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The Crystal Structure of Nitratotriaquo(2,2′-bipyridine)copper(II) Nitrate $[Cu(NO_3)(H_2O)_3(bipy)]NO_3$*

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Synopsis. The crystal structure of the title compound has been determined from three-dimensional X-ray data. The crystal is composed of the nitrate anions and the distorted-octahedral $[Cu(NO_3)(H_2O)_3(bipy)]^+$ cations, where the nitrato-groups act as a monodentate ligand and the three coordinated water molecules occupy a facet of the octahedron.

It has been found that the bis(2,2′-bipyridine)copper(II) complexes have a variety of stereochemistries: distorted trigonal bipyramid and *cis*- and *trans*-distorted octahedrons.[1-4] As a part of our structural studies on such complexes, a single crystal X-ray analysis has been carried out on $[Cu(NO_3)(H_2O)_3(bipy)]NO_3$.

Experimental

The crystals of $[Cu(NO_3)(H_2O)_3(bipy)]NO_3$ were easily prepared by adding a methanol solution of 2,2′-bipyridine (8 mmol in 20 cm^3 of the solvent) to an aqueous solution of cupric nitrate (10 mmol in 30 cm^3 of water), and were recrystallized from a water–methanol mixture. Found: C, 30.29; H, 3.75; N, 14.05%. Calcd for $[Cu(NO_3)(H_2O)_3(bipy)]NO_3$: C, 30.20; H, 3.55; N, 14.09%.

The lattice parameters were obtained by the least-squares refinement of the data from the higher-angle reflections of the (0*kl*), (*h*0*l*) and (*hk*0) Weissenberg photographs, on which aluminum powder lines were superimposed for calibration. Cu*K*α radiation (λ=1.5418 Å) was used throughout the diffraction study. The density was measured by the flotation technique, using a benzene–bromoform mixture. Of the two possible triclinic space groups, $P\bar{1}$ and P1, the former was chosen initially; it was subsequently verified by the successful refinements of the derived structure. Crystal data: $[Cu(NO_3)(H_2O)_3(bipy)]NO_3$, *F.W.*=397.8, triclinic $P\bar{1}$, a=9.52(1), b=7.80(1), c=13.62(2) Å, α=110.4(2), β=124.3(2), γ=77.3(1)°, Z=2, D_m=1.65, D_c=1.69 g·cm^{-3}, μ=25.3 cm^{-1} (for Cu*K*α radiation). The intensity data of 0*kl* to 5*kl*, and *h*0*l* to *h*4*l* were collected by the multiple-film equi-inclination technique from two cylindrically shaped crystals with approximate dimensions of 0.2×0.2×0.8 mm. The intensities of 2890 independent reflections were visually estimated by comparison with a standard scale; 374 of them were too weak to be measured and so were assumed to be zero. After the intensity data have been corrected for Lorentz-polarization, spot-extension, and absorption effects, the structure factors were placed on a common arbitrary scale by the least-squares method.

Structure Determination

The crystal structure was determined by the heavy-atom method. The position of the copper atoms was determined from a three-dimensional Patterson map, and a Fourier synthesis phased with the Cu atoms revealed all the atoms except the hydrogen atoms and those of the uncoordinated NO_3^- ion; the NO_3^- ion was found from the subsequent Fourier and difference Fourier maps. The structure was refined by the block-diagonal least-squares method, using the HBLS-IV program coded by Prof. Ashida. The weighting scheme used was: w=0.2 when F_o=0, and w=1.0 when F_o>0. The atomic scattering curves were taken from the International Tables for X-ray Crystallography,[5] the real part of the anomalous dispersion correction ($\Delta f'$=−2.1) being applied for the neutral copper atom. Refinement of the positional and thermal parameters, at first isotropic and subsequently anisotropic, reduced the R value to 0.124 for 2516 non-zero reflections, and no other significant peak was obtained in the final Fourier and difference Fourier maps. Final atomic coordinates and thermal parameters are listed in Table 1. The observed and calculated structure factors are listed in Table 2.***

Results and Discussion

The crystal is composed of the $[Cu(NO_3)(H_2O)_3(bipy)]^+$ cations and the nitrate anions. Figure 1 shows a schematic drawing of the complex cation. The coordination geometry about the copper atom is a tetragonally distorted octahedron: two nitrogen atoms of the bipy ligand[Cu–N(1)=2.02(1) and Cu–N(2)=1.99(1) Å], and two oxygen atoms of the coordinated water molecules[Cu–O(1)=1.99(1) and Cu–O(2)=

