Crystal and Molecular Structures of Dinitrato(1,10-phenanthroline)-copper(II) and Diaquanitrato(1,10-phenanthroline)copper(II) Nitrate

By **Dennis L. McFadden** and **Andrew T. McPhail**,* Paul M. Gross Chemical Laboratory, Duke University, Durham, North Carolina 27706, U.S.A.

The crystal structures of the title compounds, (I) $[Cu(C_{12}H_8N_2)(NO_3)_2]$ and (II) $[Cu(C_{12}H_8N_2)(NO_3)(H_2O)_2][NO_3]$, have been determined from three-dimensional *X*-ray diffractometer data and refined by full-matrix least-squares calculations to *R* 0.045 [(I), 1 181 reflections] and 0.058 [(II), 1 525 reflections].

Crystals of (I) and (II) are monoclinic, space group $P2_1/c$, with $Z = 4$ in cells of dimensions: (I) $a = 8.76(1)$, $b = 9.12(1)$, $c = 17.63(1)$ Å, $\beta = 107.4(1)°$; (II) $a = 7.03(1)$, $b = 20.20(1)$, $c = 11.49(1)$ Å, $\beta = 109.9(1)°$.

Crystals of (I) contain polymeric $Cu(C_{12}H_8N_2)(NO_3)_2$ units in which one of the nitrato-groups is terdentate and serves to bridge the units along the 2_1 screw axis. The copper atom is seven co-ordinate: Cu–N(phen) 1.994(5), 2.018(5); Cu–O(NO_3) 1.960(5), 1.996(4), 2.326(4), 2.814(5), and 2.863(5) Å.

In (II) the copper atom is in a distorted octahedral environment with Cu–N(phen) 2.005(6), 2.008(6), Cu–O(NO_3) 1.983(5), and Cu–O(H_2O) 2.005(6) Å defining the basal plane. A second water oxygen [Cu–O 2.261(6) Å], and an oxygen of the asymmetrically bidentate nitrato-group [Cu–O 2.594(6) Å] occupy the axial sites. The nitrate ion is involved in three hydrogen bonds to the co-ordinated water molecules.

THE reaction of 1,10-phenanthroline (phen) with a large excess of copper(II) nitrate in ethanol was reported[1] to yield a 1 : 1 complex. As part of our continuing studies on the co-ordination geometry of first-row transition metals with bidentate ligands, we repeated the described procedure and found it to yield two crystalline complexes, $[Cu(phen)(NO_3)_2]$ (I), and $[Cu(phen)(NO_3)(H_2O)_2][NO_3]$ (II), which we have subjected to single-crystal *X*-ray analysis to investigate the nature of the metal-atom co-ordination.

EXPERIMENTAL

The complexes were prepared by addition of an ethanolic solution of 1,10-phenanthroline monohydrate (0.28 g, 0·0014 mol) to a solution of $Cu(NO_3)_2,3H_2O$ (0.25 mol) in a minimum of ethanol. The solid which precipitated overnight and which contained a few small dark blue crystals of (I) was filtered off and the filtrate set aside to evaporate slowly. After several days long fibrous pale blue crystals of (II) were harvested in large yield. The filtrate was allowed to evaporate further and more large dark blue crystals of (I) formed.

Crystal Data.—(I), $C_{12}H_8CuN_4O_6$, $M = 359.7$, Monoclinic, $a = 8.76(1)$, $b = 9.12(1)$, $c = 17.63(1)$ Å, $\beta = 107.4(1)°$, $U = 1\,344$ Å^3, $D_c = 1.78$, $Z = 4$, $D_m = 1.75$, $F(000) = 740$. Mo-K_α radiation, $\lambda = 0.710\,69$ Å; μ(Mo-K_α) = 13.7 cm^{-1}. Space group $P2_1/c$ (C^5_{2h}) from systematic absences: $h0l$ when $l \neq 2n$, $0k0$ when $k \neq 2n$.

(II), $C_{12}H_{12}CuN_4O_8$, $M = 403.7$, Monoclinic, $a = 7.03(1)$, $b = 20.20(1)$, $c = 11.49(1)$ Å, $\beta = 109.9(1)°$, $U = 1\,534$ Å^3, $D_c = 1.75$, $Z = 4$, $D_m = 1.72$, $F(000) = 1\,108$. Mo-K_α radiation, μ(Mo-K_α) = 15.3 cm^{-1}. Space group $P2_1/c$ (C^5_{2h}) from systematic absences: $h0l$ when $l \neq 2n$, $0k0$ when $k \neq 2n$.

Crystallographic Measurements.—For both complexes preliminary unit cell dimensions and space-group information were obtained from precession photographs taken with Mo-K_α radiation, and rotation and Weissenberg photographs taken with Cu-K_α ($\lambda = 1.542$ Å) radiation.

Single crystals of dimensions (I) *ca.* 0.6 × 0.2 × 0.15 mm and (II) *ca.* 0.2 × 0.3 × 1.2 mm were oriented on glass fibres such that the $[10\bar{1}]$ direction for (I) and the $[30\bar{2}]$ direction for (II) were parallel to the ϕ axis of an Enraf–Nonius CAD 3 automated diffractometer (Zr-filtered Mo-K_α radiation, take-off angle 3°). Refined cell parameters were obtained from least-squares treatment of the θ, ϕ, and χ angles for 25 (I) and 36 (II) high-order reflections. Intensities for all unique reflections having $2\theta < 50°$ were collected by the θ—2θ scanning technique as described previously,[2] with scanwidths $(0.90 + 0.40 \tan\theta)°$ for (I) and $(1.60 + 0.50 \tan\theta)°$ for (II). Instrument and crystal stability were monitored throughout data collection by remeasuring the intensity of a standard strong reflection periodically and no significant variation was noted. Only those reflections for which $I > 2.0\sigma(I)$, where $\sigma^2(I)$ = (scan count + total background count), were corrected for Lorentz and polarization effects to yield 1 181 (I) and 1 525 (II) reflections which were used in the structure solutions and refinements; no allowance was made for absorption.

