

**A Fluxional Pseudo-Jahn-Teller Complex: The Structure of  
(Acetato)bis(1,10-phenanthroline)copper(II) Perchlorate, [Cu(C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)]ClO<sub>4</sub>,  
at 298 and 173 K**

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### Abstract

$M_r = 582.5$ , monoclinic,  $P2_1/c$ , Mo  $K\alpha$ ,  $\lambda = 0.71073 \text{ \AA}$ ,  $\mu = 1.05 \text{ mm}^{-1}$ ,  $F(000) = 1188$ ;  $a = 8.258(3)$ ,  $b = 19.070(9)$ ,  $c = 16.755(3) \text{ \AA}$ ,  $\beta = 111.79(2)^\circ$ ,  $V = 2450(2) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_m = 1.57(1)$ ,  $D_x = 1.579 \text{ Mg m}^{-3}$ ,  $T = 298 \text{ K}$ ;  $a = 8.246(9)$ ,  $b = 19.009(4)$ ,  $c = 16.717(3) \text{ \AA}$ ,  $\beta = 111.61(1)^\circ$ ,  $V = 2436.18(7) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_x = 1.588 \text{ Mg m}^{-3}$ ,  $T = 173 \text{ K}$ . 2607 (298 K) and 3488 (173 K) unique and significant reflections gave final  $R_w$  0.040 and 0.052, respectively. The acetato group coordinates asymmetrically to  $\text{Cu}^{\text{II}}$  and the stereochemistry of the  $[\text{Cu}(\text{phen})_2(\text{CH}_3\text{CO}_2)]^+$  cation is intermediate between five and six coordinate. The molecular geometry of the  $\text{CuN}_4\text{O}_2$  chromophore is temperature dependent; the Cu-O bond distances are 2.220 (4) and 2.421 (5)  $\text{ \AA}$  at 298 K and 2.155 (4) and 2.528 (5)  $\text{ \AA}$  at 173 K. The distortional behavior is rationalized in terms of a pseudo-Jahn-Teller formalism.

### Introduction

The realization that the purported *cis*-distorted octahedral geometry of  $[\text{Cu}(\text{bpy})_2(\text{ONO})]\text{NO}_3$  (Procter & Stephens, 1969) is not a genuine static stereochemistry has been recently demonstrated by the determination of its crystal structure over the temperature range 296 to 20 K (Simmons, Clearfield, Santarsiero & Hathaway, 1984). These results have confirmed the initial suggestion of fluxional behavior from the temperature variability of the ESR spectra

of a  $\text{Cu}^{\text{II}}$ -doped  $[\text{Zn}(\text{bpy})_2(\text{ONO})]\text{NO}_3$  system (Fitzgerald, Murphy, Tyagi, Walsh, Walsh & Hathaway, 1981). Because the ESR spectral results of a series of  $[\text{Cu}(\text{phen})_2(\text{CH}_3\text{CO}_2)]Y$  complexes (phen = 1,10-phenanthroline,  $Y = \text{BF}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{ClO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{ClO}_4$  and  $\text{BF}_4$ ) also suggest a fluxional  $\text{CuN}_4\text{O}_2$  chromophore (Clifford, Counihan, Fitzgerald, Seff, Simmons, Tyagi & Hathaway, 1982), we have determined the crystal structure of  $[\text{Cu}(\text{phen})_2(\text{CH}_3\text{CO}_2)]\text{ClO}_4$  at room temperature and at low temperature in order to confirm this suggestion.

### Experimental

Synthesis of  $[\text{Cu}(\text{phen})_2(\text{CH}_3\text{CO}_2)]\text{ClO}_4$  previously reported (Clifford, Counihan, Fitzgerald, Seff, Simmons, Tyagi & Hathaway, 1982). Composition found: C = 53.33, H = 3.38, N = 9.70, Cl = 6.39, Cu = 10.93%; calculated for  $\text{C}_{26}\text{H}_{19}\text{ClCuN}_4\text{O}_6$ : C = 53.60, H = 3.26, N = 9.62, Cl = 6.10, Cu = 10.91%.  $D_m$  by flotation.

