Crystal Structure and Electronic Properties of Bis(2,2'-bipyridyl)-nitratocopper(II) Nitrate Monohydrate

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The crystal structure of the title compound [Cu(bipy)$_2$(ONO$_2$)][NO$_3$]·H$_2$O (bipy = 2,2'-bipyridyl) has been redetermined by *X*-ray analysis in the triclinic space group *P*$\bar{1}$ with *a* = 7.488(2), *b* = 10.017(2), *c* = 15.061(2) Å, α = 106.183(4), β = 91.335(3), γ = 89.662(3)°, and *Z* = 2. The six-co-ordinate CuN$_2$N'$_2$OO' chromophore has a (4 + 1 + 1*) stereochemistry related to the original square-based pyramidal stereochemistry by an asymmetrically co-ordinated nitrate group to give an unsymmetrical bicapped square-pyramidal structure. The single-crystal e.s.r. and polarised electronic spectra are reported and together are shown to offer the possibility of distinguishing this bicapped square-pyramidal structure from that of a (4 + 1 + 1*) distorted square-pyramidal structure or *cis*-distorted octahedral structure. A structural pathway is suggested to connect these three geometries of the [Cu(bipy)$_2$(OXO)]$^+$ (OXO = ONO$^-$, O$_2$CMe$^-$, or O$_2$CH$^-$) cation by a linear combination of the S_{1a} and S_{2a} modes of vibration of the parent tris(chelate)copper(II) complex.

A NUMBER of recent *X*-ray crystallographic structure determinations[1-7] have established that the *cis*-distorted octahedral structure for the [Cu(chelate)$_2$(OXO)]$^+$ cation exists [chelate = 2,2'-bipyridyl (bipy), 1,10-phenanthroline (phen), or di-2-pyridylamine (bipyam); OXO = ONO$^-$, O$_2$CMe$^-$, or O$_2$CH$^-$], but generally undergoes distortion along the structural pathway[6,8,9] E or F, Figure 1, determined by the S_{2a} mode of vibration[10] of a regular tris(chelate)copper(II) complex, Figure 2(*b*). The extreme form of this distortion, as in [Cu(bipy)$_2$(O$_2$CH)][BF$_4$],[6] involves a clear (4 + 1 + 1*) type of distortion of the CuN$_2$N'$_2$OO' chromophore structure involving a very asymmetric bonding role of the OXO$^-$ anion. The alternative sense of distortion of a *cis*-distorted octahedral structure,[1] route D, Figure 1, involving the S_{1a} mode of vibration, Figure 2(*a*), is characterised in the three complexes having a regular *cis*-distorted octahedral CuN$_2$N'$_2$O$_2$ chromophore structure, namely, [Cu(bipyam)$_2$(ONO)][NO$_2$],[5] [Cu(phen)$_2$(O$_2$CMe)][BF$_4$]·2H$_2$O,[4] and [Cu(phen)$_2$(O$_2$CH)][BF$_4$],[11] in which the Cu–O distances range over 2.26—2.34 Å. No examples are known for the *regular* bicapped square-pyramidal structure in the [Cu(chelate)$_2$(OXO)]Y type complexes, nevertheless, an asymmetrical *cis*-distorted octahedral structure could exist, routes G (and H), Figure 1, if a linear combination of the S_{1a} and S_{2a} modes of vibration were involved. The original communication of the crystal structure of [Cu(bipy)$_2$(ONO$_2$)][NO$_3$]·H$_2$O, (1), reported a distorted trigonal-pyramidal structure, but a closer examination indicated that the O(2) atom was also within bonding

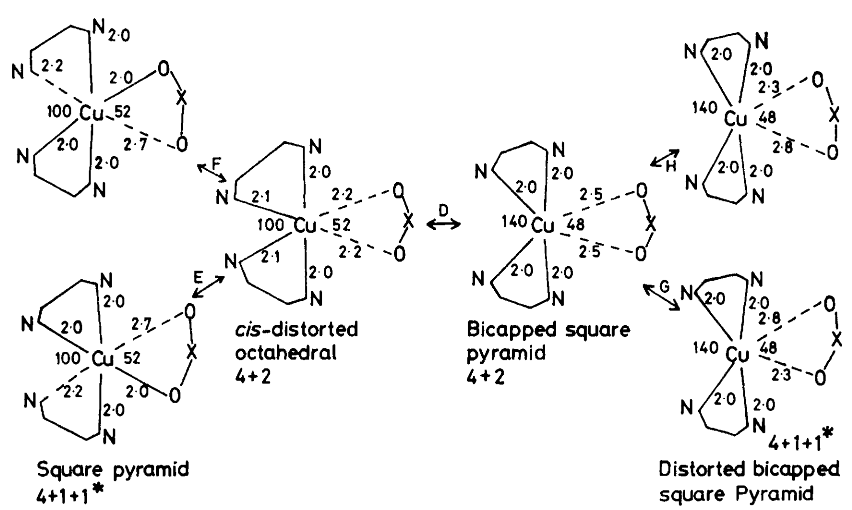

FIGURE 1 Structural pathways for the CuN$_2$N'$_2$OO' chromophore of the [Cu(bipy)$_2$(OXO)]$^+$ cation for distortion from regular *cis*-distorted octahedral to distorted square pyramid (route E and F) and to bicapped square pyramid (route D, and E or F): bond lengths (Å), angles (°)

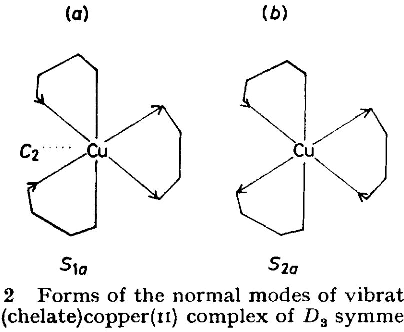

FIGURE 2 Forms of the normal modes of vibration of a tris(chelate)copper(II) complex of D_3 symmetry