Structure Analysis.—The structures were solved by the heavy-atom method. In each case copper atom co-ordinates were determined from the three-dimensional Patterson map and the non-hydrogen atoms were located in copper-phased [*R* (I) 0.42, *R* (II) 0.54] three-dimensional F_0 Fourier syntheses. Refinement of the positional and thermal parameters, at first isotropic and subsequently anisotropic, reduced *R* (I) to 0.051 and *R* (II) to 0.074. 1,10-Phenanthroline hydrogen-atom positions were then calculated assuming C–H 1.05 Å and ideal geometry at the carbon atoms, and confirmed to coincide with regions of significant positive electron density in the difference-Fourier syntheses. For (I), least-squares adjustment of hydrogen-atom positions and isotropic thermal parameters produced meaningful results except for H(6) and H(7) which were therefore placed at their calculated positions. Several further cycles of least-squares calculations brought the refinement of (I) to convergence at *R* 0.045. For (II), the water hydrogen atoms were placed to coincide with electron-density maxima in the difference map. Attempts to refine the hydrogen-atom parameters did not yield acceptable results and so they were all included in the subsequent calculations with fixed positions and *B* 5.0 Å^2. Refinement of (II) converged at *R* 0.058 following several further rounds of least-squares adjustment of the non-hydrogen atom parameters.

Final atomic co-ordinates and thermal parameters are listed in Tables 1 and 2. Observed and calculated structure factors for both complexes are in Supplementary Publication No. SUP 21377 (16 pp., 1 microfiche).† For all

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† See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

[1] P. Spacu, M. Brezeanu, F. Zalaru, O. Constantinescu, and I. Pascaru, *Anal. Univ. Bucuresti, Ser. St. Natur.*, 1966, **15**, 139.

[2] D. L. McFadden and A. T. McPhail, *J.C.S. Dalton*, 1974, **363**.

TABLE 1

Fractional atomic co-ordinates (×10^4) and anisotropic temperature-factor parameters *, with estimated standard deviations in parentheses