Single crystal  $0.36 \times 0.26 \times 0.08 \text{ mm}$ . Syntex  $P\bar{I}$  four-circle computer-controlled diffractometer used for preliminary experiments and for measurement of diffraction intensities at 298 K. Cell constants and their standard deviations determined from angular coordinates of 15 independent reflections with  $2\theta$  values up to  $23.8^\circ$ .  $\theta$ - $2\theta$  scan mode with constant scan speed ( $\omega$ ) in  $2\theta$  of  $1^\circ \text{ min}^{-1}$ . Background time to scan time ratio 1.0; scan range varied from  $-1.0$  to  $+1.0^\circ$  ( $2\theta$ ) about  $K\alpha_1$ - $K\alpha_2$  angles. Intensities of three standard reflections, measured after every 100 reflections, decreased by  $\sim 2\%$  during data collection, correction applied. Standard deviations assigned according to  $\sigma(I) = [\omega^2(CT + B_1 + B_2) + (pI)^2]^{1/2}$ ,  $CT$

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is total integrated count,  $B_1$  and  $B_2$  are background counts,  $p$  (0.02), is a factor to downweight intense reflections, and  $I = \omega(CT - B_1 - B_2)$ . 4334 symmetry-independent reflections measured ( $3 < 2\theta < 50^\circ$ ), 2607 with  $I > 3\sigma(I)$ . All diffraction intensities corrected for Lorentz-polarization and absorption (Ottersen, 1974, 1976; Busing & Levy, 1957); calculated transmission coefficients from 0.79 to 0.93.

Data at 173 K collected on Syntex  $P2_1$  four-circle diffractometer with LT-1 low-temperature attachment. Single crystal  $0.43 \times 0.68 \times 0.60$  mm.  $\theta$ - $2\theta$  scan mode with variable scan speed  $6$ – $29^\circ \text{ min}^{-1}$ , depending on intensity of 2 s pre-scan. Background time to scan time ratio 0.5; scan range varied from  $-1.0$  to  $+1.1^\circ$  ( $2\theta$ ) about the  $K\alpha_1$ - $K\alpha_2$  angles. Three standard reflections, measured after every 500 reflections, showed no systematic variation in intensity during data collection. 3488 reflections with  $I > 3\sigma(I)$  ( $0 < 2\theta < 50^\circ$ ) obtained. All diffraction intensities corrected for Lorentz-polarization and absorption (Alcock, 1970); calculated transmission coefficients from 0.68 to 0.75.

Space group  $P2_1/c$  assigned unambiguously on basis of systematic absences,  $l = 2n + 1$  for  $h0l$  and  $k = 2n + 1$  for  $0k0$ . Position of  $\text{Cu}^{\text{II}}$  ion determined from three-dimensional Patterson function; all other non-H atoms subsequently determined from Fourier difference syntheses (Hubbard, Quicksall & Jacobson, 1971). phen H positions calculated assuming C-H of  $0.89 \text{ \AA}$ , these atoms assigned isotropic thermal parameters equal to corresponding values of C atoms to which they are bonded. Full-matrix least-squares refinements on  $F$  (Gantzel, Sparks & Trueblood, 1976) with anisotropic thermal parameters for all non-H atoms,  $R = 0.043$ ,  $R_w = 0.040$ ,  $S = 1.82$  ( $T = 298 \text{ K}$ ). 2607 observations in least-squares refinements, 343 parameters,  $w = [\sigma(F_o)]^{-2}$ . Atomic scattering factors (*International Tables for X-ray Crystallography*, 1974, pp. 72–98) corrected for anomalous dispersion (*International Tables for X-ray Crystallography*, 1974, pp. 148–150). Max.  $\Delta$  in final cycle of least squares was 20% of corresponding e.s.d. Final difference Fourier syntheses showed no excursions above background.

Positional parameters from room-temperature structure used as starting coordinates for refinement of low-temperature structure. Full-matrix least-squares refinements on  $F$  [all calculations with *SHELX 76* (Sheldrick, 1976)] with anisotropic thermal parameters for all non-H atoms (phen H positions calculated assuming C-H =  $1.08 \text{ \AA}$ , not refined),  $R = 0.049$  and  $R_w = 0.052$ . 3488 observations used in least squares,  $w = 4.4335[\sigma^2(F_o) + 2.35 \times 10^{-4}(F_o)^2]^{-1}$ . Atomic scattering factors (*International Tables for X-ray Crystallography*, 1974, pp. 72–98) corrected for anomalous dispersion (*International Tables for X-ray Crystallography*, 1974, pp. 148–150). Max.  $\Delta$  in final cycle of least squares was 1% of corresponding e.s.d.

Final difference Fourier syntheses showed no excursions above background.\*

## Discussion

The final positional coordinates are given in Table 1 and bond lengths and selected bond angles appear in Table 2.