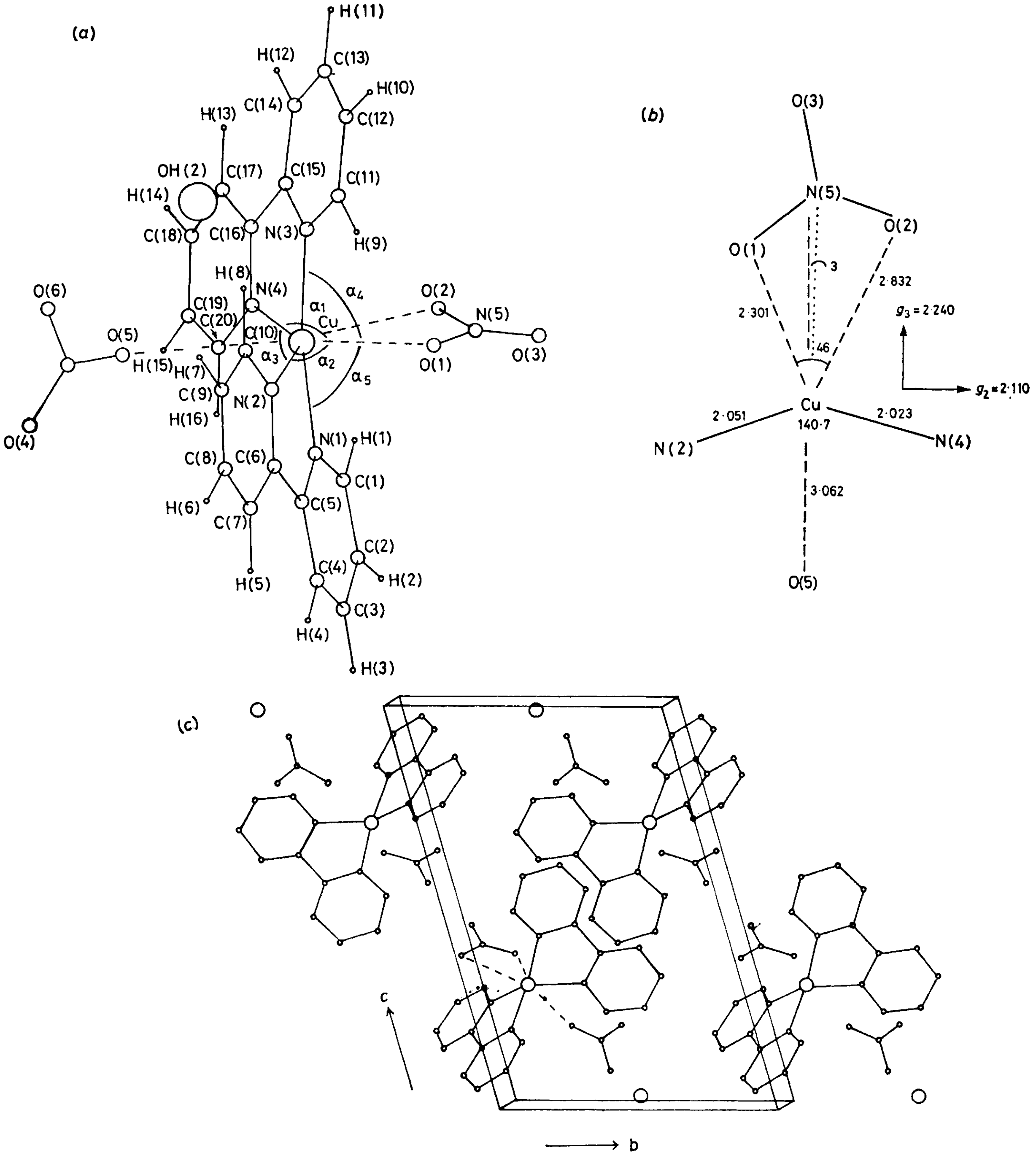

FIGURE 3 [Cu(bipy)$_2$(ONO$_2$)][NO$_3$]·H$_2$O, (1): (*a*) local molecular structure and atom-numbering scheme used; (*b*) projection down the N(1)–N(3) direction, bond lengths (Å), angles (°); (*c*) crystal packing

distance of the copper atom, at 2.832 Å, to give an unsymmetrically co-ordinated chelate nitrato-group, and an unsymmetrical bicapped square-pyramidal CuN$_2$N'$_2$OO' chromophore structure, Figure 3(*a*), corresponding to the G (or H) route distortion of the regular structure, Figure 1.

As the original data [12] for (1) were only refined to an *R* value of 0.13, and not reported in full,* in view of the novelty of the above structure the data for (1) were redetermined for comparison with those for [Cu(bipy)$_2$(OS$_2$O$_7$)]·H$_2$O, (2).[13] The electronic properties of (1) are also reported.

EXPERIMENTAL

Preparation.—Complexes (1) [14,15] and (2) [13] were prepared as previously described, and characterised by microanalysis.

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* A copy of the full set of co-ordinates was provided by the authors (to R. J. F.) in 1971.

Crystal Data.*—$C_{20}H_{18}CuN_6O_7$, $M = 517.54$, Triclinic, $a = 7.488(2)$, $b = 10.017(2)$, $c = 15.061(2)$ Å, $\alpha = 106.183(4)$, $\beta = 91.335(3)$, $\gamma = 89.662(3)$ °, $U = 1\,084.63$ Å^3, D_m (flotation) $= 1.58 \pm 0.02$ g cm^{-3}, $Z = 2$, $D_c = 1.60$ g cm^{-3}, $F(000) = 529.98$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) $= 10.18$ cm^{-1}, space group $P\bar{1}$, no systematic absences.

The unit-cell dimensions were determined and refined on a Philips PW 1100 four-circle diffractometer. The intensities were collected on the diffractometer with graphite-monochromatised Mo-K_α radiation. A θ—2θ scan mode was used and reflections with $3.0 < \theta < 30°$ in one quadrant were examined. A constant scan speed of 0.05° s^{-1} was used with a variable scan width of $(0.7 + 0.1 \tan\theta)°$. With the acceptance criterion of $I > 2.5\sigma(I)$, 3 683 reflections were retained. Lorentz and polarisation corrections were applied but no correction was made for absorption. The structure was solved by Patterson and Fourier techniques and refined by blocked-matrix least squares with anisotropic temperature factors for all of the non-hydrogen atoms, except the oxygen of the water molecule. The positions of the hydrogens were calculated geometrically and floated on the associated carbon or oxygen atoms, assuming C–H or O–H 1.08 Å, and a fixed temperature factor of 0.07 Å^2. The refinement converged when the shift-to-error ratio of any parameter was less than 0.05, with a refined weighting scheme, $w = k/[\sigma(F_o) + g(F_o)^2]$ and the final values of k and g were 1.835 2 and 0.000 886 respectively. Complex atomic scattering factors [17] were employed and the Cu atom was corrected for anomalous dispersion. The final R value was 0.054 6 and the maximum residual electron density was 0.65 e Å^{-3}.

