oxygens of the water molecules is 2·43 (2) Å. The average O–O distance in the first ring is 2·62 (2) Å, whereas in the second ring it is 2·66 (4) Å. This is indicative of the coordination of the first ring to the samarium. The present Sm–O distance agrees fairly well with the average value found in the $Sm(ClO_4)_3$-(dibenzo-18-crown-6) complex, where the Sm—O distances range from 2·36 (1) to 2·59 (1) Å with an average value of 2·51 (1) Å and Sm is ten coordinated (Ciampolini, Nardi, Cini, Mangani & Orioli, 1979). The perchlorate ions are disordered, as can be seen from the fact that the bond lengths between chlorine and oxygens in the ions are not equal.

A structure determination on the lanthanum complex of the same ligand was also performed, which gave rise to an identical structure except for the replacement of

samarium by a lanthanum atom. The report will be published elsewhere.

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Pseudo-Jahn–Teller Complexes: The Structures of Nitritobis(1,10-phenanthroline)copper(II) Tetrafluoroborate (I), $[Cu(C_{12}H_8N_2)_2(NO_2)]BF_4$, and Acetatobis(1,10-phenanthroline)copper(II) Tetrafluoroborate Dihydrate (II), $[Cu(C_{12}H_8N_2)_2(C_2H_3O_2)]BF_4 \cdot 2H_2O$

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Abstract. (I): $M_r = 556 \cdot 8$, triclinic, $P\bar{1}$, $a = 10 \cdot 442$ (4), $b = 16 \cdot 022$ (3), $c = 7 \cdot 408$ (2) Å, $\alpha = 93 \cdot 13$ (2), $\beta = 101 \cdot 86$ (2), $\gamma = 110 \cdot 13$ (2)°, $V = 1128 \cdot 2$ (5) Å^3, $Z = 2$, $D_m = 1 \cdot 62$ (1), $D_x = 1 \cdot 639$ Mg m^{-3}, $F(000) = 562$, $\mu(Mo\,K\alpha) = 1 \cdot 03$ mm^{-1}. (II): $M_r = 605 \cdot 8$, monoclinic, $P2/c$, $a = 9 \cdot 639$ (2), $b = 8 \cdot 237$ (2), $c = 17 \cdot 575$ (4) Å, $\beta = 108 \cdot 66$ (2)°, $V = 1322 \cdot 1$ (5) Å^3, $Z = 2$, $D_m = 1 \cdot 53$ (1), $D_x = 1 \cdot 522$ Mg m^{-3}, $F(000) = 618$, $\mu(Mo\,K\alpha) = 0 \cdot 86$ mm^{-1}. The crystal structures of $[Cu(phen)_2(ONO)]BF_4$ (I) and $[Cu(phen)_2(CH_3CO_2)]$-$BF_4 \cdot 2H_2O$ (II) (phen = 1,10-phenanthroline) have been determined at room temperature by single-crystal X-ray diffraction techniques using counter methods and Mo $K\alpha$ radiation ($\lambda\,K\alpha_1 = 0 \cdot 70930$ Å; $\lambda\,K\alpha_2 = 0 \cdot 71359$ Å). The structures have been refined by full-matrix least-squares procedures using 3266 (3σ) and 1834 (2σ) unique and significant reflections to the final weighted R indices of 0·059 and 0·056 respectively. In (I), the nitrito group coordinates asymmetrically to Cu^{II} and the $[Cu(phen)_2(ONO)]^+$ cation has a stereochemistry intermediate between five- and six-coordinate. In contrast, the acetato group in (II) appears to coordinate symmetrically to Cu^{II}; however, it has unusually large thermal motion which suggests that the $[Cu(phen)_2(CH_3CO_2)]^+$ cation is either statically or dynamically disordered with respect to its twofold axis. ESR results for (II) indicate that the disorder is dynamic with the complex interconverting, through a form with C_2 symmetry, between two stereochemically equivalent asymmetric forms. The distortional behavior of (I), (II), and other [Cu(phen or bpy)$_2$(OXO)]Y complexes (OXO$^-$ = $CH_3CO_2^-$, HCO_2^-, and NO_2^-) is rationalized in terms of a pseudo-Jahn–Teller formalism.

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Introduction. The first crystal structure of a [Cu(bpy)$_2$-(OXO)]Y complex (OXO$^-$ = a bidentate ligand) to be reported was that of bis(2,2'-bipyridyl)nitrito-copper(II) nitrate (Procter & Stephens, 1969). The stereochemistry of the [Cu(bpy)$_2$(ONO)]$^+$ cation was classified as *cis*-distorted octahedral, with one N atom from each bpy ligand axial and the other two N atoms and both nitrito O atoms equatorial. The nitrito ligand is nearly symmetric in its coordination to Cu^{II}. The crystal structures of six other such complexes have since been determined: [Cu(bpy)$_2$(ONO)]BF$_4$ (Walsh, Walsh, Murphy & Hathaway, 1981), [Cu(bpy)$_2$-(ONO)]PF$_6$ (Tyagi, Fitzgerald, Hathaway & Simmons, 1983), [Cu(bpy)$_2$(CH$_3$CO$_2$)]BF$_4$ and [Cu(bpy)$_2$(CH$_3$-CO$_2$)]ClO$_4$.H$_2$O (Hathaway, Ray, Kennedy, O'Brien & Murphy, 1980), [Cu(bpy)$_2$(ONO$_2$)]NO$_3$.H$_2$O (Nakai, 1980; Fereday, Hodgson, Tyagi & Hathaway, 1981), and [Cu(bpy)$_2$(HCO$_2$)]BF$_4$.½H$_2$O (Fitzgerald & Hathaway, 1981). It is found that the molecular geometry varies significantly between corresponding pairs of 'cation-distortion isomers', a result, apparently, of differing crystalline environments. For example, the Cu—O bond distances in [Cu(bpy)$_2$(ONO)]NO$_3$ are 2·230 (5) and 2·320 (5) Å (Simmons, Clearfield, Fitzgerald, Tyagi & Hathaway, 1983), while the corresponding bonds in [Cu(bpy)$_2$(ONO)]BF$_4$ show a greater disparity, 2·117 (6) and 2·462 (6) Å. The structures of the two [Cu(bpy)$_2$(CH$_3$CO$_2$)]$^+$ cations are also quite different and their acetato groups coordinate even more asymmetrically to Cu^{II}: the Cu—O bond distances are 1·980 (4) and 2·785 (5) Å in the BF$_4^-$ complex and 2·031 (5) and 2·648 (5) Å in the ClO$_4^-$.H$_2$O complex.

To study the distortional behavior and spectroscopic properties of such complexes further, we replaced bpy with phen (phen = 1,10-phenanthroline) and have determined the crystal structures of [Cu(phen)$_2$-(ONO)]BF$_4$ (I) and [Cu(phen)$_2$(CH$_3$CO$_2$)]BF$_4$.2H$_2$O (II).