The crystal and molecular structure of  $[\text{Cu}(\text{phen})_2(\text{CH}_3\text{CO}_2)]\text{ClO}_4$  is shown in Figs. 1 and 2. The acetato group coordinates asymmetrically to  $\text{Cu}^{\text{II}}$  and the stereochemistry of the  $[\text{Cu}(\text{phen})_2(\text{CH}_3\text{CO}_2)]^+$  cation is intermediate between five and six coordinate. The Cu–O bond distances are  $2.220(4)$  and  $2.421(5) \text{ \AA}$  at 298 K and  $2.155(4)$  and  $2.528(5) \text{ \AA}$  at 173 K, indicating that the molecular geometry of the  $\text{CuN}_4\text{O}_2$  chromophore is temperature dependent (see below). The nearly equivalent and slightly temperature dependent Cu(1)–N(13) and Cu(1)–N(27) axial bonds [ $1.999(4)$ ,  $2.006(4) \text{ \AA}$  ( $T = 298 \text{ K}$ ) and  $2.002(3)$ ,  $2.012(3) \text{ \AA}$  ( $T = 173 \text{ K}$ ) respectively] are shorter than the nonequivalent and moderately temperature dependent Cu(1)–N(2) and Cu(1)–N(16) equatorial bonds [ $2.098(4)$ ,  $2.130(4) \text{ \AA}$  ( $T = 298 \text{ K}$ ) and  $2.097(3)$ ,  $2.141(3) \text{ \AA}$  ( $T = 173 \text{ K}$ ) respectively]. [The bonds between Cu(1) and the nearly coplanar N(2), N(16), O(30), O(31) atoms are classified as 'equatorial', while those bonds between Cu(1) and N(13) and N(27), which are nearly perpendicular to this equatorial plane, are classified as 'axial'.] The axial N(13)–Cu(1)–N(27) angle is within  $2^\circ$  of  $180^\circ$ , and all eight out-of-plane  $N_{\text{ax}}\text{--Cu--}N_{\text{eq}}$  and  $N_{\text{ax}}\text{--Cu--O}_{\text{eq}}$  bond angles are within  $\pm 10^\circ$  of  $90^\circ$ .

Although it is not entirely apparent in Fig. 1, the thermal motion of the ligating acetato group is anomalously large at room temperature, suggesting that the  $\text{CuN}_4\text{O}_2$  chromophore is either statically or dynamically disordered. The r.m.s. values of the O and C thermal ellipsoids,  $U_{ii}^{1/2}(\text{ \AA}^2)$ , are ( $T = 298 \text{ K}$ ): O(30) =  $0.42, 0.27, 0.24$ ; O(31) =  $0.56, 0.29, 0.20$ ; C(32) =  $0.24, 0.20, 0.19$ ; and C(33) =  $0.58, 0.29, 0.26$ . More importantly, the angles between the major axes of the extremely anisotropic O thermal ellipsoids and the Cu–O bond vectors are only  $18$  and  $25^\circ$ . Thus, the vibrational amplitudes of the O atoms are not only considerable along the Cu–O bonds but, because of the near  $90^\circ$  Cu(1)–O(30, 31)–C(32) angles, they are also considerably perpendicular to the C–O bonds, which undoubtedly accounts for their foreshortening. The mean observed C–O distances,

\* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and a full list of bond angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39701 (41 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates for nonhydrogen atoms with e.s.d.'s in parentheses