(*a*) (I) $[Cu(phen)(NO_3)_2]$

Atom	x	y	z	10^4b_{11}	10^4b_{22}	10^5b_{33}	10^4b_{12}	10^4b_{13}	10^4b_{23}
Cu	1 367.3(9)	721.3 (8)	3 033.9(4)	108(1)	65(1)	196(2)	11(2)	32(1)	−2(1)
N(1)	1 124(6)	1 340(6)	4 077(3)	121(7)	58(6)	251(18)	8(13)	42(6)	10(6)
C(2)	258(8)	2 447(7)	4 242(4)	141(10)	62(8)	282(24)	50(16)	33(8)	14(8)
C(3)	296(8)	2 736(8)	5 022(4)	135(10)	79(9)	299(23)	14(16)	55(7)	1(8)
C(4)	1 213(8)	1 922(8)	5 633(4)	139(10)	94(9)	190(20)	−42(17)	37(7)	1(8)
C(4a)	2 121(7)	749(7)	5 481(4)	94(8)	77(8)	231(20)	−24(15)	41(6)	−22(7)
C(5)	3 135(8)	−186(6)	6 079(4)	133(10)	130(11)	203(22)	−7(19)	31(7)	3(9)
C(6)	3 917(8)	−1 334(8)	5 884(4)	127(10)	100(9)	241(24)	36(18)	22(8)	38(8)
C(6a)	3 737(7)	−1 650(7)	5 071(4)	82(8)	46(8)	297(24)	18(14)	13(7)	−5(7)
C(7)	4 433(8)	−2 891(8)	4 798(4)	126(10)	100(10)	350(27)	44(17)	30(8)	26(9)
C(8)	4 190(8)	−3 094(8)	4 017(4)	143(10)	88(9)	343(27)	52(17)	42(8)	1(9)
C(9)	3 240(8)	−2 109(8)	3 464(4)	126(10)	79(9)	238(22)	7(16)	31(7)	2(8)
N(10)	2 598(6)	−951(5)	3 686(3)	106(7)	45(6)	330(20)	13(12)	40(6)	−18(6)
C(10a)	2 817(7)	−722(7)	4 477(4)	83(8)	51(7)	273(21)	−44(14)	36(6)	−15(7)
C(10b)	2 005(7)	490(6)	4 685(3)	90(8)	36(7)	208(20)	−15(13)	27(6)	17(7)
N(11)	2 833(8)	235(7)	1 844(4)	145(10)	58(8)	270(22)	−31(16)	27(7)	−16(7)
O(12)	1 539(6)	−55(6)	2 026(3)	146(7)	91(7)	290(16)	−69(13)	75(5)	−47(6)
O(13)	2 921(6)	−292(6)	1 218(3)	220(8)	144(8)	341(16)	−73(14)	−111(5)	−54(6)
O(14)	3 832(6)	1 000(7)	2 281(3)	157(8)	236(11)	355(19)	−153(15)	45(6)	−62(8)
N(15)	1 622(5)	3 724(6)	2 779(3)	81(7)	100(8)	333(20)	39(13)	45(6)	−7(7)
O(16)	646(5)	2 653(5)	2 520(2)	109(6)	81(6)	210(15)	−17(11)	12(5)	−3(5)
O(17)	1 272(5)	4 952(4)	2 486(3)	142(6)	52(5)	404(17)	33(11)	66(5)	39(5)
O(18)	2 871(5)	3 480(6)	3 310(3)	97(7)	112(7)	503(25)	−25(13)	−33(7)	30(7)
(*b*) (II) $[Cu(phen)(NO_3)(H_2O)_2][NO_3]$						†			
Cu	−351.3(13)	1 048.1(4)	2 016.8(7)	154(2)	16(1)	46(1)	12(1)	14(2)	3(1)
N(1)	1 102(9)	1 200(3)	3 828(6)	209(15)	14(2)	66(5)	−4(8)	35(14)	5(5)
C(2)	1 452(12)	1 745(5)	4 467(8)	212(19)	23(2)	73(7)	0(11)	−17(19)	−1(7)
C(3)	2 514(14)	1 760(5)	5 751(8)	253(23)	38(3)	63(7)	2(15)	−41(22)	−42(8)
C(4)	3 201(14)	1 175(5)	6 367(8)	273(22)	34(3)	56(7)	−23(13)	9(20)	9(7)
C(4a)	2 858(10)	580(4)	5 710(6)	159(15)	21(2)	51(6)	−8(10)	30(15)	19(6)
C(5)	3 564(11)	−39(5)	6 252(7)	184(17)	32(3)	68(7)	22(12)	49(18)	41(7)
C(6)	3 222(12)	−602(4)	5 568(8)	186(17)	24(2)	103(8)	19(11)	62(18)	48(7)
C(6a)	2 119(10)	−591(4)	4 245(7)	151(14)	21(2)	88(7)	2(10)	93(15)	17(6)
C(7)	1 746(14)	−1 143(5)	3 475(9)	331(9)	25(3)	135(9)	11(13)	190(22)	29(8)
C(8)	733(15)	−1 058(5)	2 231(9)	356(22)	24(3)	126(8)	−11(14)	220(19)	−21(8)
C(9)	82(13)	−440(4)	1 748(7)	288(20)	20(2)	70(7)	2(11)	92(18)	−6(7)
N(10)	413(8)	101(3)	2 470(5)	154(12)	16(2)	66(5)	−2(7)	58(12)	5(5)
C(10a)	1 442(10)	21(4)	3 705(7)	121(13)	21(2)	78(6)	17(9)	89(14)	9(6)
C(10b)	1 798(10)	610(4)	4 435(6)	128(14)	22(2)	58(6)	16(9)	36(14)	22(6)
N(11)	−3 839(10)	773(9)	226(6)	208(16)	19(2)	62(6)	−4(9)	−29(16)	5(6)
O(12)	−2 006(8)	820(3)	289(5)	270(13)	24(2)	53(4)	5(8)	78(11)	−6(4)
O(13)	−5 130(10)	650(4)	−766(6)	315(18)	39(2)	70(6)	−43(11)	−169(18)	6(6)
O(14)	−4 229(8)	849(3)	1 189(5)	221(13)	31(2)	79(5)	6(8)	77(12)	−8(5)
O(15)	2 273(8)	1 374(3)	1 438(5)	251(12)	28(2)	151(6)	−6(9)	227(13)	7(6)
O(16)	−1 303(8)	1 990(3)	1 784(5)	228(13)	19(1)	69(5)	18(7)	23(12)	3(4)
N(17)	6 070(10)	2 480(3)	3 769(6)	267(16)	18(2)	78(6)	−19(9)	85(15)	0(5)
O(18)	5 664(9)	2 207(4)	2 740(5)	308(16)	37(2)	75(5)	20(10)	31(14)	−35(6)
O(19)	4 779(11)	2 633(6)	4 149(8)	382(16)	120(6)	228(8)	−205(16)	441(15)	−170(11)
O(20)	7 818(10)	2 607(4)	4 388(6)	298(18)	55(3)	102(6)	−7(12)	51(16)	−74(6)

* In the form $B\sin^2\theta/\lambda^2 = b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl$. †$10^4b_{33}$.

structure-factor calculations neutral-atom scattering factors for copper, carbon, nitrogen, and oxygen were those from ref. 3 with anomalous dispersion corrections [4] included; for hydrogen the scattering factor of ref. 5 was used. In the least-squares calculations, $\Sigma w\Delta^2$ was minimized, with weights w being assigned according to the scheme $\sqrt{w} = 1$ for $|F_o| \leqslant 20.0$ and $\sqrt{w} = 20.0/|F_o|$ for $|F_o| > 20.0$ and showed no systematic dependence of $\langle w\Delta^2\rangle$ when analyzed in ranges of $|F_o|$.

RESULTS AND DISCUSSION

The immediate environment of the copper atoms and the atom numbering schemes in (I) and (II) are shown in Figures 1 and 2. Interatomic distances and angles are in Table 3, and displacements of selected atoms from various least-squares planes in Table 4.

Crystals of (I) contain polymeric $Cu(phen)(NO_3)_2$ units in which one of the nitrato-groups is terdentate and serves to bridge these units in a *syn–anti* manner along the 2_1 screw axis. The shortest Cu ··· Cu separation [5.233(1) Å] within the polymer chain implies no direct metal–metal interaction. Figure 3 shows a view of the crystal packing.