Experimental. The synthesis of [Cu(phen or bpy)$_2$-(OXO)]Y compounds has been previously reported (Hathaway, Procter, Slade & Tomlinson, 1969). Single crystals of (I) and (II), 0·32 × 0·18 × 0·10 and 0·32 × 0·13 × 0·13 mm, mounted along their longest dimensions. Syntex four-circle computer-controlled $P\bar{1}$ diffractometer, graphite-monochromatized Mo $K\alpha$ radiation. Cell constants determined by a least-squares treatment of the angular coordinates of 15 independent high-angle reflections. θ–2θ scan mode with a constant scan speed (ω) in 2θ of 1° min^{-1} for (I) and 2° min^{-1} for (II); scan width ($\Delta 2\theta$) from 1·03 to 1·32° for (I) and from 1·66 to 1·96° for (II). Three standard reflections, measured after every 100 reflections, showed no systematic variation in intensity for either crystal. Intensities calculated as $I = \omega[\text{CT} - (t_c/t_b)$-$(B_1 + B_2)]$ with $\sigma(I) = \{[\text{CT} + (t_c/t_b)^2(B_1 + B_2)]\omega^2 +$

$(pI)^2\}^{1/2}$, where CT is the total integrated count, t_c/t_b is the ratio of total scan time to total background time (1·25), B_1 and B_2 are the background counts, and p is a factor used to downweight intense reflections (0·02). Of the 3992 unique reflections measured (3° $\leq 2\theta \leq$ 50°) for (I), 3266 had $I > 3\sigma(I)$, and of the 2996 unique reflections measured (3° $\leq 2\theta \leq$ 55°) for (II), 1834 had $I > 2\sigma(I)$. All diffraction intensities corrected for Lorentz–polarization effects and for absorption (Ottersen, 1974, 1976; Busing & Levy, 1957); calculated transmission coefficients ranged from 0·83 to 0·90 for (I) and from 0·78 to 0·89 for (II).

Normalized structure factor amplitudes for the 300 reflections with $|E| > 1·40$ for (I) and 1·38 for (II) were used in the computer program *MULTAN* (Germain, Main & Woolfson, 1971). Three-dimensional E functions, phased by the solutions with the largest combined figures of merit (2·71 and 2·00), revealed the positions of the Cu^{II} ion, one complete phen ring, and seven atoms of the other phen ring for (I) and the positions of the Cu^{II} ion and phen rings for (II). The BF$_4^-$, NO$_2^-$, and remaining phen C atoms for (I) and the BF$_4^-$, CH$_3$CO$_2^-$, and H$_2$O atoms for (II) were all subsequently located on Fourier difference syntheses (Hubbard, Quicksall & Jacobson, 1971). Although the only systematic-absence condition observed for (II), $l = 2n + 1$ for $h0l$, is consistent with two space groups (Pc and $P2/c$), the proximity of the Cu^{II} position as determined by *MULTAN* (0·499, 0·956, 0·748) to the special position in $P2/c$ ($\frac{1}{2}, \bar{y}, \frac{3}{4}$) suggests that it is the correct space group. {The space group $P2/c$ is further substantiated by the following observations: (1) a strongly correlated structure results when (II) is refined in the noncentrosymmetric space group Pc [for example, the correlation coefficients between symmetry-related parameters for atoms N(13) and N(13'), N(2) and N(2'), and O(16) and O(16') vary from 0·79–0·89 (mean = 0·85), 0·28–0·96 (mean = 0·70), and 0·04–0·86 (mean = 0·49), respectively]; (2) the acetato geometry in Pc is unacceptable: the O(16)—C(17)—C(18) and O(16')—C(17)—C(18) angles, 129 and 115°, are too dissimilar; and (3) the pattern of Cu—O$_{eq}$ and Cu—N$_{eq}$ bond distances in Pc is contrary to that observed in other [Cu(phen or bpy)$_2$(OXO)]Y structures; *i.e.*, the shorter Cu—O$_{eq}$ and Cu—N$_{eq}$ bonds and the longer Cu—O$_{eq}$ and Cu—N$_{eq}$ bonds are *cis* rather than *trans* to each other (see Table 3 and Fig. 2).} Full-matrix least-squares refinements (Gantzel, Sparks & Trublood, 1976) with anisotropic thermal parameters for all non-hydrogen atoms [except for the B atom and one F atom in (II) which were refined isotropically] and isotropic thermal parameters for the H atoms [the phen H positions in (I) were calculated assuming a C—H distance of 0·89 Å and were not refined] led to the final error indices: $R = 0·051, 0·070$; $R_w = 0·059, 0·056$; and $S = 3·20, 2·23$ for (I) and (II) respectively. The weights (w) of the 3266 and 1834

observations used in the least-squares refinements of the 334 and 224 parameters for (I) and (II) were equal to $[\sigma(F)]^{-2}$. The atomic scattering factors used (*International Tables for X-ray Crystallography*, 1974*a*) were corrected for anomalous-dispersion effects (*International Tables for X-ray Crystallography*, 1974*b*). The largest shift in a positional or thermal parameter in the final cycle of least squares was 41 and 80% of its e.s.d. for (I) and (II). Final Fourier difference functions showed no real excursions above background, the largest residual peaks being *ca* 0·7 e Å^{-3} for both structures.

Discussion. The final positional coordinates for both structures are given in Table 1;* bond lengths and selected bond angles appear in Table 2.

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* Lists of structure factors, anisotropic thermal parameters, bond angles and details of least-squares planes for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38566 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
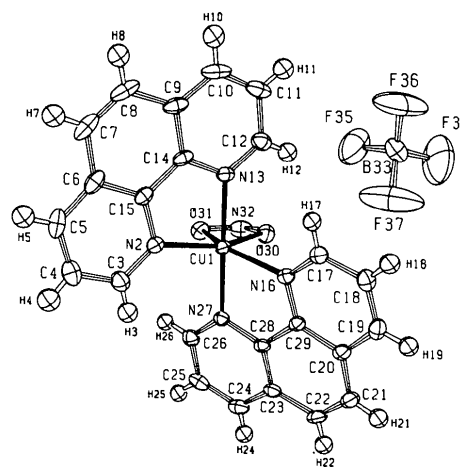

Fig. 1. *ORTEP* drawing (Johnson, 1971) of [Cu(phen)$_2$(ONO)]BF$_4$ (I) using ellipsoids of 20% probability.

