorption corrections were not considered necessary for a crystal of the size used, transmission coefficients being of the order 74—76%. Of the 4 016 measured reflexions, 2 485 with $I > 3\sigma(I)$ were used throughout the solution and refinement of the structure. All calculations were carried out on an IBM 370/155 computer using our local modification of the '*X*-ray '72' system.[4]

Structural Solution and Refinement.—An estimate of the overall scale factor was obtained using Wilson's method. The fractional co-ordinates of the isomorphous nickel complex, [LNi(NO$_3$)$_2$],[2] and isotropic U values of 0.05 Å^2 were used as a starting set of atomic parameters which were refined by full-matrix least-squares with the atomic scattering functions of ref. 5 for neutral copper, carbon, nitrogen, and oxygen. Two cycles of refinement reduced R to 0.157 for the 1 591 observed reflexions with $\theta < 20°$.

Two further cycles of refinement by block-diagonal least-squares calculations with anisotropic thermal parameters for the atoms, reduced R to 0.052 for the 2 485 observed reflexions. A (final) difference Fourier synthesis revealed electron-density maxima in chemically reasonable positions for all hydrogen atoms and no other chemically significant features; the hydrogen atoms were then allowed for (in chemically expected positions with isotropic U values of 0.063 Å^2 and scattering factors from ref. 6), but not refined in subsequent calculations. A weighting scheme was then chosen such that $\sqrt{w} = 1/[\sigma^2(F) + pF^2]^{1/2}$ with $p = 2 \times 10^{-3}$, and an analysis of variance indicated that $\Sigma w\Delta^2$ was independent of $|F_o|$ and $\sin\theta/\lambda$. The real and imaginary parts of the anomalous dispersion correction [7] for the copper atom were incorporated and two additional

[1] E. C. Alyea and P. H. Merrell, *Synthetic Reactions Inorg. Metalorg. Chem.*, 1974, **4**, 535; E. C. Alyea and P. H. Merrell, 168th Nat. Meeting Amer. Chem. Soc., Atlantic City, N.J., September, 1974, Abstracts, No. INORG. 103.

[2] E. C. Alyea, G. Ferguson, R. J. Restivo, and P. H. Merrell, *J.C.S. Chem. Comm.*, 1975, 269; R. J. Restivo, G. Ferguson, and E. C. Alyea, 25th Anniversary Meeting Amer. Cryst. Assocn., Charlottesville, Va., March 1975, Abstracts, No. J12; E. C. Alyea, G. Ferguson, and R. J. Restivo, *Inorg. Chem.*, 1975, **14**, 2491.

[3] A. F. Cameron, D. W. Taylor, and H. R. Nuttall, *J.C.S. Dalton*, 1972, 1603.

[4] A locally modified version of DATCO5 from '*X*-Ray '72' system was used for data handling, '*X*-Ray '72,' ed. J. M. Stewart, Technical Report TR 192, 1972, University of Maryland Computer Science Center, College Park, Maryland.

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refinement cycles converged to R 0.037 and $R'\{= [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|)^2]^{1/2}\}$ 0.056 for 2 485 observed reflexions; the overall R for the entire set of 4 017 reflexions is 0.055. The standard deviation of an observation of unit weight is 1.45.

TABLE 1

Final fractional co-ordinates (Cu × 10^5, others × 10^4) for non-hydrogen atoms, with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Cu	37 691(5)	17 351(3)	5 195(3)
O(41)	5 470(4)	1 451(3)	−24(3)
O(42)	5 503(3)	2 476(2)	970(2)
O(43)	7 097(4)	2 522(3)	609(3)
O(51)	3 270(3)	2 532(2)	1 463(2)
O(52)	1 800(5)	3 028(3)	1 804(4)
O(53)	1 034(4)	2 217(3)	521(3)
N(1)	2 289(3)	826(2)	−166(2)
N(2)	4 647(3)	631(2)	1 470(2)
N(3)	2 393(3)	2 452(2)	−740(2)
N(4)	6 048(4)	2 151(3)	510(3)
N(5)	2 016(4)	2 588(2)	1 258(3)
C(2)	2 443(4)	−8(3)	242(3)
C(3)	1 377(5)	−668(3)	−230(4)
C(4)	161(5)	−433(4)	−1 127(4)
C(5)	25(5)	430(4)	−1 544(3)
C(6)	1 125(4)	1 064(3)	−1 037(3)
C(7)	3 846(4)	−96(3)	1 217(3)
C(8)	4 157(6)	−970(3)	1 799(4)
C(9)	1 205(4)	2 037(3)	−1 330(3)
C(10)	−49(5)	2 434(4)	−2 258(3)
C(21)	6 050(4)	684(3)	2 347(3)
C(22)	6 326(5)	1 398(3)	3 004(3)
C(23)	7 692(5)	1 495(3)	3 853(3)
C(24)	8 752(5)	899(4)	4 019(4)
C(25)	8 493(5)	203(4)	3 362(4)
C(26)	7 131(5)	97(3)	2 511(4)
C(31)	2 672(4)	3 390(3)	−907(3)
C(32)	3 286(6)	3 526(3)	−1 432(4)
C(33)	3 634(5)	4 423(4)	−1 545(4)
C(34)	3 388(5)	5 173(3)	−1 137(3)
C(35)	2 787(6)	5 023(3)	−603(4)
C(36)	2 450(5)	4 134(3)	−470(3)