Crystals of (II) comprise discrete $[Cu(phen)(NO_3)(H_2O)_2]^+$ cations and nitrate anions bridged by the co-ordinated water molecules (Figure 4).

Copper Co-ordination Geometry.—(I). The copper atom is co-ordinated by five oxygen atoms from three

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[3] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

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

[5] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

nitrato-groups and two nitrogen atoms of the 1,10-phenanthroline ligand. Constraints imposed by the rigidity of the bidentate ligands prevent the attainment of a regular geometrical arrangement around the copper atom, and the co-ordination may be viewed either as a distorted monocapped trigonal prismatic 1 : 4 : 2 arrangement of seven electron pairs [6] or as a distorted octahedral arrangement in which one axial site is shared by a pair of oxygen atoms. For either description the equatorial plane is defined by two bidentate 1,10-phenanthroline nitrogen atoms [Cu–N 1.994(5) and 2.018(5) Å] and O(12) and O(16) of two asymmetrically bidentate nitrato-groups [Cu–O 1.960(5) and 1.996(4) Å]. Occupying the mono-capped trigonal-prism axial position is O(17^{I}) of a

TABLE 2

Fractional atomic co-ordinates ($\times 10^3$) and isotropic temperature factors for hydrogen atoms, with estimated standard deviations in parentheses. The atoms are labelled according to their bonded carbon and oxygen atoms

(*a*) (I) [$Cu(phen)(NO_3)_2$]

Atom	*x*	*y*	*z*	*B*/Å²
H(2)	−55(13)	297(12)	370(6)	6.0(22)
H(3)	−42(18)	355(9)	510(4)	2.6(14)
H(4)	108(9)	207(9)	619(5)	3.1(15)
H(5)	337(11)	16(11)	665(6)	2.2(19)
H(6)	461	−272	635	*
H(7)	514	−362	527	*
H(8)	466(13)	−398(13)	378(7)	7.3(27)
H(9)	306(10)	−230(11)	288(5)	4.5(18)

(*b*) (II) [$Cu(phen)(NO_3)(H_2O)_2$][NO_3]

Atom	*x*	*y*	*z*
H(2)	93	222	410
H(3)	280	218	629
H(4)	404	114	733
H(5)	433	−10	719
H(6)	373	−108	592
H(7)	230	−161	386
H(8)	46	−149	171
H(9)	−72	−39	80
H(15α)	138	158	207
H(15β)	300	100	138
H(16α)	−280	207	163
H(16β)	−250	167	120

* These atoms and all of those in (II) were included at their calculated positions with *B* 5.0 Å² and not refined.

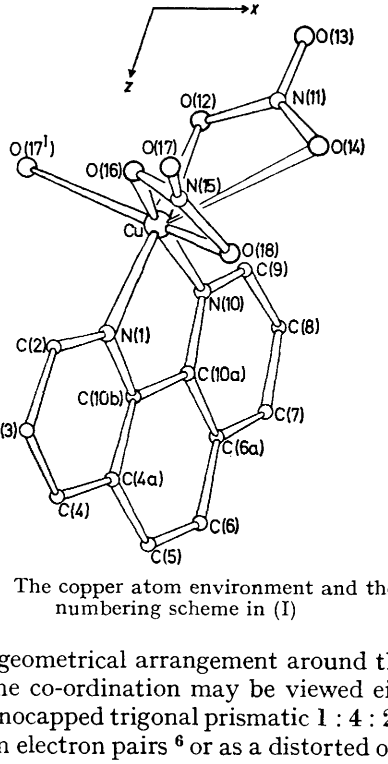

FIGURE 1 The copper atom environment and the atom numbering scheme in (I)

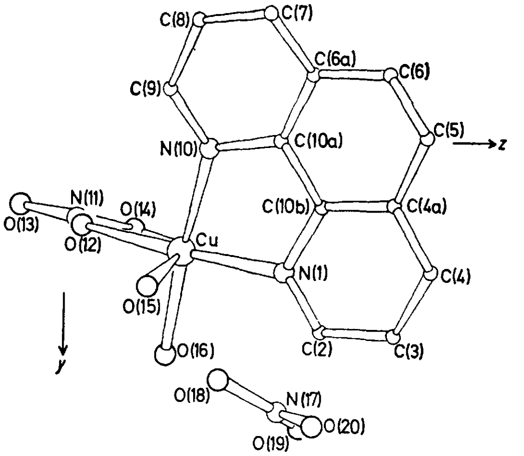

FIGURE 2 The copper atom environment and the atom numbering scheme in (II)