The structure of [Cu(phen)$_2$(ONO)]BF$_4$ is shown in Fig. 1. The nitrito ligand coordinates asymmetrically to Cu^{II} with Cu—O bond distances of 2·072 (4) and

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Table 1. *Fractional atomic coordinates* ($\times 10^4$, $\times 10^3$ *for* H) *with e.s.d.'s in parentheses*

The equivalent isotropic temperature factors, B_{eq}(Å^2), have been calculated by $B_{eq} = \frac{4}{3}(\beta_{11}a^2 + \cdots + \beta_{23}bc\cos\alpha)$; $\sigma(B_{eq}) = [(8/9)a^4\sigma^2(\beta_{11}) + \cdots + (8/9)b^2c^2\cos^2\alpha\,\sigma^2(\beta_{23})]^{1/2}$. This expression differs from that obtained from the usual propagation-of-error expression by a factor of $1/\sqrt{2}$ (Schomaker & Marsh, 1981).

	(I) [Cu(phen)$_2$(ONO)]BF$_4$					(II) [Cu(phen)$_2$(CH$_3$CO$_2$)]BF$_4$.2H$_2$O			
	x	*y*	*z*	B_{eq}		*x*	*y*	*z*	B_{eq}, B_{iso}
Cu(1)	3741·4 (5)	2260·5 (3)	2550·5 (7)	3·5 (1)	Cu(1)	0	445·8 (12)	2500	3·9 (1)
N(2)	5482 (4)	3169 (2)	1952 (5)	3·9 (1)	N(2)	−1365 (5)	1836 (5)	1531 (2)	4·0 (1)
C(3)	6580 (5)	3065 (3)	1475 (8)	5·5 (1)	C(3)	−2707 (7)	2421 (8)	1407 (4)	5·4 (2)
C(4)	7700 (6)	3761 (4)	1206 (8)	6·4 (2)	C(4)	−3451 (8)	3265 (8)	703 (5)	6·8 (2)
C(5)	7742 (6)	4615 (4)	1467 (8)	6·2 (1)	C(5)	−2812 (8)	3518 (9)	136 (5)	6·6 (2)
C(6)	6600 (6)	4769 (3)	1931 (6)	5·0 (1)	C(6)	−1408 (7)	2912 (7)	244 (3)	4·9 (1)
C(7)	6461 (7)	5622 (3)	2152 (8)	6·7 (2)	C(7)	−646 (10)	3057 (9)	−327 (4)	6·3 (2)
C(8)	5321 (8)	5714 (3)	2511 (7)	6·2 (2)	C(8)	675 (10)	2444 (9)	−184 (4)	6·2 (2)
C(9)	4155 (6)	4956 (3)	2744 (6)	5·1 (1)	C(9)	1407 (7)	1568 (7)	529 (3)	4·7 (1)
C(10)	2921 (8)	4989 (4)	3141 (7)	6·7 (2)	C(10)	2781 (8)	852 (9)	699 (5)	6·1 (2)
C(11)	1904 (7)	4232 (5)	3365 (7)	6·3 (2)	C(11)	3353 (7)	−28 (9)	1387 (5)	6·6 (2)
C(12)	2098 (5)	3420 (3)	3219 (7)	5·2 (1)	C(12)	2568 (6)	−133 (8)	1920 (4)	5·2 (2)
N(13)	3252 (4)	3355 (2)	2828 (5)	4·0 (1)	N(13)	1271 (4)	537 (5)	1797 (2)	4·1 (1)
C(14)	4267 (5)	4109 (3)	2598 (5)	4·0 (1)	C(14)	677 (6)	1383 (6)	1101 (3)	3·9 (1)
C(15)	5482 (5)	4014 (3)	2160 (5)	3·9 (1)	C(15)	−734 (6)	2052 (6)	959 (3)	3·8 (1)
N(16)	2137 (4)	1553 (2)	57 (5)	3·6 (1)	O(16)	−949 (4)	−1985 (6)	1995 (3)	7·8 (1)
C(17)	1161 (5)	1763 (3)	−1022 (6)	4·2 (1)	C(17)	0	−2767 (11)	2500	4·5 (2)
C(18)	93 (5)	1163 (3)	−2442 (6)	4·7 (1)	C(18)	0	−4508 (16)	2500	12·9 (5)
C(19)	29 (5)	312 (3)	−2726 (6)	4·6 (1)	O(19)	−3807 (6)	−2155 (9)	1033 (3)	10·0 (2)
C(20)	1048 (5)	48 (3)	−1634 (6)	4·0 (1)	B(20)*	4586 (29)	5089 (26)	2372 (19)	9·0 (7)
C(21)	1069 (5)	−834 (3)	−1815 (7)	5·0 (1)	F(21)	5026 (13)	5641 (14)	3105 (5)	27·2 (4)
C(22)	2056 (6)	−1052 (3)	−706 (8)	5·1 (1)	F(22)*	3369 (13)	5109 (20)	2199 (9)	18·0 (5)
C(23)	3172 (5)	−399 (3)	683 (6)	3·9 (1)	F(23)*	4659 (19)	3636 (15)	2271 (9)	15·6 (4)
C(24)	4283 (6)	−565 (3)	1803 (7)	4·9 (1)	H(3)	−314 (5)	226 (5)	185 (3)	3·8 (11)
C(25)	5325 (5)	109 (4)	3002 (7)	4·8 (1)	H(4)	−435 (6)	362 (6)	67 (3)	5·5 (15)
C(26)	5255 (5)	971 (3)	3202 (6)	4·2 (1)	H(5)	−323 (6)	426 (8)	−30 (4)	7·7 (17)
N(27)	4203 (4)	1148 (2)	2187 (5)	3·5 (1)	H(7)	−106 (5)	366 (6)	−75 (3)	5·5 (14)
C(28)	3184 (4)	482 (3)	902 (6)	3·4 (1)	H(8)	114 (8)	243 (8)	−52 (4)	7·9 (24)
C(29)	2092 (4)	700 (3)	−252 (5)	3·3 (1)	H(10)	319 (5)	87 (6)	32 (3)	5·4 (14)
O(30)	2501 (4)	1644 (2)	4304 (5)	5·6 (1)	H(11)	431 (7)	−59 (7)	152 (3)	8·2 (17)
O(31)	4464 (4)	2172 (3)	6085 (6)	7·3 (1)	H(12)	285 (5)	−75 (5)	232 (3)	2·8 (12)
N(32)	3242 (6)	1720 (3)	5912 (6)	5·8 (1)	H(18A)†	38	−483	295	9·3
B(33)	8909 (12)	3082 (9)	6406 (19)	6·6 (3)	H(18B)†	34	−477	215	9·3
F(34)	7873 (10)	2443 (9)	6711 (21)	21·7 (5)	H(18C)†	−83	−477	226	9·3
F(35)	9818 (9)	3249 (5)	7965 (15)	15·9 (3)	H(19A)‡	−429 (8)	−295 (9)	129 (5)	10·0
F(36)	8686 (13)	3770 (7)	5937 (13)	17·5 (5)	H(19B)‡	−294 (8)	−193 (9)	141 (4)	10·0
F(37)	9304 (15)	2702 (7)	5128 (16)	20·0 (6)					

* B(20), F(22), and F(23) were refined with occupancies of 0·5. B(20), F(23), and the eight H positions, H(3)–H(12), were refined isotropically.