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

| T = 298 K |             |             |             |                        | T = 173 K   |             |             |                        |  |
|-----------|-------------|-------------|-------------|------------------------|-------------|-------------|-------------|------------------------|--|
|           | x           | y           | z           | $U_{eq}(\text{\AA}^2)$ | x           | y           | z           | $U_{eq}(\text{\AA}^2)$ |  |
| Cu(1)     | 0-3788 (1)  | 0-33356 (3) | 0-32675 (3) | 0-0426 (3)             | 0-38103 (5) | 0-33411 (2) | 0-32603 (3) | 0-0281 (3)             |  |
| N(2)      | 0-1697 (5)  | 0-2776 (2)  | 0-2387 (2)  | 0-044 (3)              | 0-1712 (4)  | 0-2783 (2)  | 0-2384 (2)  | 0-030 (2)              |  |
| C(3)      | 0-0931 (8)  | 0-2185 (3)  | 0-2463 (3)  | 0-057 (4)              | 0-0940 (5)  | 0-2187 (2)  | 0-2465 (3)  | 0-041 (2)              |  |
| C(4)      | -0-0365 (8) | 0-1863 (3)  | 0-1782 (4)  | 0-064 (4)              | -0-0375 (6) | 0-1872 (2)  | 0-1786 (3)  | 0-049 (3)              |  |
| C(5)      | -0-0876 (7) | 0-2156 (3)  | 0-0990 (4)  | 0-062 (4)              | -0-0894 (6) | 0-2160 (2)  | 0-0979 (3)  | 0-043 (2)              |  |
| C(6)      | -0-0106 (7) | 0-2782 (3)  | 0-0865 (3)  | 0-049 (3)              | -0-0112 (5) | 0-2789 (2)  | 0-0861 (2)  | 0-035 (2)              |  |
| C(7)      | -0-0532 (8) | 0-3133 (3)  | 0-0058 (3)  | 0-059 (4)              | -0-0553 (6) | 0-3138 (2)  | 0-0049 (3)  | 0-040 (2)              |  |
| C(8)      | 0-0257 (8)  | 0-3720 (3)  | -0-0013 (3) | 0-061 (4)              | 0-0262 (4)  | 0-3741 (2)  | -0-0025 (2) | 0-041 (2)              |  |
| C(9)      | 0-1567 (7)  | 0-4042 (3)  | 0-0721 (3)  | 0-048 (3)              | 0-1579 (5)  | 0-4050 (2)  | 0-0707 (2)  | 0-034 (2)              |  |
| C(10)     | 0-2456 (7)  | 0-4660 (3)  | 0-0692 (3)  | 0-058 (4)              | 0-2481 (6)  | 0-4670 (2)  | 0-0672 (3)  | 0-044 (2)              |  |
| C(11)     | 0-3703 (8)  | 0-4901 (3)  | 0-1421 (4)  | 0-065 (4)              | 0-3747 (6)  | 0-4914 (2)  | 0-1406 (3)  | 0-046 (3)              |  |
| C(12)     | 0-4088 (7)  | 0-4532 (3)  | 0-2186 (3)  | 0-057 (4)              | 0-4142 (6)  | 0-4541 (2)  | 0-2168 (3)  | 0-041 (2)              |  |
| N(13)     | 0-3267 (5)  | 0-3953 (2)  | 0-2243 (2)  | 0-044 (3)              | 0-3303 (4)  | 0-3963 (2)  | 0-2230 (2)  | 0-032 (2)              |  |
| C(14)     | 0-2010 (6)  | 0-3706 (3)  | 0-1520 (3)  | 0-042 (3)              | 0-2029 (5)  | 0-3716 (2)  | 0-1506 (2)  | 0-029 (2)              |  |
| C(15)     | 0-1177 (6)  | 0-3071 (2)  | 0-1594 (3)  | 0-039 (3)              | 0-1184 (5)  | 0-3078 (2)  | 0-1587 (2)  | 0-029 (2)              |  |
| N(16)     | 0-3054 (5)  | 0-4030 (2)  | 0-4071 (2)  | 0-042 (3)              | 0-3064 (4)  | 0-4041 (2)  | 0-4068 (2)  | 0-029 (2)              |  |
| C(17)     | 0-2448 (7)  | 0-4671 (3)  | 0-3954 (3)  | 0-057 (4)              | 0-2457 (5)  | 0-4697 (2)  | 0-3949 (3)  | 0-039 (2)              |  |