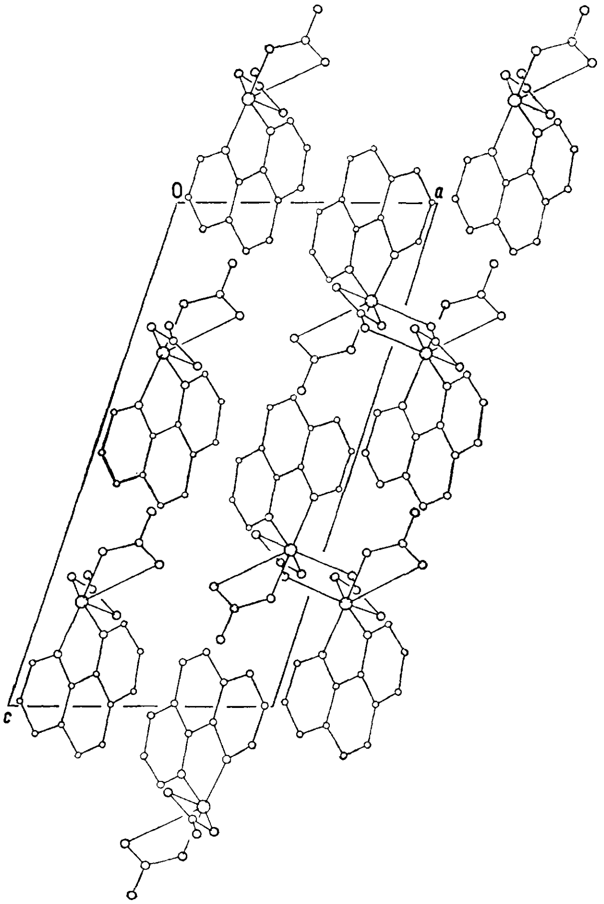

FIGURE 3 Crystal structure of (I), viewed in projection along the *b* axis

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[6] R. J. Gillespie, 'Molecular Geometry,' Van Nostrand, London, 1972.

bridging nitrato-group [Cu–O(17$^{\rm I}$) 2.326(4) Å]. In the remaining two sites are oxygen atoms from bidentate nitrato-groups which span the axial and equatorial positions [Cu–O(14) 2.863(5) and Cu–O(18) 2.814(5) Å],

Table 3

Interatomic distances (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) Bond lengths

(i) At Cu

	(I)	(II)
Cu–N(1)	1.994(5)	2.005(6)
Cu–N(10)	2.018(5)	2.008(6)
Cu–O(12)	1.960(5)	1.983(5)
Cu–O(16)	1.996(4)	2.005(6)
Cu–O(18)	2.814(5)	
Cu–O(17$^{\rm I}$)	2.326(4)	
Cu–O(14)	2.863(5)	2.594(6)
Cu–O(15)		2.261(6)
Cu–O(16$^{\rm I}$)	3.297(4)	

(ii) In the phen ligand

	(I)	(II)
N(1)–C(2)	1.331(9)	1.300(11)
N(1)–C(10b)	1.362(8)	1.384(10)
C(2)–C(3)	1.397(10)	1.408(13)
C(3)–C(4)	1.356(10)	1.379(14)
C(4)–C(4a)	1.405(9)	1.396(12)
C(4a)–C(5)	1.439(9)	1.410(12)
C(4a)–C(10b)	1.396(8)	1.400(10)
C(5)–C(6)	1.351(10)	1.357(13)
C(6)–C(6a)	1.424(9)	1.452(12)
C(6a)–C(7)	1.435(9)	1.391(13)
C(6a)–C(10a)	1.399(9)	1.393(11)
C(7)–C(8)	1.342(10)	1.374(14)
C(8)–C(9)	1.402(10)	1.381(13)
C(9)–N(10)	1.310(8)	1.343(11)
N(10)–C(10a)	1.365(8)	1.365(10)
C(10a)–C(10b)	1.421(8)	1.427(11)

(iii) In the nitrate ion and nitrato-groups

	(I)	(II)
N(11)–O(12)	1.294(8)	1.269(9)
N(11)–O(13)	1.227(8)	1.217(9)
N(11)–O(14)	1.202(9)	1.237(9)
N(15)–O(16)	1.289(7)	
N(15)–O(17)	1.233(7)	
N(15)–O(18)	1.230(7)	
N(17)–O(18)		1.246(10)
N(17)–O(19)		1.175(11)
N(17)–O(20)		1.219(10)

(*b*) Angles

(i) At Cu

	(I)	(II)
N(1)–Cu–N(10)	82.8(2)	83.1(2)
N(1)–Cu–O(12)	175.0(2)	172.9(2)
N(1)–Cu–O(14)	134.8(2)	120.3(2)
N(1)–Cu–O(15)		94.7(2)
N(1)–Cu–O(16)	93.6(2)	91.3(2)
N(1)–Cu–O(18)	76.2(2)	
N(1)–Cu–O(17$^{\rm I}$)	94.7(2)	
N(10)–Cu–O(12)	94.1(2)	93.0(2)
N(10)–Cu–O(14)	89.0(2)	95.9(2)
N(10)–Cu–O(15)		100.4(2)
N(10)–Cu–O(16)	165.7(2)	170.8(2)
N(10)–Cu–O(18)	115.7(2)	
N(10)–Cu–O(17$^{\rm I}$)	107.2(2)	
O(12)–Cu–O(14)	48.7(2)	54.0(2)
O(12)–Cu–O(15)		91.9(2)
O(12)–Cu–O(16)	90.4(2)	91.8(2)
O(12)–Cu–O(18)	108.7(2)	
O(12)–Cu–O(17$^{\rm I}$)	82.5(2)	
O(14)–Cu–O(15)		142.9(2)
O(14)–Cu–O(16)	83.8(2)	80.6(2)
O(14)–Cu–O(18)	67.8(2)	
O(14)–Cu–O(17$^{\rm I}$)	130.0(2)	
O(15)–Cu–O(16)		87.3(2)
O(16)–Cu–O(18)	50.0(2)	
O(16)–Cu–O(17$^{\rm I}$)	86.8(2)	
O(18)–Cu–O(17$^{\rm I}$)	134.2(2)	

Table 3 (*Continued*)