† The coordinates of the half-occupancy C(18) methyl H atoms were taken from a Fourier difference function and were not refined.

‡ H(19A) and H(19B) were refined with *B*'s fixed at 10·0 Å^2.

2·597 (4) Å. This type of coordination, with five ligands near and a sixth distant, has been termed 4 + 1 + 1* (Hathaway, 1973). The axial Cu(1)—N(13) and Cu(1)—N(27) bonds, which are nearly equivalent [1·999 (4) and 2·019 (3) Å], are shorter than the equatorial Cu(1)—N(2) and Cu(1)—N(16) bonds [2·049 (3) and 2·167 (3) Å]. The axial N(13)—Cu(1)—N(27) angle is almost linear (178·2°). The mean N—O bond distance (1·23 Å) and the O—N—O angle (113·4°) in the coordinated nitrite group are nearly the same as in an uncoordinated nitrite ion, 1·24 Å and 114·9° (Kay & Frazer, 1961).

The structure of [Cu(phen)$_2$(CH$_3$CO$_2$)]BF$_4$.2H$_2$O is shown in Fig. 2. Unlike the nitrito group in (I), the acetato group in (II) appears to coordinate symmetrically to Cu^{II} at 2·261 (5) Å. Its thermal motion, however, is remarkably large, which suggests that the [Cu(phen)$_2$(CH$_3$CO$_2$)]$^+$ cation is either statically or dynamically disordered about its twofold axis, in contrast to the apparent rigid stereochemistry of (I) (see below).

The bond lengths and angles in the phen ligands of (I) and (II) agree well with the mean values of chemically equivalent bonds in other phen complexes (Frenz & Ibers, 1972) and with the weighted-mean values reported for molecular 1,10-phenanthroline (Nishigaki, Yoshioka & Nakatsu, 1978). Each phen ligand has approximate C$_{2v}$ symmetry: the maximum difference between chemically equivalent bonds in each
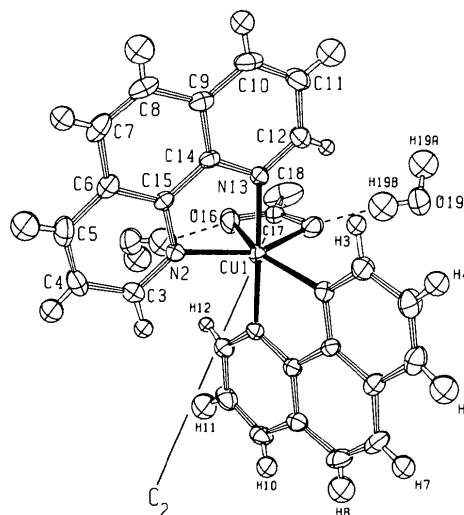

Fig. 2. ORTEP drawing (Johnson, 1971) of [Cu(phen)$_2$-(CH$_3$CO$_2$)]BF$_4$.2H$_2$O (II) using ellipsoids of 20% probability. The average C$_2$ axis and hydrogen bonds are indicated.

ligand is only 0·022 Å. Least-squares-plane calculations indicate small deviations from planarity for the phen ligands.

The BF$_4^-$ group in (I) has large thermal motion. The mean B—F bond length of 1·28 Å (1·26 to 1·31 Å), compared with the value of ca 1·42 Å for a well defined BF$_4^-$ group (Sutton, 1965), indicates considerable bond

Table 2. *Bond lengths (Å) and selected bond angles (°) with e.s.d.'s in parentheses*

Bond lengths involving H atoms are given only if those H positions were refined. The symmetry operation used to generate the positions of the primed atoms is: $\bar{x}$, y, $\frac{1}{2}-z$.

(I) [Cu(phen)$_2$(ONO)]BF$_4$

Cu(1)—N(2)	2·049 (3)	O(30)—N(32)	1·254 (6)
Cu(1)—N(13)	1·999 (4)	O(31)—N(32)	1·207 (7)
Cu(1)—N(16)	2·167 (3)	B(33)—F(34)	1·277 (17)
Cu(1)—N(27)	2·019 (3)	B(33)—F(35)	1·283 (17)
Cu(1)—O(30)	2·072 (4)	B(33)—F(36)	1·256 (17)
Cu(1)—O(31)	2·597 (4)	B(33)—F(37)	1·306 (18)

N(2)—C(3)	1·327 (6)	N(16)—C(17)	1·312 (6)
N(2)—C(15)	1·354 (5)	N(16)—C(29)	1·356 (5)
C(3)—C(4)	1·369 (8)	C(17)—C(18)	1·394 (7)
C(4)—C(5)	1·354 (9)	C(18)—C(19)	1·345 (7)
C(5)—C(6)	1·401 (8)	C(19)—C(20)	1·399 (6)
C(6)—C(7)	1·428 (7)	C(20)—C(21)	1·420 (6)
C(6)—C(15)	1·409 (6)	C(20)—C(29)	1·403 (6)
C(7)—C(8)	1·326 (10)	C(21)—C(22)	1·338 (7)
C(8)—C(9)	1·442 (8)	C(22)—C(23)	1·436 (7)
C(9)—C(10)	1·397 (10)	C(23)—C(24)	1·396 (7)
C(9)—C(14)	1·401 (6)	C(23)—C(28)	1·406 (6)
C(10)—C(11)	1·354 (9)	C(24)—C(25)	1·352 (7)
C(11)—C(12)	1·386 (8)	C(25)—C(26)	1·409 (7)
C(12)—N(13)	1·332 (6)	C(26)—N(27	1·323 (6)
N(13)—C(14)	1·353 (6)	N(27)—C(28)	1·367 (5)
C(14)—C(15)	1·427 (6)	C(28)—C(29)	1·435 (6)

N(2)—Cu(1)—N(13)	81·7 (1)	N(16)—Cu(1)—N(27)	79·9 (1)
N(2)—Cu(1)—N(16)	112·1 (1)	N(16)—Cu(1)—O(30)	93·2 (1)
N(2)—Cu(1)—N(27)	98·4 (1)	N(16)—Cu(1)—O(31)	141·3 (1)
N(2)—Cu(1)—O(30)	154·5 (1)	N(27)—Cu(1)—O(30)	89·1 (1)
N(2)—Cu(1)—O(31)	105·3 (1)	N(27)—Cu(1)—O(31)	85·3 (1)
N(13)—Cu(1)—N(16)	98·4 (1)	O(30)—Cu(1)—O(31)	50·7 (1)
N(13)—Cu(1)—N(27)	178·2 (1)		
N(13)—Cu(1)—O(30)	91·6 (1)	O(30)—N(32)—O(31)	113·4 (5)
N(13) Cu(1) O(31)	96·4 (1)		