| C(18)     | 0-2178 (8)  | 0-5059 (3)  | 0-4597 (4)  | 0-071 (4)              | 0-2184 (6)  | 0-5084 (2)  | 0-4598 (3)  | 0-051 (3)              |  |
| C(19)     | 0-2556 (8)  | 0-4780 (3)  | 0-5383 (4)  | 0-068 (4)              | 0-2559 (6)  | 0-4796 (2)  | 0-5391 (3)  | 0-048 (3)              |  |
| C(20)     | 0-3217 (7)  | 0-4096 (3)  | 0-5544 (3)  | 0-046 (3)              | 0-3219 (5)  | 0-4102 (2)  | 0-5549 (2)  | 0-034 (2)              |  |
| C(21)     | 0-3701 (8)  | 0-3756 (3)  | 0-6353 (3)  | 0-061 (4)              | 0-3693 (6)  | 0-3760 (2)  | 0-6361 (2)  | 0-042 (2)              |  |
| C(22)     | 0-4338 (8)  | 0-3105 (3)  | 0-6475 (3)  | 0-060 (4)              | 0-4325 (6)  | 0-3100 (2)  | 0-6474 (2)  | 0-042 (2)              |  |
| C(23)     | 0-4549 (6)  | 0-2715 (3)  | 0-5784 (3)  | 0-047 (3)              | 0-4539 (5)  | 0-2716 (2)  | 0-5780 (2)  | 0-031 (2)              |  |
| C(24)     | 0-5179 (7)  | 0-2024 (3)  | 0-5851 (4)  | 0-056 (4)              | 0-5196 (5)  | 0-2018 (2)  | 0-5861 (3)  | 0-039 (2)              |  |
| C(25)     | 0-5281 (7)  | 0-1698 (3)  | 0-5153 (4)  | 0-055 (3)              | 0-5301 (5)  | 0-1687 (2)  | 0-5155 (3)  | 0-040 (2)              |  |
| C(26)     | 0-4793 (7)  | 0-2059 (3)  | 0-4376 (3)  | 0-049 (3)              | 0-4811 (5)  | 0-2053 (2)  | 0-4370 (3)  | 0-035 (2)              |  |
| N(27)     | 0-4218 (5)  | 0-2707 (2)  | 0-4285 (2)  | 0-040 (3)              | 0-4234 (4)  | 0-2710 (1)  | 0-4284 (2)  | 0-028 (2)              |  |
| C(28)     | 0-4070 (6)  | 0-3039 (3)  | 0-4973 (3)  | 0-038 (3)              | 0-4085 (4)  | 0-3040 (2)  | 0-4974 (2)  | 0-027 (2)              |  |
| C(29)     | 0-3440 (6)  | 0-3744 (3)  | 0-4861 (3)  | 0-039 (3)              | 0-3441 (5)  | 0-3752 (2)  | 0-4861 (2)  | 0-026 (2)              |  |
| O(30)     | 0-6547 (6)  | 0-3679 (2)  | 0-3859 (3)  | 0-114 (3)              | 0-6486 (6)  | 0-3682 (2)  | 0-3824 (3)  | 0-094 (3)              |  |
| O(31)     | 0-6315 (7)  | 0-2822 (2)  | 0-3092 (2)  | 0-144 (4)              | 0-6454 (8)  | 0-2783 (3)  | 0-3097 (2)  | 0-126 (4)              |  |
| C(32)     | 0-7143 (6)  | 0-3277 (2)  | 0-3512 (3)  | 0-044 (3)              | 0-7224 (5)  | 0-3268 (2)  | 0-3516 (2)  | 0-034 (2)              |  |
| C(33)     | 0-8969 (10) | 0-3373 (5)  | 0-3600 (7)  | 0-173 (8)              | 0-9042 (8)  | 0-3404 (4)  | 0-3638 (6)  | 0-124 (6)              |  |
| Cl(34)    | 0-1528 (2)  | 0-0147 (1)  | 0-3138 (1)  | 0-058 (9)              | 0-1491 (1)  | 0-0151 (1)  | 0-3134 (1)  | 0-039 (1)              |  |
| O(35)     | 0-1695 (6)  | 0-0101 (2)  | 0-2332 (3)  | 0-106 (3)              | 0-1646 (5)  | 0-0100 (2)  | 0-2321 (2)  | 0-073 (2)              |  |
| O(36)     | 0-2672 (6)  | 0-0683 (2)  | 0-3614 (3)  | 0-117 (4)              | 0-2639 (5)  | 0-0688 (2)  | 0-3617 (3)  | 0-077 (3)              |  |
| O(37)     | -0-0211 (5) | 0-0351 (2)  | 0-3027 (2)  | 0-091 (3)              | -0-0265 (4) | 0-0344 (2)  | 0-3021 (2)  | 0-063 (2)              |  |
| O(38)     | 0-1942 (7)  | -0-0484 (2) | 0-3564 (3)  | 0-142 (5)              | 0-1942 (6)  | -0-0487 (2) | 0-3577 (3)  | 0-092 (3)              |  |