(ii) In the phen ligand

	(I)	(II)
Cu–N(1)–C(2)	129.4(4)	130.4(6)
Cu–N(1)–C(10b)	112.0(4)	111.1(5)
C(2)–N(1)–C(10b)	118.6(5)	118.6(7)
N(1)–C(2)–C(3)	121.1(6)	122.8(8)
C(2)–C(3)–C(4)	120.4(6)	119.2(9)
C(3)–C(4)–C(4a)	120.0(6)	119.6(8)
C(4)–C(4a)–C(5)	124.9(6)	123.7(7)
C(4)–C(4a)–C(10b)	116.4(6)	117.5(7)
C(5)–C(4a)–C(10b)	118.7(6)	118.8(7)
C(4a)–C(5)–C(6)	121.4(6)	121.4(8)
C(5)–C(6)–C(6a)	120.1(6)	121.3(8)
C(6)–C(6a)–C(7)	124.5(6)	124.8(8)
C(6)–C(6a)–C(10a)	119.8(6)	117.3(7)
C(7)–C(6a)–C(10a)	115.7(6)	117.8(8)
C(6a)–C(7)–C(8)	120.0(7)	118.7(9)
C(7)–C(8)–C(9)	120.3(7)	121.0(9)
C(8)–C(9)–N(10)	121.8(6)	121.5(8)
Cu–N(10)–C(9)	130.0(5)	129.8(5)
Cu–N(10)–C(10a)	110.8(4)	112.4(5)
C(9)–N(10)–C(10a)	119.2(5)	117.8(7)
C(6a)–C(10a)–N(10)	123.0(5)	123.1(7)
C(6a)–C(10a)–C(10b)	119.9(6)	120.9(7)
N(10)–C(10a)–C(10b)	117.0(5)	116.0(7)
N(1)–C(10b)–C(4a)	123.3(5)	122.4(7)
N(1)–C(10b)–C(10a)	116.7(5)	117.4(6)
C(4a)–C(10b)–C(10a)	120.0(5)	120.2(7)

(iii) In the nitrate ion and nitrato-groups

	(I)	(II)
O(12)–N(11)–O(13)	115.9(6)	119.1(7)
O(12)–N(11)–O(14)	118.9(6)	118.0(6)
O(13)–N(11)–O(14)	125.1(7)	122.8(7)
Cu–O(12)–N(11)	117.4(4)	108.2(4)
Cu–O(14)–N(11)	75.0(4)	79.7(4)
O(16)–N(15)–O(17)	118.9(5)	
O(16)–N(15)–O(18)	118.6(5)	
O(17)–N(15)–O(18)	122.5(5)	
Cu–O(16)–N(15)	114.9(3)	
Cu–O(17$^{\rm I}$)–N(15$^{\rm I}$)	122.2(3)	
Cu–O(18)–N(15)	76.5(4)	
O(18)–N(17)–O(19)		120.9(8)
O(18)–N(17)–O(20)		120.4(7)
O(19)–N(17)–O(20)		118.7(8)

(*c*) (i) Separations <3.6 Å between the polymer chains in (I)

C(6) ··· O(14$^{\rm II}$)	3.26	C(4) ··· O(13$^{\rm III}$)	3.44
O(13) ··· C(8$^{\rm IV}$)	3.35	C(4) ··· C(10b$^{\rm VI}$)	3.49
O(14) ··· C(8$^{\rm IV}$)	3.36	C(3) ··· O(13$^{\rm III}$)	3.50
C(5) ··· O(17$^{\rm III}$)	3.36	C(7) ··· O(18$^{\rm II}$)	3.51
C(5) ··· O(14$^{\rm II}$)	3.37	C(4) ··· O(16$^{\rm III}$)	3.53
C(6) ··· O(18$^{\rm II}$)	3.37	C(2) ··· C(5$^{\rm VI}$)	3.54
O(17) ··· C(9$^{\rm V}$)	3.37	C(6) ··· N(10$^{\rm II}$)	3.59
C(4) ··· N(11$^{\rm III}$)	3.39	O(17) ··· C(8$^{\rm V}$)	3.59

Roman numeral superscripts refer to the following transformations of the co-ordinates of Table 1:

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

(ii) Interionic separations $\leqslant 3.5$ Å in (II)

O(20) ··· O(16$^{\rm I}$)	2.73	O(20) ··· O(12$^{\rm I}$)	3.33
O(18) ··· O(16$^{\rm II}$)	2.75	O(19) ··· O(16$^{\rm I}$)	3.41
O(15) ··· O(14$^{\rm II}$)	2.78	O(19) ··· N(11$^{\rm I}$)	3.47
O(15) ··· O(18)	2.88	O(19) ··· O(13$^{\rm I}$)	3.47
C(2) ··· O(19)	3.07	N(17) ··· O(16$^{\rm I}$)	3.49
O(20) ··· C(2$^{\rm II}$)	3.07	O(20) ··· O(16$^{\rm II}$)	3.49
C(5) ··· O(14$^{\rm IV}$)	3.26	C(5) ··· C(10a$^{\rm III}$)	3.49
O(18) ··· O(14$^{\rm II}$)	3.29	C(7) ··· C(4$^{\rm III}$)	3.50
C(3) ··· O(18$^{\rm V}$)	3.32	C(6) ··· C(10b$^{\rm III}$)	3.50

Roman numeral superscripts refer to the following transformations of the co-ordinates of Table 1:

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

and lie approximately equidistant from the O(17^I)–Cu polar axis. For the alternative distorted octahedral description, one axial position is again occupied by O(17^I) but the other is vacant and is shared by that pair of oxygen atoms which lie approximately equidistant from the O(17^I)–Cu polar axis as already described. The co-ordination geometry in (I) bears a strong similarity to that found[7] around the copper atom in dimeric [$Cu(py)_2(NO_3)_2$],py (py = pyridine) where two *trans*-related pyridine nitrogen atoms [Cu–N 1.995(7) and 2.006(8) Å] and two nitrato-oxygen atoms [Cu–O 2.035(6) and 2.042(6) Å] define the equatorial plane, one nitrato-oxygen atom at 2.542(8) Å occupies an axial site, and two other oxygen atoms at 2.618(8) and 2.906(7) Å complete the co-ordination.