(II) [Cu(phen)$_2$(CH$_3$CO$_2$)]BF$_4$.2H$_2$O

Cu(1)—N(2)	2·123 (4)	O(16)—C(17)	1·233 (6)
Cu(1)—N(13)	2·000 (4)	C(17)—C(18)	1·434 (16)
Cu(1)—O(16)	2·261 (5)	B(20)—F(21)	1·30 (3)
		B(20)—F(21')	1·12 (3)
		B(20)—F(22)	1·11 (3)
		B(20)—F(23)	1·21 (3)

N(2)—C(3)	1·331 (7)	C(3)—H(3)	1·00 (4)
N(2)—C(15)	1·343 (6)	C(4)—H(4)	0·90 (5)
C(3)—C(4)	1·400 (10)	C(5)—H(5)	0·97 (6)
C(4)—C(5)	1·345 (11)	C(7)—H(7)	0·88 (5)
C(5)—C(6)	1·397 (10)	C(8)—H(8)	0·85 (7)
C(6)—C(7)	1·425 (10)	C(10)—H(10)	0·88 (5)
C(6)—C(15)	1·407 (8)	C(11)—H(11)	1·00 (6)
C(7)—C(8)	1·318 (13)	C(12)—H(12)	0·84 (4)
C(8)—C(9)	1·421 (9)		
C(9)—C(10)	1·392 (9)	O(19)—H(19A)	1·00 (7)
C(9)—C(14)	1·408 (8)	O(19)—H(19B)	0·90 (5)
C(10)—C(11)	1·366 (11)		
C(11)—C(12)	1·382 (10)		
C(12)—N(13)	1·320 (7)		
N(13)—C(14)	1·365 (6)		
C(14)—C(15)	1·414 (7)		

N(2)—Cu(1)—N(2')	114·7 (2)	N(13)—Cu(1)—O(16)	92·4 (2)
N(2)—Cu(1)—N(13)	80·2 (2)	N(13)—Cu(1)—O(16')	91·5 (2)
N(2)—Cu(1)—N(13')	97·5 (2)	O(16)—Cu(1)—O(16')	55·4 (1)
N(2)—Cu(1)—O(16)	95·4 (2)	O(16)—C(17)—O(16')	117·0 (7)
N(2)—Cu(1)—O(16')	149·5 (2)	O(16)—C(17)—C(18)	121·5 (2)
N(13)—Cu(1)—N(13')	175·7 (2)		

foreshortening. The observed angles range from 102 to 117° and are reasonably close to tetrahedral. The BF$_4^-$ group in (II) is disordered about a twofold axis; the mean B–F bond length of 1·19 Å (1·11 to 1·30 Å) indicates even greater bond foreshortening. The observed bond angles (95 to 118°) are also reasonably close to tetrahedral. The F(21) atoms in the BF$_4^-$ groups of (II) participate in hydrogen bonding to water molecules [the F(21)···H(19A)–O(19) distance is 2·85 Å and the angle at H(19A) is 173°], as do the acetato O atoms [the O(16)···H(19B)–O(19) distance is 2·74 Å and the angle at H(19B) is 161°].

In addition to (I) and (II), the crystal structures of other [M(phen or bpy)$_2$(OXO)]Y (M = Cu, Zn) complexes have been determined; the metal–ligand bond distances are given in Table 3. Several observations can be made by examining the data in Table 3: (1) The molecular geometry varies significantly between corresponding pairs of cation-distortion isomers. For example, the Cu–O bond lengths in [Cu(phen)$_2$-(CH$_3$CO$_2$)]ClO$_4$ are 2·220 (4) and 2·421 (5) Å, while the corresponding bonds in [Cu(phen)$_2$(CH$_3$CO$_2$)]BF$_4$ show a greater disparity, 1·999 (4) and 2·670 (5) Å (Clifford, Counihan, Fitzgerald, Seff, Simmons, Tyagi & Hathaway, 1982). (2) The molecular geometry of the CuN$_4$O$_2$ chromophore is temperature dependent. For

example, the Cu–O bond distances in [Cu(bpy)$_2$-(ONO)]NO$_3$ are 2·051 (2) and 2·536 (2) Å at 20 K and 2·230 (5) and 2·320 (5) Å at 296 K (Simmons, Clearfield, Fitzgerald, Tyagi & Hathaway, 1983). (3) A pattern of continuous distortion from C_2 symmetry exists for the Cu^{II} complexes: as a pair of *trans* Cu–O$_{eq}$ and Cu–N$_{eq}$ bonds lengthen, the other pair concomitantly shorten. Furthermore, the Cu–N$_{ax}$ bonds become slightly unequal: the N atoms in the shorter Cu–N$_{ax}$ bonds always belong to the same phen (or bpy) ligands as do the N atoms in the shorter Cu–N$_{eq}$ bonds. (4) The distortion from C_2 symmetry in [Zn(bpy)$_2$(ONO)]NO$_3$, an orbitally non-degenerate d^{10} complex, is considerably less (as measured by the so-called δ value; see Table 3) and qualitatively different from that in [Cu(bpy)$_2$(ONO)]NO$_3$, even though both crystals are isostructural; thus, the distortional behavior in the Cu^{II} systems is unattributable to crystal-packing forces.

A Cu^{II} complex with D_3 symmetry, such as [Cu(phen)$_3$]$^{2+}$, has an ^2E electronic ground state and is susceptible to Jahn–Teller distortion (Jotham & Kettle, 1971). If one of the phen groups is replaced by a chelating OXO$^-$ group, the resulting symmetry is C_2 and the electronic degeneracy is lifted: the ^2E term splits into a ^2A ground state and a ^2B excited state (Procter,

Table 3. *Molecular geometries for* [M(phen or bpy)$_2$(OXO)]Y *complexes* (M = Cu, Zn)