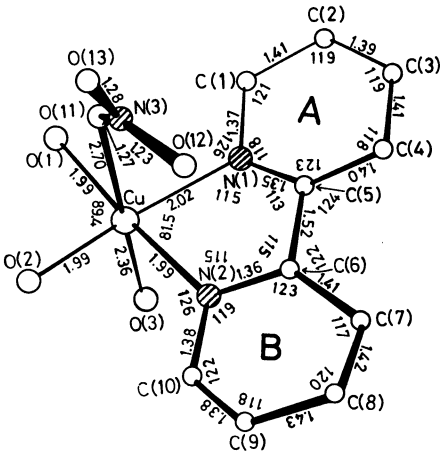

Fig. 1. A schematic drawing of the complex cation $[Cu(NO_3)(H_2O)_3(bipy)]^+$.

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*** Table 2 has been deposited at the Office of the Chemical Society of Japan, Document No. 7704.

Table 1. Atomic parameters ($\times 10^4$) and their standard deviations
The anisotropic thermal factors are of the form
$\exp\{-(h^2B_{11}+k^2B_{22}+l^2B_{33}+hkB_{12}+hlB_{13}+klB_{23})\}$.

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	4761(2)	3832(2)	1949(1)	32(2)	79(3)	14(1)	38(4)	45(2)	14(2)
O(1)	5847(11)	1826(11)	1192(8)	139(16)	115(17)	65(8)	96(27)	164(19)	55(18)
O(2)	2959(10)	4115(11)	277(7)	90(13)	104(16)	33(6)	65(24)	67(15)	37(15)
O(3)	3370(10)	1682(12)	1950(8)	77(13)	124(18)	83(9)	-7(25)	120(18)	54(20)
O(11)	6552(12)	6047(12)	1924(9)	141(16)	94(17)	116(11)	-12(28)	196(23)	86(21)
N(3)	6531(11)	7779(12)	2189(8)	64(13)	88(18)	39(7)	21(26)	63(17)	47(18)
O(12)	6106(15)	8751(14)	2919(9)	273(26)	192(24)	77(10)	65(40)	251(28)	16(24)
O(13)	7004(12)	8498(11)	1709(8)	176(17)	84(16)	71(8)	-8(27)	187(21)	34(18)
N(1)	6723(10)	4068(12)	3706(7)	40(12)	74(16)	36(7)	-3(24)	48(15)	17(17)
C(1)	8170(12)	2982(17)	4083(10)	18(13)	147(25)	45(9)	33(31)	32(18)	62(24)
C(2)	9492(13)	3311(19)	5334(11)	37(15)	206(31)	44(9)	45(36)	28(20)	57(27)
C(3)	9338(14)	4787(19)	6210(10)	51(16)	185(29)	40(9)	-65(36)	29(20)	27(26)
C(4)	7829(14)	5866(18)	5830(10)	82(18)	152(26)	29(8)	-64(36)	50(20)	8(23)
C(5)	6563(12)	5449(14)	4573(9)	36(13)	96(20)	32(8)	22(28)	59(17)	32(20)
C(6)	4869(12)	6487(14)	4044(9)	37(13)	94(20)	31(7)	16(28)	63(17)	23(19)
C(7)	4423(14)	7956(16)	4792(10)	98(18)	95(22)	49(9)	-20(34)	116(23)	-5(22)
C(8)	2794(16)	8814(16)	4192(11)	126(21)	98(23)	63(11)	72(37)	147(26)	35(25)
C(9)	1686(16)	8182(17)	2876(12)	117(20)	115(24)	75(12)	139(38)	147(27)	89(27)
C(10)	2246(13)	6736(17)	2228(10)	62(16)	144(25)	53(10)	103(34)	87(22)	76(25)
N(2)	3826(11)	5906(13)	2796(8)	66(14)	111(19)	31(7)	17(27)	63(17)	24(18)
O(21)	2739(9)	7576(12)	-37(8)	49(11)	152(19)	73(8)	58(24)	77(16)	112(20)
N(4)	1124(12)	7952(13)	-696(9)	76(15)	84(18)	55(8)	22(28)	73(19)	38(20)
O(22)	87(12)	7159(18)	-706(12)	81(15)	332(33)	162(15)	23(37)	106(26)	334(39)
O(23)	624(15)	8961(22)	-1353(16)	137(21)	446(46)	255(24)	152(51)	120(37)	583(59)