TABLE 4

Equations of least-squares planes in the form * $AX + BY + CZ + D = 0$, and, in square brackets, displacements (Å) of atoms from the planes

Plane (I*a*): phen

$$-0.8125X - 0.5803Y - 0.0562Z + 0.0798 = 0$$

[N(1) −0.074, C(2) −0.007, C(3) 0.091, C(4) 0.072, C(4a) −0.003, C(5) −0.031, C(6) −0.046, C(6a) −0.021, C(7) 0.050, C(8) 0.070, C(9) 0.041, N(10) −0.041, C(10a) −0.054, C(10b) −0.048, Cu −0.266]

Plane (I*b*): N(1), N(10), O(12), O(16)

$$-0.8831X - 0.4187Y - 0.2119Z + 1.0960 = 0$$

[N(1) 0.154, N(10) −0.154, O(12) 0.145, O(16) −0.145, O(14) −2.004, O(18) −2.097, O(17^I) 2.369, Cu 0·090]

Plane (I*c*): N(11), O(12)—(14)

$$-0.3039X + 0.8138Y - 0.4954Z + 1.8167 = 0$$

[N(11) −0.005, O(12) 0.002, O(13) 0.002, O(14) 0.002, Cu −0.056]

Plane (I*d*): N(15), O(16)—(18)

$$0.6971X - 0.2065Y - 0.6866Z + 3.9399 = 0$$

[N(15) −0.001, O(16) 0.000, O(17) 0.000, O(18) 0.000, Cu 0.022]

Plane (II*a*): phen

$$0.9784X + 0.1296Y - 0.1613Z + 1.0458 = 0$$

[N(1) −0.014, C(2) 0.013, C(3) 0.032, C(4) 0.008, C(4a) −0.017, C(5) 0.004, C(6) 0.003, C(6a) −0.016, C(7) 0.011, C(8) 0.030, C(9) 0.014, N(10) −0.019, C(10a) −0.021, C(10b) −0.028, Cu −0.045]

Plane (II*b*): N(1), N(10), O(12), O(16)

$$0.9430X + 0.1885Y - 0.2373Z + 1.2660 = 0$$

[N(1) 0.013, N(10) −0.013, O(12) 0.012, O(16) −0.012, Cu 0.121, O(14) −2.032, O(15) 2.367]

Plane (II*c*): N(11), O(12)—(14)

$$-0.0666X + 0.9795Y - 0.1903Z - 1.6654 = 0$$

[N(11) 0.003, O(12) −0.001, O(13) −0.001, O(14) −0.001, Cu 0.063]

Plane (II*d*): N(17), O(18)—(20)

$$0.0790X + 0.8927Y - 0.4436Z - 2.8944 = 0$$

[N(17) −0.008, O(18) 0.003, O(19) 0.003, O(20) 0.003]

* Cartesian co-ordinates (X, Y, Z) are related to the fractional atomic co-ordinates (x, y, z) of Table 1 by the transformation $[X, Y, Z] = [xa + zc\cos\beta, yb, zc\sin\beta]$

Dihedral angles (°) between planes

(I*a*)–(I*c*)	78.6	(I*c*)–(I*d*)	87.7
(I*a*)–(I*d*)	65.9	(II*a*)–(II*c*)	84.7

(II). The copper atom is in a distorted octahedral environment where two nitrogen atoms of the bidentate 1,10-phenanthroline ligand [Cu–N(1) 2.005(6) and Cu–N(10) 2.008(6) Å], one oxygen atom of an asymmetrically bidentate nitrato-group [Cu–O(12) 1.983(5) Å], and one water molecule oxygen [Cu–O(16) 2.005(6) Å] define the equatorial plane. Occupying one of the axial sites is the second water molecule [Cu–O(15) 2.261(6) Å], while an oxygen atom of the nitrato-group [Cu–O(14) 2.594(6) Å] completes the metal-ion co-ordination. The mean Cu–N distance [2.007(6) Å] is in excellent agreement with that [2.006(5) Å] for [$Cu(phen)(NO_3)_2$].

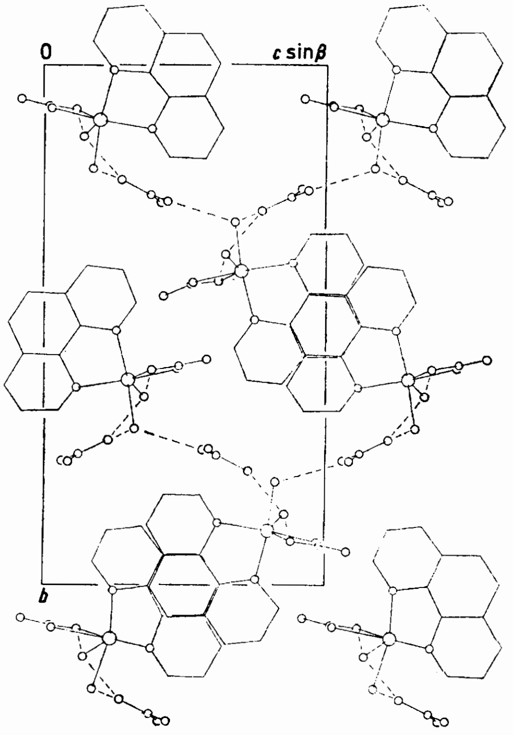

FIGURE 4 Crystal structure of (II), viewed in projection along the *a* axis; hydrogen bonds are denoted by broken lines

Nitrate Geometry.—The atoms in each of the nitrato-groups and the nitrate ion are coplanar and, in accord with the commonly observed geometry, the copper atom lies close to the least-squares planes through the nitrato-groups (Table 4). The dihedral angle between the nitrato-planes in (I) is 87.7°.