TABLE 2

Fractional co-ordinates (× 10^3) for the hydrogen atoms

Atom	*x*	*y*	*z*
H(3)	149	−134	11
H(4)	−69	−93	−151
H(5)	−92	62	−224
H(22)	550	188	286
H(23)	789	203	436
H(24)	981	99	467
H(25)	933	−27	350
H(26)	691	−43	198
H(32)	352	294	−173
H(33)	408	454	−197
H(34)	366	586	−123
H(35)	258	560	−29
H(36)	204	401	−3
H(81)	336	−105	194
H(82)	411	−153	136
H(83)	514	−104	249
H(101)	−27	200	−285
H(102)	−94	242	−219
H(103)	−1	313	−248

Final positional parameters for non-hydrogen atoms are listed in Table 1, calculated hydrogen atom positions in Table 2, and interatomic distances and angles in Table 3. Details of mean planes through various portions of the molecule, anisotropic thermal parameters, and observed and calculated structure factors are listed in Supplementary Publication No. SUP 21557 (36 pp., 1 microfiche).*

TABLE 3

Interatomic distances (Å) and angles (°)

(*a*) Distances

Cu–O(41)	2.533(5)	C(2)–C(7)	1.500(5)
Cu–O(42)	1.968(3)	C(6)–C(9)	1.493(7)
Cu–O(51)	2.213(4)	C(7)–C(8)	1.491(6)
		C(9)–C(10)	1.500(5)
Cu–N(1)	1.913(3)		
Cu–N(2)	2.046(3)	C(2)–C(3)	1.380(6)
Cu–N(3)	2.035(3)	C(3)–C(4)	1.380(6)
		C(4)–C(5)	1.378(8)
N(4)–O(41)	1.250(5)	C(5)–C(6)	1.381(6)
N(4)–O(42)	1.283(6)		
N(5)–O(51)	1.255(6)	C(21)–C(22)	1.385(6)
		C(22)–C(23)	1.392(5)
N(4)–O(43)	1.217(6)	C(23)–C(24)	1.364(8)
N(5)–O(52)	1.216(9)	C(24)–C(25)	1.370(9)
N(5)–O(53)	1.214(5)	C(25)–C(26)	1.392(6)
		C(21)–C(26)	1.375(7)
N(1)–C(2)	1.331(5)		
N(1)–C(6)	1.337(4)	C(31)–C(32)	1.370(9)
		C(32)–C(33)	1.386(8)
N(2)–C(7)	1.286(5)	C(33)–C(34)	1.369(8)
N(3)–C(9)	1.281(5)	C(34)–C(35)	1.376(10)
		C(35)–C(36)	1.380(7)
N(2)–C(21)	1.428(4)	C(31)–C(36)	1.377(7)
N(3)–C(31)	1.441(6)		