TABLE 1

Atom co-ordinates (× 10^4) of $[Cu(bipy)_2(ONO_2)][NO_3]\cdot H_2O$ with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
Cu	3 854(1)	1 887(1)	2 941(1)
N(1)	2 781(4)	2 741(3)	4 152(2)
C(1)	2 262(5)	2 028(4)	4 743(3)
C(2)	1 660(6)	2 685(5)	5 611(3)
C(3)	1 615(5)	4 141(4)	5 894(3)
C(4)	2 183(5)	4 858(4)	5 302(3)
C(5)	2 748(4)	4 131(3)	4 426(2)
C(6)	3 426(4)	4 814(3)	3 736(2)
C(7)	3 331(5)	6 230(4)	3 864(3)
C(8)	3 977(6)	6 765(4)	3 180(4)
C(9)	4 677(6)	5 887(5)	2 398(3)
C(10)	4 694(5)	4 478(4)	2 316(3)
N(2)	4 097(4)	3 939(3)	2 975(2)
N(3)	5 214(4)	891(3)	1 836(2)
C(11)	6 792(5)	1 290(5)	1 592(3)
C(12)	7 731(6)	457(5)	867(3)
C(13)	7 088(7)	−834(5)	408(3)
C(14)	5 497(6)	−1 257(4)	674(3)
C(15)	4 555(5)	−375(3)	1 381(2)
C(16)	2 825(5)	−727(3)	1 708(2)
C(17)	1 906(6)	−1 934(4)	1 306(3)
C(18)	273(7)	−2 159(4)	1 664(3)
C(19)	−407(6)	−1 138(5)	2 401(3)
C(20)	580(5)	49(4)	2 776(3)
N(4)	2 194(4)	247(3)	2 454(2)
N(5)	6 671(4)	852(3)	4 001(2)
O(1)	6 491(4)	1 947(3)	3 766(2)
O(2)	5 577(5)	−95(3)	3 688(3)
O(3)	7 896(4)	762(3)	4 544(2)
N(6)	9 701(6)	6 280(4)	−1 499(3)
O(4)	10 940(6)	5 485(4)	−1 841(3)
O(5)	9 208(6)	7 200(4)	−1 859(3)
O(6)	9 081(6)	6 244(4)	−746(3)
OH(2)	6 965(12)	5 000(7)	249(5)

TABLE 2

Selected bond lengths (Å) for $[Cu(bipy)_2(ONO_2)][NO_3]\cdot H_2O$ with estimated standard deviations in parentheses

N(1)–Cu	1.973(5)	O(1)–N(5)	1.249(5)
N(2)–Cu	2.051(5)	O(2)–N(5)	1.239(5)
N(3)–Cu	1.986(5)	O(3)–N(5)	1.234(6)
N(4)–Cu	2.023(5)	O(4)–N(6)	1.244(7)
O(1)–Cu	2.301(5)	O(5)–N(6)	1.243(8)
O(2)–Cu	2.832(5)	O(6)–N(6)	1.244(8)
O(5)–Cu	3.062(6)		

TABLE 3

Selected bond angles (°) for $[Cu(bipy)_2(ONO_2)][NO_3]\cdot H_2O$ with estimated standard deviations in parentheses

N(2)–Cu–N(1)	81.0(2)	O(2)–N(5)–O(1)	117.9(4)
N(3)–Cu–N(1)	170.7(1)	O(3)–N(5)–O(1)	119.3(4)
N(3)–Cu–N(2)	103.7(2)	O(3)–N(5)–O(1)	122.7(5)
N(4)–Cu–N(1)	100.0(2)	O(5)–N(6)–O(4)	119.9(6)
N(4)–Cu–N(2)	140.7(1)	O(6)–N(6)–O(4)	119.7(6)
N(4)–Cu–N(3)	81.5(2)	O(6)–N(6)–O(5)	119.9(5)
O(1)–Cu–N(1)	85.5(2)		
O(1)–Cu–N(2)	91.8(2)		
O(1)–Cu–N(3)	86.3(2)		
O(1)–Cu–N(4)	127.5(2)		

TABLE 4

Summary of some relevant mean planes (r.m.s.d. = root-mean-square deviation in Å) for $[Cu(bipy)_2(ONO_2)][NO_3]\cdot H_2O$

		r.m.s.d.
Plane (1):	N(1), C(1)—C(5)	0.0070
Plane (2):	N(2), C(6)—C(10)	0.0053
Plane (3):	N(1), C(1)—C(10), N(2)	0.0521
Plane (4):	N(3), C(11)—C(15)	0.0111
Plane (5):	N(4), C(16)—C(20)	0.0130
Plane (6):	N(3), C(11)—C(20), N(4)	0.0295
Plane (7):	N(5), O(1)—O(3)	0.0038
Plane (8):	N(6), O(4)—O(6)	0.0197
Plane (9):	Cu, N(1)—N(4)	0.3906
Plane (10):	Cu, N(2), N(4), O(1)	0.0000

Dihedral angles (°) between planes: (1)—(2), 6.0; (4)—(5), 3.1; (3)—(6), 44.6; (7)—(10), 10.5; (7)—(8), 85.9

All calculations were carried out using the SHELX 76 and XANADU (G. M. Sheldrick), PLUTO (S. Motherwell), and XPUB (R. Taylor) systems of programs on an IBM 370/138 computer. The final atomic co-ordinates are given in Table 1, selected bond lengths in Table 2, and selected bond angles in Table 3. Table 4 gives some relevant mean-plane data. The final structure factors, anisotropic temperature factors, calculated hydrogen-atom positions, full bond-length, bond-angle, and mean-plane data are in Supplementary Publication No. SUP 23101 (31 pp.).† Figure 3(*a*) illustrates the structure of (1) and the atom-numbering scheme used, and Figure 3(*c*), the crystal packing.

Electronic Properties.—These were recorded as previously described.[18,19] Figure 4(*a*) illustrates the electronic reflectance spectrum of (1) and Figure 4(*b*), the polycrystalline e.s.r. spectrum of (1). The single-crystal e.s.r. spectra of (1) showed only one signal in any direction, using the six-position method.[20] The crystal g values were determined, along with their directions, and are reported in Table 5, along with the direction of some relevant Cu–N, Cu–S, and N–N directions. As the space group of (1) is triclinic $P\bar{1}$,

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* The original data were collected using the following unit-cell data: $a = 7.53$, $b = 10.05$, $c = 15.65$ Å, $\alpha = 111.8$, $\beta = 91.0$, $\gamma = 90.5°$, transformation matrix [16] $[100, 0\bar{1}1, 001]$.