1.99(1) Å] define the equatorial plane, while the axial positions are occupied by the O(3) atom of the third coordinated water molecule[Cu–O(3)=2.36(1) Å], and by the O(11) atom of the nitrato-group[Cu–O(11)= 2.70 Å]. The copper atom is 0.12 Å distant from the equatorial plane, towards the O(3) atom. The angles of N(1)–Cu–O(11), N(1)–Cu–O(3), N(2)–Cu–O(11), and N(2)–Cu–O(3) are 84.9(4), 94.0(4), 93.2(4), and 91.7(4)° respectively.

The bipyridine ligand is in the *cis*-planar configuration with the maximum deviation of 0.04 Å, and the "bite" angle, N(1)–Cu–N(2), is 81.5°; the planarities of the two pyridine rings, A and B, are good with the maximum deviations of 0.02 and 0.01 Å respectively, and the dihedral angle between the A and B planes is 3°. The C(5)–C(6) bond length is 1.52(2) Å, and the aromatic C–C(1.38—1.43 Å) and C–N(1.35—1.38 Å) bond lengths are 1.41 and 1.36 Å on the average. It should be noted that the angles of C(4)–C(5)–C(6) and C(5)–C(6)–C(7) are larger than those of N(1)–C(5)–C(6) and C(5)–C(6)–N(2) by 8—10°; the same trend has been observed in the 2,2′-bipyridine[6] and its copper complexes.[1–4,7,8] The dihedral angle between the equatorial plane and the plane of the bipy ligand is 8°.

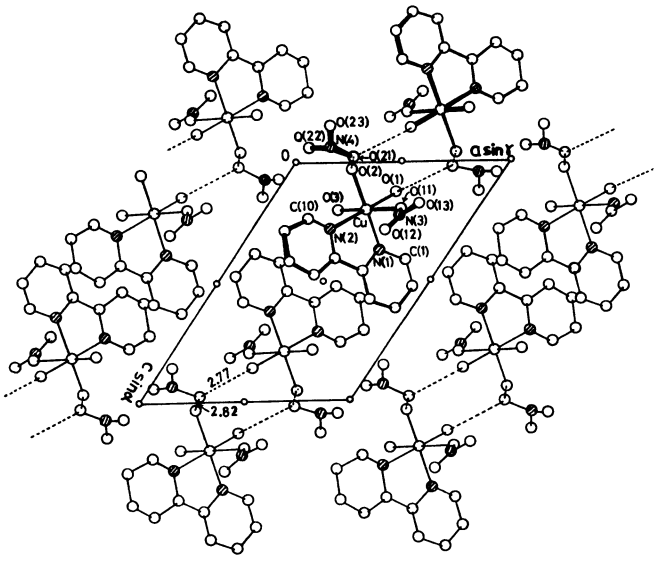

Fig. 2. Projection of the structure along the b axis. Dotted lines are hydrogen bonds.

The nitrato-group is planar and acts as a monodentate ligand. The O(11) is bonded to the copper atom (2.70 Å), while the O(13) is linked to the O(1)′[x,1+ y,z] by a hydrogen bond (2.76 Å). The plane of the nitrato-group makes the dihedral angles of 72° with the equatorial plane and of 79° with the plane of the bipy ligand.

The uncoordinated nitrate ion is also planar and is linked to the two water molecules by hydrogen bonds, which are indicated by the dotted lines in Fig. 2 [O(21) ···O(2)=2.82(2) and O(21)···O(11)″[1−x, 1−y, −z]= 2.77(2) Å]. The bond lengths of N(4)–O(21), N(4)–O(22), and N(4)–O(23) are 1.32(2), 1.27(2), and 1.22(2) Å respectively. The O–N(4)–O angles in the nitrate ion range from 119(1) to 121(1)°. The plane of the nitrate ion makes the angles of 74° with the plane of the coordinated nitrato-group and of 79° with the equatorial plane of the complex cation.

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