(*b*) Angles

N(1)–Cu–N(2)	79.2(1)	N(3)–Cu–O(42)	98.5(1)
N(1)–Cu–N(3)	80.0(1)	N(1)–Cu–O(51)	106.6(2)
N(3)–Cu–O(41)	91.8(2)	N(3)–Cu–O(51)	95.4(1)
O(41)–Cu–O(42)	55.9(1)	O(41)–Cu–O(51)	147.9(1)
O(42)–Cu–O(51)	92.1(1)	O(42)–Cu–N(1)	161.2(2)
N(2)–Cu–O(51)	94.5(1)	N(2)–Cu–N(3)	158.8(1)
N(1)–Cu–O(41)	105.4(2)		
N(2)–Cu–O(41)	89.8(2)		
N(2)–Cu–O(42)	99.9(1)		
O(41)–N(4)–O(43)	122.5(5)	C(6)–N(1)–C(2)	122.6(3)
O(41)–N(4)–O(42)	117.7(4)	N(1)–C(2)–C(3)	120.3(3)
O(42)–N(4)–O(43)	119.9(4)	C(2)–C(3)–C(4)	117.9(4)
O(51)–N(5)–O(52)	118.8(4)	C(3)–C(4)–C(5)	121.0(4)
O(51)–N(5)–O(53)	120.6(5)	C(4)–C(5)–C(6)	118.6(4)
O(52)–N(5)–O(53)	120.6(5)	C(5)–C(6)–N(1)	119.5(4)
Cu–O(41)–N(4)	80.8(3)	C(21)–C(22)–C(23)	119.6(4)
Cu–O(42)–N(4)	106.0(2)	C(22)–C(23)–C(24)	119.7(5)
		C(23)–C(24)–C(25)	121.0(4)
Cu–O(51)–N(5)	121.4(3)	C(24)–C(25)–C(26)	119.9(5)
		C(25)–C(26)–C(21)	119.6(5)
Cu–N(2)–C(7)	115.2(2)	C(26)–C(21)–C(22)	120.2(3)
Cu–N(3)–C(9)	114.6(3)		
Cu–N(2)–C(21)	121.2(3)	C(31)–C(32)–C(33)	119.2(5)
Cu–N(3)–C(31)	122.5(2)	C(32)–C(33)–C(34)	121.4(7)
C(7)–N(2)–C(21)	123.6(3)	C(33)–C(34)–C(35)	118.6(5)
C(9)–N(3)–C(31)	122.5(3)	C(34)–C(35)–C(36)	120.9(5)
Cu–N(1)–C(2)	119.4(2)	C(35)–C(36)–C(31)	119.6(6)
Cu–N(1)–C(6)	118.0(3)	C(36)–C(31)–C(32)	120.2(5)

DISCUSSION

The crystal structure consists of monomeric units of $[LCu(NO_3)_2]$ separated by distances which are close to van der Waals contacts (Figure 1). A view of the molecule and our numbering scheme are shown in Figure 2. The copper atom is six-co-ordinated to the three nitrogens of the terdentate ligand and three oxygens of two nitrato-groups. Thus atoms N(1)—(3) and O(42) describe an equatorial plane with Cu displaced 0.234 Å from it towards the axial oxygen O(51) of the unidentate NO_3 group; the remaining axial site is occupied by O(41) of the bidentate NO_3 ligand. The N(1), N(2), N(3), and O(41) plane makes an angle of 89.8° with the plane defined by atoms O(41), O(42), O(51), and N(1). There is, however, considerably more

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* See Notice to Authors No. 7, in *J.C.S. Dalton*, 1975, Index issue.

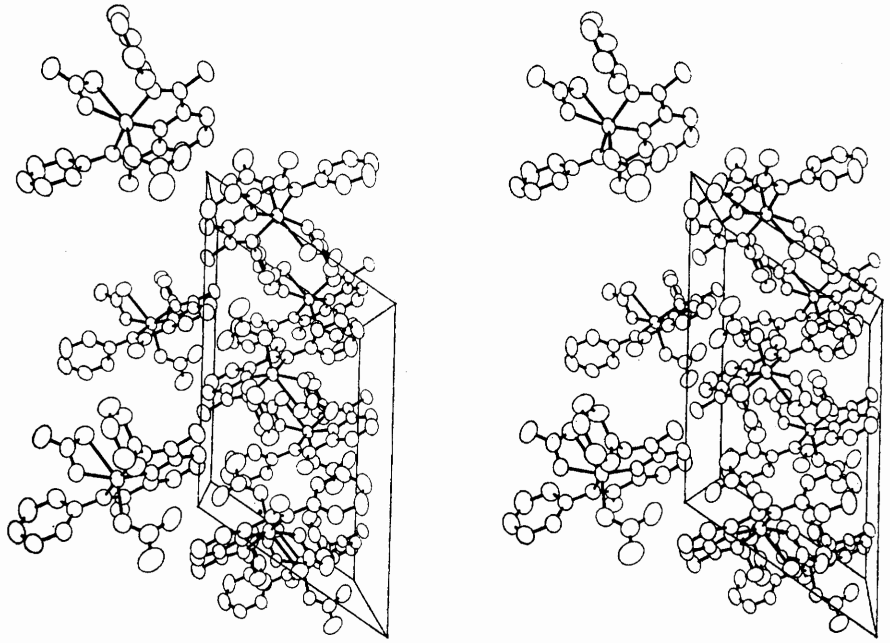

FIGURE 1 A stereoview of the molecular packing, with hydrogen atoms omitted for clarity