Table 2. Bond lengths ( $\text{\AA}$ ) and selected bond angles ( $^\circ$ ) with e.s.d.'s in parentheses

|                   | T = 298 K | T = 173 K |                   | T = 298 K | T = 173 K |
|-------------------|-----------|-----------|-------------------|-----------|-----------|
| Cu(1)-N(2)        | 2-098 (4) | 2-097 (3) | O(30)-C(32)       | 1-175 (6) | 1-219 (5) |
| Cu(1)-N(13)       | 1-994 (4) | 2-002 (3) | O(31)-C(32)       | 1-166 (6) | 1-190 (5) |
| Cu(1)-N(16)       | 2-130 (4) | 2-141 (3) | C(32)-C(33)       | 1-471 (9) | 1-459 (7) |
| Cu(1)-N(27)       | 2-006 (4) | 2-012 (3) |                   |           |           |
| Cu(1)-O(30)       | 2-220 (4) | 2-155 (4) | Cl(34)-O(35)      | 1-410 (4) | 1-413 (3) |
| Cu(1)-O(31)       | 2-421 (5) | 2-528 (5) | Cl(34)-O(36)      | 1-419 (5) | 1-424 (3) |
|                   |           |           | Cl(34)-O(37)      | 1-432 (4) | 1-438 (3) |
|                   |           |           | Cl(34)-O(38)      | 1-376 (5) | 1-398 (4) |
| N(2)-C(3)         | 1-321 (7) | 1-331 (5) | N(16)-C(17)       | 1-307 (7) | 1-327 (5) |
| N(2)-C(15)        | 1-358 (6) | 1-361 (4) | N(16)-C(29)       | 1-358 (6) | 1-360 (4) |
| C(3)-C(4)         | 1-384 (8) | 1-385 (6) | C(17)-C(18)       | 1-393 (8) | 1-398 (6) |
| C(4)-C(5)         | 1-355 (9) | 1-370 (6) | C(18)-C(19)       | 1-345 (9) | 1-360 (6) |
| C(5)-C(6)         | 1-404 (8) | 1-407 (6) | C(19)-C(20)       | 1-401 (8) | 1-414 (6) |
| C(6)-C(7)         | 1-431 (8) | 1-432 (6) | C(20)-C(21)       | 1-419 (7) | 1-425 (5) |
| C(6)-C(15)        | 1-399 (7) | 1-401 (5) | C(20)-C(29)       | 1-396 (7) | 1-397 (5) |
| C(7)-C(8)         | 1-322 (9) | 1-356 (6) | C(21)-C(22)       | 1-334 (9) | 1-346 (6) |
| C(8)-C(9)         | 1-440 (8) | 1-430 (5) | C(22)-C(23)       | 1-441 (7) | 1-433 (6) |
| C(9)-C(10)        | 1-398 (8) | 1-405 (6) | C(23)-C(24)       | 1-405 (8) | 1-422 (6) |
| C(9)-C(14)        | 1-404 (7) | 1-399 (5) | C(23)-C(28)       | 1-409 (7) | 1-401 (5) |
| C(10)-C(11)       | 1-353 (8) | 1-367 (6) | C(24)-C(25)       | 1-354 (8) | 1-367 (6) |
| C(11)-C(12)       | 1-392 (8) | 1-388 (6) | C(25)-C(26)       | 1-395 (7) | 1-407 (5) |
| C(12)-N(13)       | 1-317 (7) | 1-322 (5) | C(26)-N(27)       | 1-312 (6) | 1-326 (5) |
| N(13)-C(14)       | 1-353 (6) | 1-361 (4) | N(27)-C(28)       | 1-359 (6) | 1-356 (5) |
| C(14)-C(15)       | 1-421 (7) | 1-430 (5) | C(28)-C(29)       | 1-427 (7) | 1-441 (5) |
| N(2)-Cu(1)-N(13)  | 80-6 (2)  | 80-8 (1)  | N(16)-Cu(1)-O(30) | 91-1 (1)  | 91-3 (1)  |
| N(2)-Cu(1)-N(16)  | 114-1 (2) | 113-6 (1) | N(16)-Cu(1)-O(31) | 142-1 (1) | 142-0 (1) |
| N(2)-Cu(1)-N(27)  | 97-7 (2)  | 97-6 (1)  | N(27)-Cu(1)-O(30) | 88-2 (1)  | 88-8 (1)  |
| N(2)-Cu(1)-O(30)  | 154-7 (2) | 154-9 (1) | N(27)-Cu(1)-O(31) | 88-5 (2)  | 87-4 (1)  |
| N(2)-Cu(1)-O(31)  | 103-2 (2) | 103-6 (1) | O(30)-Cu(1)-O(31) | 52-1 (1)  | 52-3 (1)  |
| N(13)-Cu(1)-N(16) | 98-9 (2)  | 99-1 (1)  |                   |           |           |
| N(13)-Cu(1)-N(27) | 177-9 (2) | 178-1 (1) |                   |           |           |
| N(13)-Cu(1)-O(30) | 93-9 (2)  | 93-1 (1)  | O(30)-C(32)-O(31) | 121-7 (5) | 120-5 (5) |
| N(13)-Cu(1)-O(31) | 93-1 (2)  | 94-0 (1)  | O(31)-C(32)-C(33) | 118-1 (5) | 118-3 (5) |
| N(16)-Cu(1)-N(27) | 80-6 (2)  | 80-5 (1)  | O(31)-C(32)-C(33) | 120-2 (6) | 121-1 (6) |