† For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

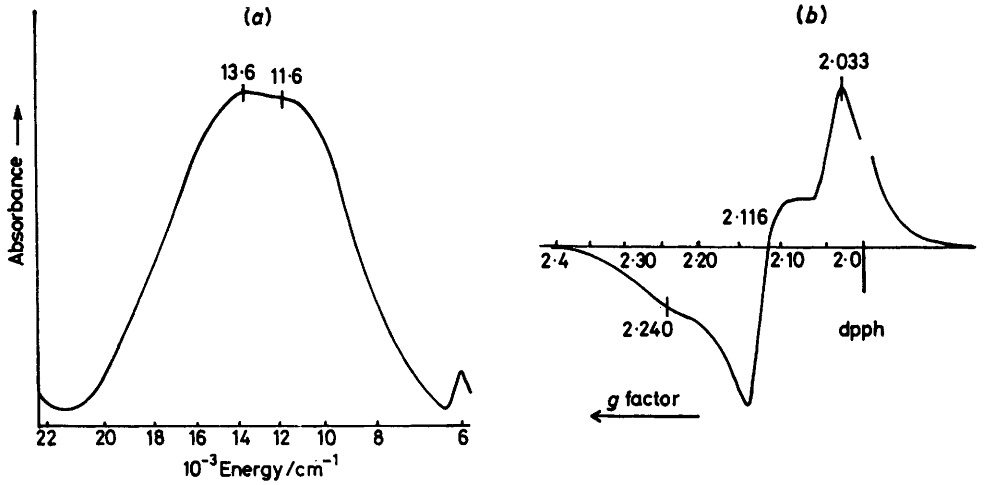

FIGURE 4 Electronic reflectance (*a*) and polycrystalline e.s.r. (*b*) spectra of [Cu(bipy)$_2$(ONO$_2$)][NO$_3$]·H$_2$O (dpph = diphenylpicrylhydrazyl)

the crystal *g* values equate with the local molecular *g* factors. The polarised single-crystal electronic spectra of (1) were recorded in the main faces of the crystal, Figure 5, and consisted of a main band at 13 400 cm^{-1} in *z* polarisation (011), at 12 200 cm^{-1} in *y* polarisation (001), and at 13 600 cm^{-1} with a substantial shoulder at 11 400 cm^{-1} in *x* polarisation (100).

TABLE 5

Single-crystal *g* factors, their angular directions (°) and those of some atom–atom directions for (*a*) [Cu(bipy)$_2$(ONO$_2$)][NO$_3$]·H$_2$O and (*b*) [Cu(bipy)$_2$(OS$_2$O$_7$)]·H$_2$O

(*a*)	*X*	*Y*	*Z*
2.023	55	82	36
2.110	119	31	79
2.240	48	60	124
N(1)–N(3)	62	63	40
Cu–N(5)	45	70	128
N(2)–N(4)	112	42	86
(*b*)			
2.047	89	38	129
2.110	107	53	41
2.246	16	80	76
N(1)–N(3)	90	48	139
Cu–S(1)	0	89	94
N(2)–N(4)	92	52	37

RESULTS AND DISCUSSION

Crystal Structure.—The structure of (1) consists of a [Cu(bipy)$_2$(ONO$_2$)]$^+$ cation and an NO$_3^-$ anion with a water molecule in the lattice. The structure of the cation is at least five-co-ordinate, with a structure intermediate between trigonal bipyramidal (as suggested previously [12]) and square-based pyramidal. In addition, the O(2) atom of the co-ordinated nitrate group is involved at a potentially bonding distance of 2.832 Å, on the same side of the Cu,N(1)—N(4) plane as O(1), to give an unsymmetrical bidentate co-ordinating nitrate group. As the [Cu–O(2)] − [Cu–O(1)] difference of 0.53 Å is less than that previously suggested [21] as the limit for an unsymmetrically co-ordinated bidentate nitrate group (0.7 Å), this indicates that the [Cu(bipy)$_2$(ONO$_2$)]$^+$ cation is best considered as six-co-ordinate, with a CuN$_2$N'$_2$OO' chromophore. There are no unusual bond lengths or angles in the bipy ligands,[22] the individual pyridine rings are reasonably planar, Table 4, and within each bipy ligand the pyridine rings are twisted with respect to each other by 6.0 and 3.1°, respectively, within the range of 0—13° previously observed [12,21] for the angle of twist of the bipy ligand. The nitrate ions involve reasonable N–O bond lengths,[21] mean 1.243 Å, and trigonal bond angles, mean 119.9°. In the co-ordinated nitrate group, the spread of the N–O bond distances is just significant and the N(5)–O(1) bond distance is longer than the N(5)–O(2) and the N(5)–O(3) bond distances, consistent with the ' predominantly ' unidentate function of the nitrate group. In the ionic nitrate group the spread of the N–O bond distances is not significant, and suggests that the Cu–O(5) distance of 3.062 Å is too long for even semi-co-ordination of this nitrate to the copper(II) ion.[23]

The Structure of the CuN$_2$N'$_2$OO' *Chromophore.*—The

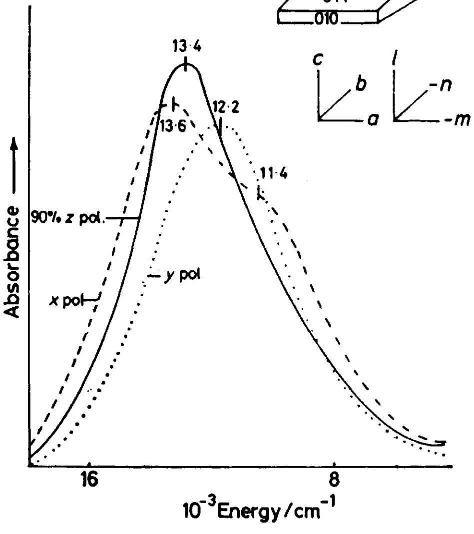

FIGURE 5 The polarised single-crystal electronic spectra of [Cu(bipy)$_2$(ONO$_2$)][NO$_3$]·H$_2$O [*x*, *y*, and *z* refer to the axes of Figure 3(*a*)]

five-co-ordinate CuN_4O chromophore may be considered as trigonal bipyramidal,[12] Figure 3(*a*), or square-based pyramidal, Figure 3(*b*). In the former, the trigonal N(1)–Cu–N(3) direction is almost linear, 170.7°, with two Cu–N distances of 1.973 and 1.986 Å, which are only just significantly different. The two in-plane Cu–N distances, 2.051 and 2.023 Å, are again significantly different, and *ca.* 0.05 Å longer than the axial Cu–N distances, rather less than the difference of 0.1 Å previously observed in trigonal-bipyramidal copper(II) complexes.[24] The in-plane Cu–O distance of 2.301 Å is significantly longer than the normal in-plane trigonal-bipyramidal Cu–O distance of 2.0—2.1 Å,[25] and suggests that the Cu–O distance is best considered as a relatively long Cu–ligand distance of a square-pyramidal structure with the N(1), N(2), N(3), and N(4) atoms forming the basal plane with the O(1) atom occupying the apical fifth ligand position as in $[Cu(bipy)_2(OS_2O_7)]\cdot H_2O$,[13] (2), and $[Cu(bipy)_2(OH_2)][S_2O_6]$,[26] (3), Figure 6(*a*) and (*b*).