All structures determined at room temperature unless indicated otherwise. $\delta = (b-a) + (d-c) + (f-e)$ and is a measure of the amount of distortion from C_2 symmetry.
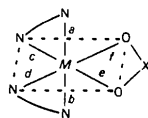
Complex	Space group	a(Å)	b(Å)	c(Å)	d(Å)	e(Å)	f(Å)	δ(Å)	Reference
[Cu(bpy)$_2$(CH$_3$CO$_2$)]BF$_4$	$P2_1/c$	1·995 (6)	2·016 (6)	2·033 (5)	2·209 (6)	1·980 (4)	2·785 (5)	1·00 (1)	(1)
[Cu(phen)$_2$(CH$_3$CO$_2$)]BF$_4$	$P\bar{1}$	2·009 (5)	2·023 (5)	2·061 (5)	2·215 (4)	1·999 (4)	2·670 (5)	0·84 (1)	(2)
[Cu(bpy)$_2$(CH$_3$CO$_2$)]ClO$_4$.H$_2$O	$P\bar{1}$	1·971 (5)	1·994 (5)	2·056 (5)	2·168 (5)	2·031 (5)	2·648 (5)	0·75 (1)	(1)
[Cu(phen)$_2$(CH$_3$CO$_2$)]ClO$_4$	$P2_1/c$	2·003 (3)	2·013 (3)	2·098 (3)	2·147 (3)	2·155 (4)	2·532 (4)	0·44 (1)*	(3)
[Cu(phen)$_2$(CH$_3$CO$_2$)]ClO$_4$	$P2_1/c$	1·994 (4)	2·006 (4)	2·098 (4)	2·130 (4)	2·220 (4)	2·421 (5)	0·25 (1)	(3)
[Cu(phen)$_2$(CH$_3$CO$_2$)]ClO$_4$.2H$_2$O	$P2/c$	1·994 (5)	1·994 (5)	2·124 (4)	2·124 (4)	2·257 (5)	2·257 (5)	0·00 (0)	(2)
[Cu(phen)$_2$(CH$_3$CO$_2$)]BF$_4$.2H$_2$O	$P2/c$	2·000 (4)	2·000 (4)	2·123 (4)	2·123 (4)	2·261 (5)	2·261 (5)	0·00 (0)	(4)
[Zn(phen)$_2$(CH$_3$CO$_2$)]BF$_4$.2H$_2$O	$P2/c$	2·143 (4)	2·143 (4)	2·114 (4)	2·114 (3)	2·183 (3)	2·183 (3)	0·00 (0)	(5)
[Cu(phen)$_2$(ONO)]BF$_4$	$P\bar{1}$	1·999 (4)	2·019 (3)	2·049 (3)	2·167 (3)	2·072 (4)	2·597 (4)	0·66 (1)	(4)
[Cu(bpy)$_2$(ONO)]BF$_4$	$P2_1/c$	1·990 (5)	2·004 (5)	2·052 (5)	2·142 (5)	2·117 (6)	2·462 (6)	0·45 (1)	(6)
[Cu(bpy)$_2$(ONO)]PF$_6$	$P\bar{1}$	1·991 (3)	1·993 (3)	2·092 (3)	2·134 (3)	2·178 (5)	2·429 (5)	0·29 (1)	(7)
[Cu(bpy)$_2$(ONO)]NO$_3$	$P2_1/c$	1·983 (2)	1·998 (2)	2·028 (2)	2·142 (2)	2·051 (2)	2·536 (2)	0·61 (1)†	(8)
[Cu(bpy)$_2$(ONO)]NO$_3$	$P2_1/c$	1·986 (2)	1·992 (2)	2·060 (2)	2·110 (2)	2·155 (2)	2·414 (2)	0·32 (1)‡	(8)
[Cu(bpy)$_2$(ONO)]NO$_3$	$P2_1/c$	1·984 (2)	1·989 (2)	2·071 (2)	2·098 (2)	2·204 (3)	2·351 (3)	0·18 (1)§	(8)
[Cu(bpy)$_2$(ONO)]NO$_3$	$P2_1/c$	1·980 (3)	1·988 (3)	2·074 (4)	2·085 (4)	2·230 (5)	2·320 (5)	0·11 (1)	(8)
[Zn(bpy)$_2$(ONO)]NO$_3$	$P2_1/c$	2·129 (9)	2·151 (9)	2·076 (9)	2·092 (9)	2·223 (9)	2·217 (8)	0·04 (2)	(6)
[Cu(bpy)$_2$(HCO$_2$)]BF$_4$.½H$_2$O	$P\bar{1}$	1·978 (5)	2·001 (5)	2·061 (5)	2·158 (5)	2·024 (5)	2·869 (12)	0·97 (2)	(9)
[Cu(phen)$_2$(HCO$_2$)]BF$_4$	$C2/c$	1·990 (6)	1·990 (6)	2·111 (6)	2·111 (6)	2·363 (8)	2·363 (8)	0·00 (0)	(10)
[Cu(phen)$_2$(HCO$_2$)]ClO$_4$	$C2/c$	1·985 (3)	1·985 (3)	2·111 (3)	2·111 (3)	2·353 (6)	2·353 (6)	0·00 (1)	(11)
[Cu(bpy)$_2$(ONO)]NO$_3$.H$_2$O	$P\bar{1}$	1·973 (5)	1·986 (5)	2·023 (5)	2·051 (5)	2·301 (5)	2·832 (5)	0·57 (1)	(12)

References: (1) Hathaway, Ray, Kennedy, O'Brien & Murphy (1980); (2) Clifford, Counihan, Fitzgerald, Seff, Simmons, Tyagi & Hathaway (1982); (3) Simmons, Alcock, Fitzgerald, Tyagi & Hathaway (1983); (4) this work; (5) Fitzgerald & Hathaway (1983); (6) Walsh, Walsh, Murphy & Hathaway (1981); (7) Tyagi, Fitzgerald, Hathaway & Simmons (1983); (8) Simmons, Clearfield, Fitzgerald, Tyagi & Hathaway (1983); (9) Fitzgerald & Hathaway (1981); (10) Hathaway (1983); (11) Escobar & Wittke (1983); (12) Fereday, Hodgson, Tyagi & Hathaway (1981); Nakai (1980).

* $T = 173$ K.   † $T = 20$ K.   ‡ $T = 100$ K.   § $T = 165$ K.

Hathaway, Billing, Dudley & Nicholls, 1969). Nevertheless, the [Cu(phen)$_2$(OXO)]$^+$ cation will be unstable with respect to pseudo-Jahn–Teller distortion if: (1) the splitting of the ^2A and ^2B states in the undistorted complex (2Δ) is sufficiently small; and (2) the vibronic

Fig. 3. *ORTEP* drawings (Johnson, 1971) of the equatorial atoms in the [M(phen or bpy)$_2$(OXO)]Y (M = Cu, Zn) complexes listed in Table 3 using ellipsoids of 50% probability. In each view, the scale is the same and the MO_2 groups lie in the plane of the page; metal–oxygen bond lengths (Å) are indicated. The thermal amplitudes of the acetato O atoms in [Cu(phen)$_2$(CH$_3$CO$_2$)]Y.2H$_2$O (Y = BF$_4^-$ and ClO$_4^-$) are reduced because of the dampening effect of the O(16)···H(19B)–O(19) hydrogen bonds, which are not shown. Notice the difference in the thermal motions of the O atoms in the two isostructural crystals, [M(phen)$_2$(CH$_3$CO$_2$)]BF$_4$.2H$_2$O (M = Cu, Zn).