1.17 (1) (298 K) and 1.20 (1) Å (173 K), are significantly shorter than the mean value of 1.26 Å determined from the literature data reported for twenty bidentate nonbridging acetato metal complexes.

The bond lengths and angles in the phen ligands of  $[\text{Cu}(\text{phen})_2(\text{CH}_3\text{CO}_2)]\text{ClO}_4$  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). The  $\text{ClO}_4^-$  group also has large thermal motion; however, a foreshortening of the Cl-O bonds is barely discernible. The mean Cl-O bond lengths, 1.41 (298 K) and 1.42 Å (173 K), compare favorably with the value of 1.43 Å reported for well defined  $\text{ClO}_4^-$  groups (Taylor, Hall & Amma, 1969). The observed O-Cl-O bond angles (108–111°) are reasonably close to tetrahedral and fall within the wide range generally found for  $\text{ClO}_4^-$  groups (Figgis, Wadley & Graham, 1972).

In addition to  $[\text{Cu}(\text{phen})_2(\text{CH}_3\text{CO}_2)]\text{ClO}_4$ , the crystal structures of other  $[\text{Cu}(\text{phen or bpy})_2(\text{OXO})]\text{Y}$  complexes ( $\text{OXO}^-$  = a bidentate chelating ligand) have been determined. Several observations can be made by examining the results (Simmons, Seff, Clifford & Hathaway, 1983). (1) The molecular geometry of the  $\text{CuN}_4\text{O}_2$  chromophore varies significantly between cation-distortion isomers. For example, the Cu-O bond distances in  $[\text{Cu}(\text{phen})_2(\text{CH}_3\text{CO}_2)]\text{ClO}_4$  are 2.220 (4) and 2.421 (5) Å ( $T=298$  K), while the corresponding bonds in  $[\text{Cu}(\text{phen})_2(\text{CH}_3\text{CO}_2)]\text{BF}_4$  are 1.999 (4) and 2.670 (5) Å ( $T=298$  K). (2) A pattern of continuous distortion from  $C_2$  symmetry exists: as a pair of *trans* Cu-O<sub>eq</sub> and Cu-N<sub>eq</sub> bonds lengthen, the other pair of *trans* Cu-O<sub>eq</sub> and Cu-N<sub>eq</sub> bonds shorten. Furthermore, the Cu-N<sub>ax</sub> bonds become slightly unequal:

the N atoms in the shorter Cu-N<sub>ax</sub> bonds always belong to the same phen (or bpy) ligands as do the N atoms in the shorter Cu-N<sub>eq</sub> bonds. {This form of distortion is indeed observed for  $[\text{Cu}(\text{phen})_2(\text{CH}_3\text{CO}_2)]\text{ClO}_4$ : the *trans* equatorial Cu(1)-O(31) and Cu(1)-N(16) bonds are longer than the other *trans* equatorial Cu(1)-O(30) and Cu(1)-N(2) bonds, and the axial Cu(1)-N(13) and Cu(1)-N(27) bonds are slightly unequal, albeit in the right sense.} (3) The amplitude and anisotropy of the thermal motions of the O atoms increase as the  $\text{OXO}^-$  group coordinates more symmetrically to  $\text{Cu}^{\text{II}}$ ; concomitantly, the angles between the major axes of the O thermal ellipsoids and the Cu-O bond vectors decrease. (4) The molecular geometry of the  $\text{CuN}_4\text{O}_2$  chromophore is temperature dependent. (5) The distortion from  $C_2$  symmetry in  $[\text{Zn}(\text{bpy})_2(\text{ONO})]\text{NO}_3$ , an orbitally nondegenerate  $d^{10}$  complex, is considerably less and qualitatively different from that in  $[\text{Cu}(\text{bpy})_2(\text{ONO})]\text{NO}_3$ , even though the crystals are isostructural; thus, the distortional behavior in the  $\text{Cu}^{\text{II}}$  systems is not attributable to crystal-packing forces. (6) The thermal motions of the acetato O atoms are remarkably large and anisotropic in the disordered complex,  $[\text{Cu}(\text{phen})_2(\text{CH}_3\text{CO}_2)]\text{BF}_4 \cdot 2\text{H}_2\text{O}$  ( $P2_1/c$ ,  $Z=2$  and the  $\text{Cu}^{\text{II}}$  ions lie on crystallographic  $C_2$  axes), in contrast with the small and nearly isotropic thermal motions of the acetato O atoms in the isostructural, but ordered, Zn analogue. Thus, a  $[\text{Cu}(\text{phen or bpy})_2(\text{OXO})]\text{Y}$  complex apparently cannot possess static  $C_2$  symmetry.