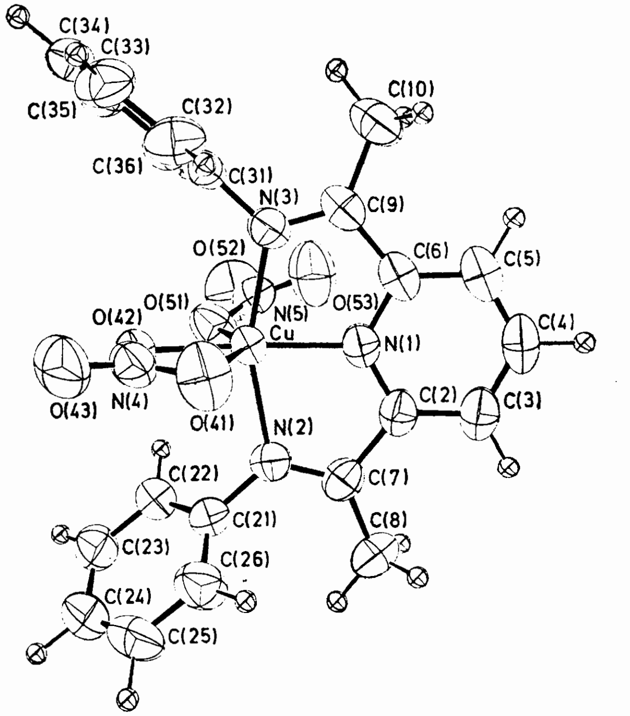

FIGURE 2 A perspective view with 50% probability ellipsoids showing the molecular geometry and atom numbering system used.

TABLE 4

Metal(II)–nitrato bidentate co-ordination in [LM(NO_3)$_2$] complexes

Metal complex	M–O(Å)	Δ *
[(py)$_3$Cd(NO_3)$_2$] [a]	2.444(9), 2.491(10)	0.047
[LNi(NO_3)$_2$] [b]	2.070(4), 2.138(5)	0.068
[(py)$_3$Co(NO_3)$_2$] [c]	2.207(9), 2.311(9)	0.104
[(py)$_3$Zn(NO_3)$_2$] [c]	2.232(13), 2.418(12)	0.186
[LCu(NO_3)$_2$] [d]	1.968(3), 2.533(5)	0.565
[(py)$_3$Cu(NO_3)$_2$] [e]	2.154(7), 2.732(9)	0.578

[a] Ref. 9. [b] Ref. 2. [c] Ref. 3. [d] This work. [e] Ref. 3.

* Δ = Difference (Å) in M–O distance

distortion from octahedral co-ordination for this Cu^{II} complex, as compared with the corresponding Ni^{II} complex;[2] this is predicted by the Jahn–Teller effect.[8] Thus, in the Cu^{II} complex, the bonding of the nitrato-group is highly asymmetric with Cu–O 1.968(3) and 2.533(5) Å [*cf.* 2.070(4) and 2.138(5) Å for the corresponding Ni–O distances[2]], together with angles Cu–O(42)–N(4) (106.0°) and Cu–O(41)–N(4) (80.3°). Similar observations with regard to highly asymmetrical nitrato-co-ordination for the Cu^{II} species have been made in the series of related trispyridine complexes [(py)$_3$M(NO_3)$_2$] [M = Co^{II}, Cu^{II}, and Zn^{II} (ref. 3), and Cd^{II} (ref. 9)] (Table 4). In these complexes both nitrato-groups are equivalent as a consequence of space-group symmetry requirements and the distorted stereochemistry about the metal atom has been described in terms of a trigonal bipyramidal geometry, using the line-of-centre approach of Cotton,[10] where the bidentate nitrato-groups are considered to occupy single co-ordination sites. The single-crystal electronic and e.s.r. spectral data[11] of [(py)$_3$Cu(NO_3)$_2$],[3] and of the related complexes [(bipy)$_2$CuNH$_3$][BF$_4$]$_2$,[12] [(bipy)$_2$CuCl]Cl·6H$_2$O,[13] and [(dchp)CuCl]CuCl$_2$[14] [dchp = dodeca(dimethylamino)cyclohexaphosphazene-*NNNN*] have also been interpreted in terms of trigonal

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[8] H. L. Schläfer and G. Gliemann, 'Basic Principles of Ligand Field Theory,' Wiley–Interscience, New York, 1969, p. 172.

[9] A. F. Cameron, D. W. Taylor, and R. H. Nuttall, *J.C.S. Dalton*, 1972, 1608.