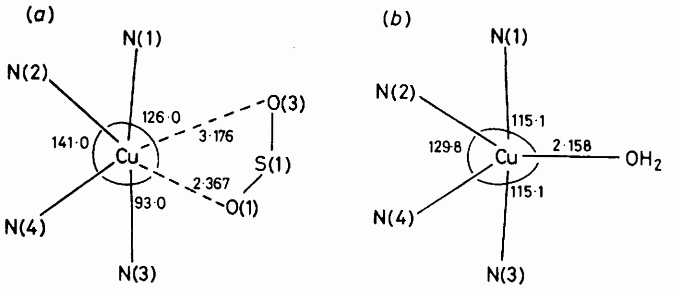

FIGURE 6 Local molecular structures of (*a*) $[Cu(bipy)_2(OS_2O_7)]\cdot H_2O$, (2), and (*b*) $[Cu(bipy)_2(OH_2)][S_2O_6]$, (3); bond lengths (Å), and angles (°)

In (1), in addition to the elongation of the Cu–O(1) distance to 2.301 Å, there is an increase of the N(2)–Cu–N(4) angle to 140.7°, and clear asymmetry in the α_1 and α_2 angles, Figure 3(*a*), 127.7 and 91.9°, respectively. The O(1) atom lies in the Cu,N(2),N(4) plane for no crystallographic reason and the O(2) atom of the co-ordinated nitrate occupies the N(2)–Cu–O(1) angle at a distance of 2.832 Å consistent with weak semi-co-ordination [23] (see above). The mean plane of this nitrate ion makes an angle of 10.5° with the Cu,N(2),N(4),O(1) plane and 85.9° with the plane of the ionic nitrate ion, Table 4. Figure 3(*b*) shows a projection of the Cu,N(2), N(4), O(1),O(2), and N(5) atoms viewed down the N(1)–N(3) direction and emphasises how symmetrically the co-ordinated nitrate group is positioned with respect to the N(1),N(2),N(3),N(4) atom basal plane, with the Cu $\cdots$ N(5) direction making an angle of only 3° to the bisector of the N(2)–Cu–N(4) angle, despite the asymmetry in the two Cu–O bond distances to this nitrate group.

Tetrahedral Distortion of the CuN_4 *Chromophore.*—In the trigonal-pyramidal description of the CuN_4O chromophore structure of (1) the out-of-plane angular distortions from 90° are ± 10°, in particular the O(1)–Cu–N(1) (α_4) and O(1)–Cu–N(3) (α_5) angles are 85.5 and 86.3° respectively, both significantly less than 90°, and imply that the N(1)–Cu–N(3) angle of 170.7° is towards the Cu–O(1) direction. This is confirmed by the mean plane, Table 4, through the N(1),N(2),N(3), and N(4) atoms, where the N(1) and N(3) atoms lie further from the plane than does the copper atom, which lies 0.26 Å from this plane. Consequently, the CuN_4 chromophore has a *genuine tetrahedral distortion* about the copper atom, with N(1)–Cu–N(3) and N(2)–Cu–N(4) angles of 170.7 and 140.7° respectively. This not only contrasts with the bulk of the $[Cu(bipy)_2L]Y$ complexes,[13,27] which have $\alpha_4 + \alpha_5 > 180°$, but with genuinely square-based pyramidal complexes,[28] where the four in-plane ligand atoms lie below the copper atom and on the side opposite to the fifth ligand direction,[18] and distort towards the trigonal-bipyramidal structure [27] rather than towards the tetrahedral structure observed in (1). Only three $[Cu(bipy)_2L]X_2$ complexes are known to involve α_4 and α_5 angles less than 90°, namely, $[Cu(bipy)_2(OS_2O_7)]\cdot H_2O$,[13] (2), $[Cu(bipy)_2(OH_2)][S_2O_6]$,[26] (3), and (1). In (3), $\alpha_1 = \alpha_2 = 115.0°$, and α_3 is greater than 120° (129.8°), but in (1) and (2) not only is there an increasing elongation of the Cu–O(1) bond distance, Figure 6, but there is an increased asymmetry (Figure 6, ref. 13) in the $\alpha_2 - \alpha_1$ angle; in (1) this is 35.7° and in (2), 32.3°.

Structural Pathways for the $CuN_2N'_2OO'$ *Chromophore.*—These distortion correlations of (1) can be rationalised using the structural pathways [8] of Figure 1, starting with a regular *cis*-distorted octahedron. The sense of the distortions of Figure 1 can be associated with the S_{1a} and S_{2a} modes of vibration of a regular tris(chelate)copper(II) complex,[10] Figure 2, where the D,E (or F) and G (or H) route distortions may be related by a linear combination of the S_{1a} and S_{2a} modes of distortion of the $CuN_2N'_2OO'$ chromophore. If the S_{1a} mode predominates, the regular *cis*-distorted octahedral structure arises as in $[Cu(bipyam)_2(ONO)][NO_2]$,[5] $[Cu(phen)_2(O_2CMe)][BF_4]\cdot 2H_2O$,[4] and $[Cu(phen)_2(O_2CH)][BF_4]$,[11] but extending to the regular bicapped square-pyramidal structure. If an equal mixture of S_{1a} and S_{2a} is involved then the distorted dicapped square-pyramidal structure will predominate, as in (1) and (2). If the S_{2a} mode alone is involved in the structural pathway the E (or F) route of distortion will predominate to give a (4 + 1 + 1 *) square-pyramidal distortion with elongation along the Cu–N(4) direction as in $[Cu(bipy)_2(O_2CMe)][BF_4]$,[2] $[Cu(bipy)_2(O_2CMe)][ClO_4]\cdot H_2O$,[2] and $[Cu(bipy)_2(O_2CH)][BF_4]$.[6]