The mean nitrato N–O lengths [1.246 (I), 1.241 Å (II)] are in excellent agreement with the mean of the means [1.246(6) Å] from several recent accurate determinations.[8-12] The mean nitrate ion N–O bond length

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

[12] A. F. Cameron, D. W. Taylor, and R. H. Nuttall, *J.C.S. Dalton*, 1973, 2130.

(1.213 Å) is slightly smaller than the nitrato-mean, probably due to neglect of correction for the more severe effects of thermal motion.

In both complexes the nitrato-groups act as asymmetrically bidentate ligands with respect to the same copper atom. Moreover, in (I) one group serves also to bridge the Cu(phen)$(NO_3)_2$ units along the 2_1 screw axis so that all three oxygen atoms are co-ordinated to copper atoms. In accord with previous observations for other nitrato-complexes,[13] the individual N–O lengths in (I) and (II) differ significantly, their values reflecting the extent of the bonding interaction with the copper atom. Thus, the shorter is the Cu–O distance, the stronger is the bonding interaction and the longer (weaker) is the N–O bond. In (I) the distances are Cu–O(12) 1.960(5), N(11)–O(12) 1.294(8); Cu–O(16) 1.996(4), N(15)–O(16) 1.289(7); Cu–O(17^{I}) 2.326(4), N(15)–O(17) 1.233(7); Cu–O(18) 2.814(5), N(15)–O(18) 1.230(7); Cu–O(14) 2.863(5), N(11)–O(14) 1.202(9) Å; and in (II) they are Cu–O(12) 1.983(5), N(11)–O(12) 1.269(9); Cu–O(14) 2.594(6), N(11)–O(14) 1.237(7) Å. Additionally, the O–N–O valency angles reveal distortions from 120° in the direction that the largest O–N–O interbond angle is always opposite to the longest N–O bond and *vice versa*. Examples of this in (I) are N(11)–O(12) 1.294(8) Å and O(13)–N(11)–O(14) 125.1(7)°, N(11)–O(14) 1.202(9) Å and O(12)–N(11)–O(13) 115.9(6)°; other lengths and angles assume appropriate values consistent with this pattern. Similar observations have been noted for a number of other nitrato-complexes and may be rationalized [13] in terms of the electron-pair repulsion model and the amount of nitrogen *p* character in the bonds involved.

1,10-*Phenanthroline Ligands*.—In the 1,10-phenanthroline ligands the means of chemically equivalent bonds, assuming C_{2v} symmetry, are N(1)–C(2) 1.321(9) [1.322(11)], N(1)–C(10b) 1.364(8) [1.375(10)], C(2)–C(3) 1.400(10) [1.395(13)], C(3)–C(4) 1.349(10) [1.377(14)], C(4)–C(4a) 1.420(9) [1.394(13)], C(4a)–C(5) 1.432(9) [1.431(12)], C(4a)–C(10b) 1.398(9) [1.397(11)], C(5)–C(6) 1.351(10) [1.357(13)], C(10a)–C(10b) 1.421(8) [1.427(11)] Å, where values in square brackets are for (II) and the other values are for (I) (the quoted standard deviations in parentheses for the mean of a pair of lengths is the larger of the individual values derived from the least-squares calculations). These distances correlate well with the bond orders predicted [14] for phenanthrene from considerations of the contributions of various resonance forms. They are also not significantly different from the corresponding mean values computed [15] from the results of a number of investigations: 1.34(3), 1.37(4), 1.42(4), 1.36(3), 1.41(3), 1.44(3), 1.43(4), 1.34(3), and 1.42(4) Å. In each complex the ligand atoms deviate significantly from coplanarity. For (I) the displacements (Table 4) indicate that the ligand is folded approximately about the line joining the mid-points of the C(5)–C(6) and C(10a)–C(10b) bonds. In contrast to this the atom displacements of (II) indicate that while there is symmetric buckling about these same mid-points there is bending about the C(4a) ··· C(6a) line in addition to the same type of folding as in (I), presumably in response to crystal-packing forces.

Crystal Packing.—The majority of the shorter intermolecular separations (Table 3) between polymer chains in (I) and ions in (II) involve oxygen atoms and correspond in (I) to normal van der Waals interactions. The shorter O ··· O separations in (II) imply that all the water hydrogen atoms participate in hydrogen bonds The equatorial water molecule bridges nitrate ions related by the *c* glide plane, O(16) ··· O(18) 2.75, O(16) ··· O(20) 2.73 Å, O(18) ··· O(16) ··· O(20) 114.6°. The axial water molecule is hydrogen bonded to nitrate and nitrato-oxygen atoms thereby bridging ions along the *a* direction: O(15) ··· O(14) 2.78, O(15) ··· O(18) 2.88 Å, O(14) ··· O(15) ··· O(18) 70.9°.

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