coupling constant, $\langle {}^2A \,|\, (\partial H^e / \partial S_i)_o \,|\, {}^2B \rangle$, is nonzero, which requires the vibrational mode(s) coupling the ^2A and ^2B electronic states to have b symmetry (Bersuker, 1975; Burdett, 1980). Thus, an isolated [Cu(phen or bpy)$_2$(OXO)]$^+$ cation is unsusceptible to distortion unless a vibronic coupling of the ^2A and ^2B electronic states occurs, in which case *static C_2 symmetry cannot be retained.*

Evidence for this coupling comes from the structures of two isostructural crystals, (II) and its Zn analogue. The metal ions lie on crystallographic twofold axes and appear to coordinate symmetrically; only the [Cu(phen)$_2$(CH$_3$CO$_2$)]$^+$ cation, however, is disordered about the twofold axis. This disorder is clearly depicted in Fig. 3, which is a montage showing the *ORTEP* drawings of the equatorial atoms in the complexes listed in Table 3. It is seen, especially for the Cu^{II} acetato complexes, that the amplitude and anisotropy of the thermal motions of the ligating O atoms increase as C_2 symmetry is approached; concomitantly, the angles between the major axes of the O thermal ellipsoids and the Cu–O bond vectors decrease. For example, these angles are only 13 and 7° in the 'symmetric' [Cu(phen)$_2$(CH$_3$CO$_2$)]Y (Y = BF$_4^-$.2H$_2$O and ClO$_4^-$.2H$_2$O) complexes, respectively, *vs* 18 and 25°, and 42 and 54° in the asymmetric Y = ClO$_4^-$ and BF$_4^-$ complexes, respectively. Increasing amplitudes with increasing symmetry is evident by the trend in the largest r.m.s. values, $U_{33}^{1/2}$ (Å), of the acetato O thermal ellipsoids in Fig. 3: 0.23 and 0.28 in [Cu(bpy)$_2$(CH$_3$CO$_2$)]BF$_4$, 0.24 and 0.36 in [Cu(phen)$_2$(CH$_3$CO$_2$)]BF$_4$, 0.27 and 0.38 in [Cu(bpy)$_2$(CH$_3$CO$_2$)]ClO$_4$.H$_2$O, 0.42 and 0.56 in [Cu(phen)$_2$(CH$_3$CO$_2$)]ClO$_4$, and 0.42 and 0.41 in the 'symmetric' [Cu(phen)$_2$(CH$_3$CO$_2$)]BF$_4$.2H$_2$O and ClO$_4^-$.2H$_2$O complexes, respectively [lower, presumably, because of the dampening effect of the O(16)···H(19B)–O(19) hydrogen bonds; see Fig. 2]. The trend is similar for the formato complexes: the angles are only 3 and 5° in the 'symmetric' [Cu(phen)$_2$-(HCO$_2$)]Y (Y = ClO$_4^-$ and BF$_4^-$; $C2/c$, Z = 4) complexes, respectively, *vs* 47 and 76° in the asymmetric [Cu(bpy)$_2$(HCO$_2$)]BF$_4$.½H$_2$O complex; the $U_{33}^{1/2}$ (Å) values (O atom) are both 0.49 in the 'symmetric' complexes *vs* 0.28 and 0.40 in the asymmetric complex. Although the $U_{ii}^{1/2}$ values (O atom) are nearly constant for the nitrito complexes, the angles do decrease as C_2 symmetry is approached: 32 and 63° in [Cu(phen)$_2$(ONO)]BF$_4$, 26 and 48° in [Cu(bpy)$_2$-(ONO)]BF$_4$, 20 and 21° in [Cu(bpy)$_2$(ONO)]PF$_6$, and 16 and 24° in [Cu(bpy)$_2$(ONO)]NO$_3$. This preferential vibration along a direction nearly parallel to a metal–ligand bond is contrary to expectations based on bond-stretching and bond-bending energies.

The small and nearly isotropic acetato O thermal ellipsoids in [Zn(phen)$_2$(CH$_3$CO$_2$)]BF$_4$.2H$_2$O [$U_{ii}^{1/2}$ (Å) values = 0.24, 0.26, 0.28 and the angles between the major axes of the O thermal ellipsoids and the Zn–O

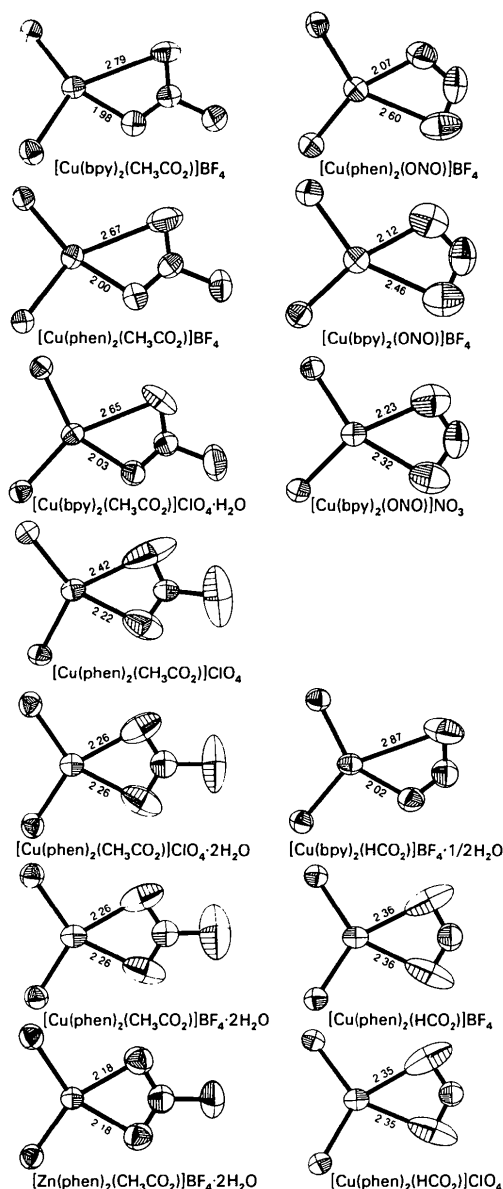bond vectors = 85°], which has *static* C_2 symmetry, are in marked contrast with those in the isostructural but disordered Cu^{II} analogue. The marked temperature dependence of the single-crystal ESR spectra of the 10% Cu-doped [Zn(phen)₂(CH₃CO₂)]Y ($Y =$ BF₄⁻.2H₂O and ClO₄⁻.2H₂O) systems (Clifford, Counihan, Fitzgerald, Seff, Simmons, Tyagi & Hathaway, 1982) and the crystallographic results reported herein suggest that (II) consists of two interconverting asymmetric structures (a 'dynamic pseudo-Jahn–Teller effect') associated with two equivalent and thermally accessible energy minima; it has average, not static C_2 symmetry.