Bicapped Square-pyramidal Structure.—This stereochemistry, Figure 1, involves a six-co-ordinate CuN_4O_2 chromophore with a clear *cis*-distortion, Cu–O = 2.5 Å, *i.e.* a (4 + 2) co-ordination; it differs from the *cis*-distorted octahedron,[1,18] not only in the magnitude of the *cis* distortion, but with increasing *cis* distortion, there is a corresponding increase of the α_3 angle from <120° in the *cis*-distorted octahedron to >120° in the bicapped square pyramid. In the $[Cu(bipy)_2(OXO)]Y$ complexes the structures of (1) and (2) are representative of a distorted bicapped square-pyramidal structure, but there are no examples known of a regular bicapped square-pyramidal structure. This structure does exist in

[Cu(tben)][BF$_4$]$_2$[29] [where tben = *NNN'N'*-tetrakis(2'-benzimidazolylmethyl)ethane-1,2-diamine], Figure 7(*a*), where tben is a sexidentate nitrogen-donor ligand able to occupy all six co-ordinate positions of a CuN$_6$ chromophore. Using the notation of Figure 1, the copper atom occupies a crystallographic two-fold position to yield a regular bicapped square pyramid, the N(1)–Cu–N(3) angle is near linear 165.6° [170.7° in (1)], and N(2)–Cu–N(4) is 142.9° [140.7° in (1)]. The *cis*-distorted Cu–N distances are equivalent, 2.50 Å, the Cu,N(1),N(2),N(3), N(4) plane has a tetrahedral twist, comparable to that described in (1), and the Cu,N(2),N(4),N(5),N(6) plane is reasonably planar, *cf.* the Cu,N(2),N(4),O(1),O(2) plane of (1). The only major difference from (1) lies in the equivalence of the Cu–N(5) and Cu–N(6) distances and the N(5)–Cu–N(6) angle of 70.3° due to the five-membered ethylenediamine copper ring system.[29] The above structure of (4) contrasts with the structure of [Cu(H$_2$edta)(OH$_2$)] [30] (5) (where H$_4$edta = ethylenediamine-tetra-acetic acid), a potentially sexidentate chelate ligand, in which the H$_2$edta co-ordinates as a quinquedentate ligand, Figure 7(*b*), and the local molecular structure of the CuN$_2$O$_4$ chromophore is elongated rhombic octahedral, as more frequently found [18] for six-co-ordinate copper(II) complexes. The marked elongation of the Cu–N(5) and Cu–N(6) distances of (4) plus their relation by the crystallographic two-fold axis all suggest that the two-fold axis of (4) equates with the principal axis of the CuN$_6$ chromophore with the N(1)—N(4) atoms, representing the equational plane, notwithstanding the clear tetrahedral twist of these four nitrogen atoms. In (1) this tetrahedral distortion of the N(1)—N(4) atoms has traditionally [31] been associated with inability of the [Cu(bipy)$_2$]$^{2+}$ cation to have a planar conformation due to the steric hindrance [31] of the C(3) and C(3') hydrogen atoms. As there are no such constraints in tben the origin of this tetrahedral distortion cannot arise from steric hindrance, as tben is a symmetrical sexidentate ligand with *four* equivalent donor atoms N(1)—N(4). While the structure of (1) bears a recognisable relationship to the D_3 symmetry of a tris(chelate)copper(II) system, Figure 1, despite the presence of non-equivalent ligands, it is impossible for the chelate ligand system of (4) to have even approximate D_3 symmetry. It is therefore surprising that the structures of (1) and (4) are so comparable, especially with the presence of a C_2 axis in (4), and its clear absence in (1), and suggests that the soft modes of vibration (which are responsible for the structural pathways of Figure 1) are basic to the nuclear framework of the CuN$_4$O$_2$ chromophore, and are only marginally influenced by the restraints introduced by the different chelate function of the ligands, *cf.* (1) and (5).

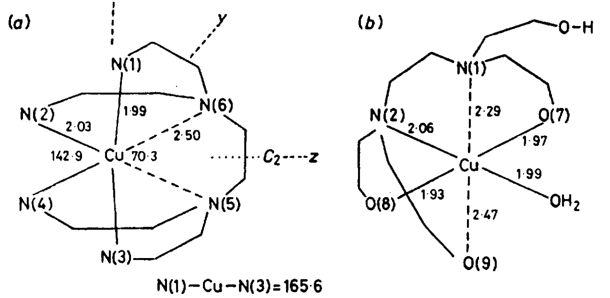

FIGURE 7 Local molecular structures of (*a*) [Cu(tben)][BF$_4$]$_2$, (4) and (*b*) [Cu(H$_2$edta)(OH$_2$)], (5); bond lengths (Å), angles (°)

Consequently, in this distorted bicapped square-pyramidal structure the principal axis is best equated with the perpendicular to the Cu,N(1)—N(4) plane [approximately the Cu–N(5) direction, and not to the Cu–O(2) direction]. Thus in the even more distorted structure [13] of (2), the principal axis is best associated with the perpendicular to the Cu,N(1)—N(4) plane, which makes an angle of 5.1° to the Cu–S(1) direction [13] [the Cu,N(2),N(4),O(1) plane makes an angle of 11.2° to the S(1),O(1),O(3) plane, Figure 6(*b*)], and the structure of (2) is also best described as distorted bicapped square pyramidal.

Electronic Properties.—The electronic reflectance spectrum of (1), Figure 4(*a*), consists of a rather broad peak with a maximum at 13 600 cm^{-1}, and a poorly resolved shoulder at 11 600 cm^{-1}. This contrasts with the single peak at 14 180 cm^{-1} for (2),[13] at 15 150 cm^{-1} for the elongated rhombic octahedral structure [32] of [Cu(bipy)$_2$(ClO$_4$)][ClO$_4$],[15] and at 12 450 cm^{-1} for (2) [26] and emphasises the insensitivity of these electronic spectra to the various stereochemistries present in these [Cu(bipy)$_2$(OXO)]Y complexes. Nevertheless, they clearly distinguish the present complex from the regular *cis*-distorted octahedral complexes,[33] and from the distorted square-pyramidal (4 + 1 + 1*) complex,[2,6] route E (or F), both of which are characterised by two broad well resolved peaks in the region 9 000—15 700 cm^{-1}. The electronic spectrum of (1) also contrasts with that of (4), which consists [34] of a peak at 14 600 cm^{-1}, and a medium shoulder at 9 400—10 500 cm^{-1}, despite the comparable structures of (1) and (4).