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bipyramidal structures. It is likewise possible to describe [$LCu(NO_3)_2$] in terms of a distorted trigonal bipyramidal structure if the line-of-centre approach is used for the bidentate NO_3 ligand. In this description, the terminal nitrogen atoms of the ligand L are axial with the central nitrogen atom, O(51) of the unidentate NO_3 group, and the midpoint [X] of O(41) and O(42) equatorial. This leads to angles X–Cu–O(51) 123.8 and X–Cu–N(1) 129.5°.

The Cu–O bond length to the unidentate nitrato-ligand, 2.213(4) Å, is intermediate between the distances for the bidentate group; by contrast, in the corresponding nickel complex,[2] the Ni–O(unidentate) distance [2.027(5) Å] is shorter than the Ni–O(bidentate) distances. The N–O(Cu) bond lengths are in the range 1.250—1.283(6) Å, the shorter distances being associated with the longer Cu–O bonds, as expected. The non-co-ordinated N–O bonds are much shorter and do not differ from their mean [1.216(7) Å].

In the terdentate ligand, the N(1)–Cu–N(2) and N(1)–Cu–N(3) angles, 79.2(1) and 80.0(1)° respectively, are considerably distorted from 90° by the bite of the ligand which, with the exception of the phenyl rings, is essentially planar. The copper atom lies 0.062 below, and O(42) 0.513 Å above, this plane. The central Cu–N(1) bond [1.913(3) Å] is significantly shorter than the terminal Cu–N(2) and Cu–N(3) bonds [2.046 and 2.035(3) Å respectively]; an exactly analogous situation was found in the related nickel complex.[2] The mean N–C distance in the pyridine ring is 1.334(5) Å whereas the N(2)–C(7) and N(3)–C(9) distances are much shorter [mean 1.284(5) Å], consistent with the double-bond character of the azomethine bonds. The other distances within the ligand are close to the expected values [*e.g.* mean C–C(py) 1.380(7), mean C–C(aromatic) 1.378(9), C(sp^2)–C(Me) 1.496(6), C(sp^2)(aromatic)–C(sp^2) 1.497(5) Å].

Other details of the conformation of the molecule are explicable in terms of intra- and inter-molecular overcrowding effects. The plane of the unidentate nitrato-group N(5), O(51), O(52), O(53) is rotated about the Cu–O(51) bond [torsion angle N(1)–Cu–O(51)–N(5) 24.3°] to reduce intramolecular interactions between nitrato-oxygen O(53) and atoms N(1), C(6), C(9), and N(3) of the terdentate ligand; O(53) is almost equidistant from these atoms with separations 2.987, 3.069, 3.122, and 3.168 Å respectively. Relief from severe intramolecular strain is also achieved by an increase in the N(1)–Cu–O(51) angle to 106.6(2)° from the regular octahedral value.

The plane of the bidentate nitrato-group is inclined at 4.6° to the N(1), O(41), O(42), O(51) plane; the folding about the O(41) · · · O(42) line being towards the N(3) side of the molecule. Inspection of the intermolecular contacts (Table 5) shows that one of the shortest contacts involves the terminal nitrato-oxygen O(41) and the methyl group C(10′) of a neighbouring molecule [C · · · O 3.166(5) Å] where C(10′) is on the side of O(43) remote from N(3). In the absence of such folding, the C · · · O contact would presumably have been much too short.

Table 5

Selected non-bonded contacts

(*a*) Intermolecular contacts <3.4 Å

C(8) · · · O(41^{I})	3.203(9)	C(4) · · · O(53^{II})	3.280(8)
C(7) · · · O(41^{I})	3.121(7)	C(32) · · · O(52^{III})	3.269(7)
C(2) · · · O(41^{I})	3.283(7)	C(10) · · · O(52^{III})	3.241(10)
C(3) · · · O(43^{I})	3.394(7)	C(10) · · · O(43^{IV})	3.166(5)
C(3) · · · O(53^{II})	3.324(7)	C(25) · · · O(52^{V})	3.133(7)
		C(26) · · · O(52^{V})	3.165(7)

(*b*) Intramolecular non-bonded contacts (Å)

N(1) · · · O(53)	2.987(7)	C(6) · · · O(53)	3.069(8)
N(3) · · · O(53)	3.168(8)	C(9) · · · O(53)	3.122(8)

Roman numeral superscripts refer to the following transformations, relative to the reference molecule at x, y, z:

I $1 - x, -y, -z$
II $-x, -y, -z$
III $x, \frac{1}{2} - y, z - \frac{1}{2}$
IV $x - 1, \frac{1}{2} - y, z - \frac{1}{2}$
V $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$

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[5/1016 *Received*, 28*th May*, 1975]

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