The proposed potential-energy surface for the ^2A and ^2B pseudo-degenerate electronic states in a [Cu(phen or bpy)₂(OXO)]Y complex is shown in Fig. 4 (Bersuker, 1975; Öpik & Pryce, 1957; Ammeter, 1980) as a function of the distortion coordinate $S(b)$ of the active b mode, the form of which corresponds to the distortion pattern previously mentioned. When the average site symmetry of a complex is C_2, as in (II), the ground-state minima are equivalent (solid curve); otherwise, they are nonequivalent (dotted curve) and separated in energy by ΔE. A maximum in the ^2A curve occurs at $S(b) = 0$, i.e. for an undistorted complex with static C_2 symmetry.

The structural results of (I), (II), and other [Cu(phen or bpy)₂(OXO)]Y systems have been rationalized in terms of a pseudo-Jahn–Teller formalism. The proposed potential-energy-surface model implies that each of the observed geometries is a statistical mean weighted according to the relative thermal population of
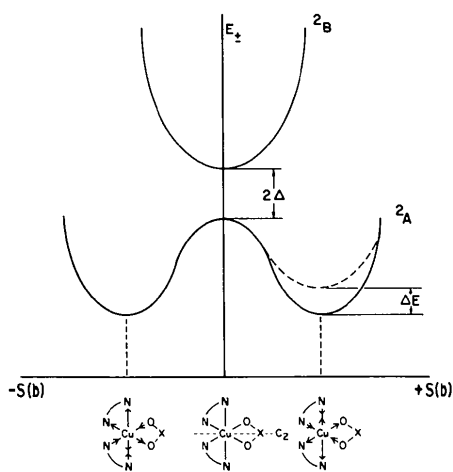
the two minima, which, at a given temperature, is a function of ΔE. The ΔE values are quite sensitive to variations in intracrystalline forces, as demonstrated by the sizeable structural differences between various cation-distortion isomers. The observed distortions from C_2 symmetry should increase with decreasing temperature, a result of depopulating the higher-energy well; this has been observed in both [Cu(bpy)₂-(ONO)]NO₃ and [Cu(phen)₂(CH₃CO₂)]ClO₄ (Table 3).

We are indebted to Dr Carmen Escobar, Universidad de Chile, for allowing us access to her unpublished data on [Cu(phen)₂(HCO₂)]ClO₄ and to Richard E. Marsh, California Institute of Technology, for his many useful comments.

Fig. 4. Proposed potential-energy surface for the pseudo-degenerate electronic ^2A ground and ^2B excited states in a [Cu(phen or bpy)₂(OXO)]Y complex as a function of the distortion coordinate $S(b)$ of the active vibrational mode, the form of which is indicated below the energy minima. If the average site symmetry of a complex is C_2, as in [Cu(phen)₂(CH₃CO₂)]BF₄.2H₂O, the ground-state minima are equivalent (solid curve); otherwise, they are nonequivalent (dotted curve).

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Structure of 2,2′-Bipyridyl(iminodiacetato)oxovanadium(IV) Dihydrate, C₁₄H₁₃N₃O₅V.2H₂O

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Abstract. $M_r = 390.2$, monoclinic, $P2_1/a$, $a = 11.878$ (1), $b = 15.698$ (3), $c = 9.027$ (1) Å, $\beta = 100.9$ (5)°, $U = 1653$ (3) Å³, $Z = 4$, $D_x = 1.57$ (1), $D_m = 1.55$ (1) g cm⁻³, $\lambda(Cu\,K\alpha) = 1.5418$ Å, $\mu = 56.7$ cm⁻¹, $F(000) = 804$, $T = 293$ K. Final $R = 0.047$ for 2450 reflections. The V atom is octahedrally coordinated to the vanadyl O, two carboxyl O atoms and one N from the tridentate iminodiacetate ligand, and to two N atoms from the bidentate bipyridyl ligand. The structure consists of individual complexes and two loosely bound molecules of water of crystallization.

Introduction. In the course of their extensive study of the chemistry of the oxovanadium ion, Dutta & Ghosh (1967, especially paper on pp. 306–313) found a general synthetic route to the oxovanadium(IV) heterochelates. The majority of the oxovanadium complexes synthesized so far are of the type [VO(X)(bidentate ligand)₂], a few being of the type [VO(X)(quadridentate ligand)], X being H₂O, some amine molecule or non-existent. The title compound is a rare example where a tridentate ligand is present along with a bidentate one. The determination of the crystal structure of this compound was undertaken to find out the details of the coordination of V in this complex.

Experimental. Very dark prismatic crystals made available to us believed to be the monohydrate. Direction of elongation of crystal arbitrarily named as c and from oscillation and Weissenberg photographs space group found to be $P2_1/a$. D_m measured by flotation in benzene/bromoform. Structure solved by Patterson and successive Fourier syntheses using a set of visually estimated photographic data. Since the reasonable model of the monohydrate structure failed to refine, a fresh set of intensity data was collected using a CAD-4 diffractometer and graphite-monochromated Cu Kα radiation, with a specimen of dimensions 0.15 × 0.15 × 0.175 mm. 25 reflections used for measuring lattice parameters. Absorption correction applied, max. 1.940, min. 1.835. $2\theta_{max} = 120°$. $h\,-13-13$, $k\,0-17$, $l\,0-10$. Three standard reflections, decay corrections: max. = 1.0682, min. = 1.0001, av. 1.0403. Intensities of 2450 independent reflections measured, 263 with $I \le \sigma\,(I)$ unobserved.

Using the refined cell parameters obtained by diffractometry, it was found that unless the crystal was assumed to be a dihydrate, a value of D_x consistent with D_m could not be obtained. For verification, a difference Fourier synthesis was made on the basis of structure factors calculated with the contribution from only the 23 atoms of the complex itself. The map distinctly revealed the positions of two water molecules. Thus the compound is a dihydrate.

Complete model subjected to least-squares refinement, using values of form factors for V, O, N, and C as given by Cromer & Waber (1965). Function $w(F_o - F_c)^2$ minimized, where $w = 1/\sigma^2(F)$, the estimation of the standard deviations $\sigma(F)$ being based on counting statistics, $S = 2.77$. Three cycles of full-matrix least-squares refinement with an individual isotropic temperature factor, followed by another three cycles of anisotropic refinement in block-diagonal approximation lowered R to 0.067. At this stage all 17 H atoms located from a difference Fourier synthesis. Thermal parameters for four H atoms belonging to the two water molecules kept fixed, parameters of other 13 H refined isotropically in subsequent cycles. Values

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