The polycrystalline e.s.r. spectrum of (1) is rhombic and yields the crystal g values 2.033, 2.116, and 2.240. As the space group of (1) is triclinic $P\bar{1}$, the crystal g values correspond to the local molecular g factors. The more accurate single-crystal g factors are listed in Table 5 along with their angular directions, and those of some significant atom–atom directions. The g factors are clearly rhombic with an R value of 0.67 [$R = (g_2 - g_1)/(g_3 - g_2)$],[18] suggesting an approximately $d_{x^2-y^2}$ ground state for the copper(II) ion in the CuN$_2$N'$_2$OO' chromophore. There is a clear correlation of the highest g factor with the Cu–N(5) direction, Table 5(*a*), and a reasonable correlation of the intermediate and lowest g factors with the N(2)–N(4) and N(1)–N(3) directions respectively. Thus, despite the relatively low g value of 2.023, Table 5(*a*), which could imply [18] an approximately d_{z^2} ground state for a trigonal-bipyramidal CuN$_4$O chromophore,[35] the g values of (1) support the square-pyramidal description of the structure of (1). As the highest g value, 2.240, correlates with the Cu–N(5) direction rather than the Cu–O(1) direction, the g factors are more consistent with the six-co-ordinate bicapped square-pyramidal description of this structure, rather than the original five-co-ordinate trigonal-bipyramidal description.[12] Similar conclusions can be deduced from the correlation of the local molecular directions and the direction of the single-crystal g factors of (2), Table 5(*b*). It is then of interest to compare the single-crystal g factors (Figure 8) of (*a*) a distorted bicapped square-pyramidal structure, as in (1), of (*b*) a *cis*-distorted octahedral structure, as in $[Cu(bipy)_2(ONO)][NO_3]$,[28] (6), and (*c*) a distorted square-pyramidal (4 + 1 + 1 *) structure as in $[Cu(bipy)_2(O_2CH)][BF_4]$,[6] (7). All *three* complexes have comparable lowest g values 2.01—2.03, which all lie parallel to the N(1)–Cu–N(3) direction. In (6) and (1) the two highest g values lie parallel to the Cu–X direction of the OXO group, and perpendicular to this direction, in the plane at right angles to the N(1)–Cu–N(3) direction, but whereas in (1), it is the g_3 factor that lies parallel to the Cu–X direction, in (6), it is the g_2 factor that lies parallel to the Cu–X direction. In (7) the g_3 factor lies at *ca.* 135° to the Cu–X direction, and approximately parallel to the Cu–N(4) direction, Figure 8(*c*). Thus, across the structural pathway of Figure 1 in the plane at right angles to the N(1)–Cu–N(3) direction, there are systematic variations, not only in the relative values of g_2 and g_3 (and hence in the R values), but also in the direction of the g_2 and g_3 factors relative to the Cu–X directions, which together offer a rational description of the distortions depicted in the structural pathways of Figure 1. In the route E (or F) distortion, from (6) to (7), the N(2)–Cu–N(4) angle remains essentially unchanged and the rotation of the g factors is primarily associated with the decrease in the length of the Cu–O(1) bond distance and the synergic increase in length of the Cu–N(4) bond distance. In the D plus H (or F) route distortion, the interchange of the g_2 and g_3 factors is primarily associated with the increase in the Cu–O(2) bond distance by *ca.* 0.5 Å and the increase in the N(2)–Cu–N(4) bond angle (103.0 to 140.7°) from (6) to (1). Within the structural pathway of Figure 1, the R values offer a means of distinguishing (6) from (1) and (7), and although the g factors cannot distinguish (1) from (7), the use of the electronic reflectance spectra to distinguish (7) with two bands, from (1) with a single broad band, offer an ' electronic criterion of stereochemistry '[36] to distinguish the distorted square-pyramidal (4 + 1 + 1 *) structure and the distorted bicapped square-pyramidal structure from a *cis*-distorted octahedral structure. The observed single-crystal g factors[37] of (4), 2.031, 2.115, and 2.292 are then consistent with the bicapped square-pyramidal structure, Figure 7(*a*).

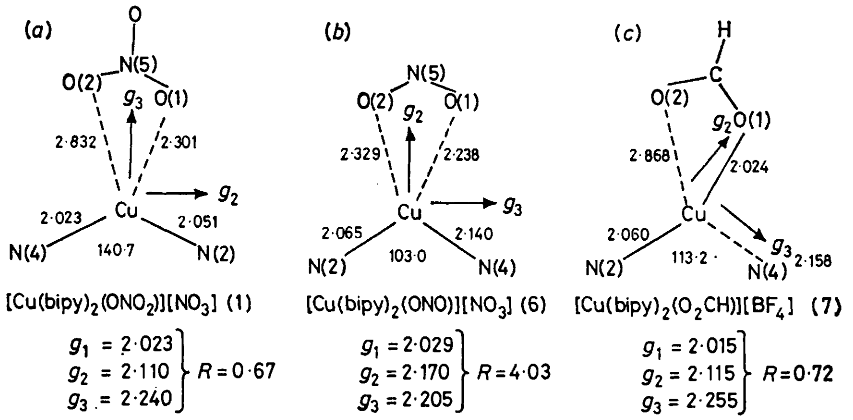

FIGURE 8 $[Cu(bipy)_2(OXO)]Y$: directions of the local molecular g factors of (*a*) a bicapped square pyramid, (*b*) *cis*-distorted octahedron, and (*c*) distorted square pyramid (4 + 1 + 1 *). Projections down the N(1)–N(3) direction; bond lengths (Å), angles (°)

The polarised single-crystal electronic spectra of (1), Figure 5, show a single peak at 13 400 cm^{-1} in z polarisation, at 12 200 cm^{-1} in y polarisation, and a maximum at 13 600 cm^{-1}, plus a shoulder at 11 400 cm^{-1}, in x polarisation. As the Cu,N(2),N(4),O(1) atoms form such a clear plane, with the Cu,N(1),N(3) plane at 80° to it, the spectra are assigned, Table 6, in C_{2v} effective symmetry[18] using the selection rules previously reported,[18] Table 6, and establish the tentative one-electron orbital sequence, $d_{x^2-y^2} > (d_{xy}) > d_{yz} > d_{z^2} > d_{xz}$.

TABLE 6

Tentative assignment of the polarised single-crystal electronic spectra of $[Cu(bipy)_2(ONO_2)][NO_3]\cdot H_2O$ in C_{2v} symmetry with a $d_{x^2-y^2}$ ground state

Transition	C_{2v}
$d_{z^2}\rightarrow d_{x^2-y^2}$	13 400 (z polarisation)
$d_{xy}\rightarrow d_{x^2-y^2}$	11 400
$d_{xz}\rightarrow d_{x^2-y^2}$	13 600 (x polarisation)
$d_{yz}\rightarrow d_{x^2-y^2}$	12 200 (y polarisation)

This sequence is consistent with long-bonded O(1) and O(2) atom positions and reflects the distortion of the N(2) and N(4) atoms out of the xy plane to interact with the d_{yz} orbital to lift it significantly above the d_{xz} level, which is essentially non-bonding. The $d_{xy}\rightarrow d_{x^2-y^2}$ transition is electronically forbidden, but is assigned to the shoulder at 11 400 cm^{-1} in x polarisation, but why it is so separated from the d_{xz} level is not clear, except that the *ca.* 80° angle of the bipy ligands could account for the destabilisation of the d_{xy} orbital.*

We acknowledge the award of a Senior Demonstratorship (to P. H. and S. T.), help in data collection by Drs. P. G. Owston, M. McPartlin, and K. Hendrick (The Polytechnic of North London, Holloway), the Computer Bureau, U.C.C. for computing facilities, Drs. G. Sheldrick, S. Motherwell, and R. Taylor (Cambridge University) for the use of their programs, the Microanalysis Section, U.C.C., for microanalysis, and B. O'Mahony for technical assistance.

[1/010 *Received, 5th January,* 1981]

* *Note added at proof*: Since this paper was accepted for publication a re-determination of the structure of (1) has appeared; see H. Nakai *Bull. Chem. Soc. Jpn.*, 1980, **53**, 1321.

REFERENCES

[1] F. S. Stephens and I. M. Procter, *J. Chem. Soc. A*, 1969, 1248.

[2] B. J. Hathaway, N. Ray, D. Kennedy, N. O'Brien, and B. Murphy, *Acta Crystallogr., Sect. B*, 1980, **36**, 1371.

[3] C. J. Simmons, P. W. Payne, K. Seff, F. Clifford, and B. J. Hathaway, *Inorg. Chem.*, submitted for publication.

[4] C. J. Simmons, K. Seff, F. Clifford, and B. J. Hathaway, *Acta Crystallogr.*, submitted for publication.

[5] P. C. Power, Ph.D. Thesis, University College, Cork, 1975; H. A. Chen and J. P. Fackler, personal communication.

[6] W. Fitzgerald and B. J. Hathaway, *J. Chem. Soc., Dalton Trans.*, 1981, 567.

[7] A. Walsh, B. Walsh, B. Murphy, and B. J. Hathaway, *Acta Crystallogr.*, accepted for publication.

[8] H. B. Burgi, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 460; E. L. Muetterties, and L. J. Guggenberger, *J. Am. Chem. Soc.*, 1974, **96**, 1748; J. D. Dunitz, '*X*-Ray Analysis and Structure of Organic Molecules,' Cornell University Press, London, 1979, ch. 7; J. D. Dunitz, at the J. M. Robertson Symposium, Glasgow, September 1980; O. Murray-Rust and J. Murray-Rust, *Acta Crystallogr., Sect. A*, 1975, **31**, S64.

[9] A. Walsh, B. Walsh, B. Murphy, S. Tayagi, and B. J. Hathaway, *J. Chem. Soc., Dalton Trans.*, in the press.

[10] H. B.Burgi, personal communication.

[11] W. Fitzgerald, V. Kasempimolporn, and B. J. Hathaway, unpublished work.

[12] H. Nakai, S. Ooi, and H. Kuroya, *Bull. Chem. Soc. Jpn.*, 1970, **43**, 577.

[13] W. D. Harrison and B. J. Hathaway, *Acta Crystallogr., Sect. B*, 1980, **36**, 1069.

[14] F. M. Jaeger and J. A. Dijk, *Z. Anorg. Allg. Chem.*, 1936, **227**, 273.

[15] B. J. Hathaway, I. M. Procter, R. C. Slade, and A. A. G. Tomlinson, *J. Chem. Soc. A*, 1969, 2219.

[16] K. Hendrick, personal communication.

[17] D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891; D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, 1965, **18**, 104.

[18] B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.*, 1970, **5**, 143.

[19] B. J. Hathaway, P. Nicholls, and D. Barnard, *Spectrovision*, 1969, **22**, 4.

[20] D. E. Billing and B. J. Hathaway, *J. Chem. Phys.*, 1969, **50**, 2258.

[21] C. C. Addison, N. Logan, S. C. Wallwork, and C. D. Garner, *Q. Rev.*, 1971, **25**, 289.

[22] F. S. Stephens, *J. Chem. Soc. A*, 1969, 833; 1248; 2081.

[23] I. M. Procter, B. J. Hathaway, and P. Nicholls, *J. Chem. Soc. A*, 1968, 1678.

[24] F. Huq and A. C. Shapski, *J. Chem. Soc. A*, 1971, 1927.

[25] B. J. Hathaway and P. G. Hodgson, *J. Inorg. Nucl. Chem.*, 1973, **35**, 4071.

[26] W. D. Harrison and B. J. Hathaway, *Acta Crystallogr., Sect. B*, 1979, **35**, 2910.

[27] W. D. Harrison, D. Kennedy, and B. J. Hathaway, *Inorg. Nucl. Chem. Lett.*, accepted for publication.

[28] M. Duggan, N. Ray, G. Tomlinson, P. Brint, and K. Pelin, *J. Chem. Soc., Dalton Trans.*, 1980, 1342.

[29] P. J. M. W. L. Birker, S. Gorter, H. M. J. Hendriks, and J. Reedijk, *Inorg. Chim. Acta Lett.*, 1980, **45**, L63.

[30] F. S. Stephens, *J. Chem. Soc. A*, 1969, 1723.

[31] C. K. Jorgensen, *Acta Chem. Scand.*, 1955, **9**, 1362.

[32] H. Nakai, *Bull. Chem. Soc. Jpn.*, 1971, **44**, 2412.

[33] I. M. Procter, B. J. Hathaway, D. E. Billing, R. J. Dudley, and P. Nicholls, *J. Chem. Soc. A*, 1969, 1192.

[34] J. Reedijk, S. Tyagi, and B. J. Hathaway, unpublished work.

[35] R. J. Dudley, B. J. Hathaway, P. G. Hodgson, P. C. Power, and D. J. Loose, *J. Chem. Soc., Dalton Trans.*, 1974, 1005.

[36] B. J. Hathaway, *J. Chem. Soc., Dalton Trans.*, 1972, 1196.

[37] S. Tyagi and B. J. Hathaway, unpublished work.