On the basis of these observations, it has been suggested that the  $[\text{Cu}(\text{phen or bpy})_2(\text{OXO})]\text{Y}$  complexes are susceptible to a pseudo-Jahn-Teller (or synonymously 'second-order Jahn-Teller') distortion away from  $C_2$  symmetry. This occurs *via* a vibronic coupling of the  $^2A$  ground and  $^2B$  excited electronic states (Simmons, Clearfield, Fitzgerald, Tyagi & Hathaway, 1983; Simmons, Seff, Clifford & Hathaway, 1983). The two-dimensional adiabatic potential-energy surface for these pseudo-degenerate elec-

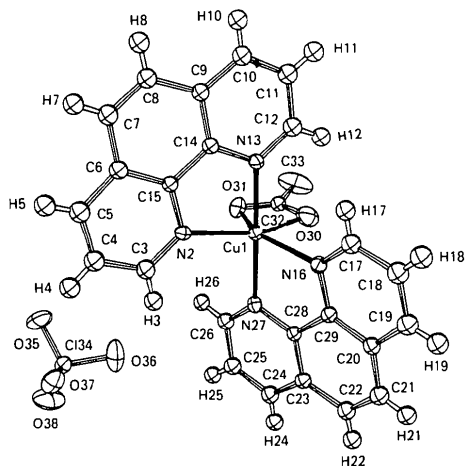


Fig. 1. ORTEP drawing of the pseudo-Jahn-Teller complex  $[\text{Cu}(\text{phen})_2(\text{CH}_3\text{CO}_2)]\text{ClO}_4$  using 20% probability ellipsoids ( $T=298$  K).

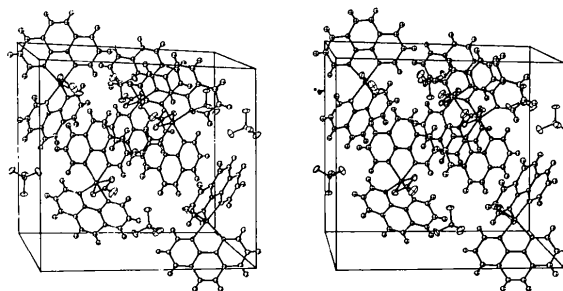


Fig. 2. ORTEP stereoview of the crystal structure of  $[\text{Cu}(\text{phen})_2(\text{CH}_3\text{CO}_2)]\text{ClO}_4$  using 15% probability ellipsoids ( $T=298$  K). The view is approximately into the  $+a$  direction, with  $+b$  extending horizontally to the right, and  $+c$  extending upwards in the plane of the page.

tronic states, which is consistent with theory (Öpik & Pryce, 1957; Hochstrasser & Marzacco, 1969; Bersuker, 1975; Henneker, Penner & Siebrand, 1978) and with the aforementioned crystallographic results, consists of a double-minimum ground-state curve and a parabolic excited-state curve. The  $\text{CuN}_4\text{O}_2$  chromophores that correspond to the minima have maximally distorted Cu-N and Cu-O bonds, which are disposed according to the distortion pattern and its inverse previously described in observation (2). Thus, if the minima are equivalent, the average site symmetry is  $C_2$ , as in  $[\text{Cu}(\text{phen})_2(\text{CH}_3\text{CO}_2)]\text{BF}_4 \cdot 2\text{H}_2\text{O}$ ; if the minima are non-equivalent and separated in energy by  $\Delta E$ , the average site symmetry is  $C_1$ , as in  $[\text{Cu}(\text{phen})_2(\text{CH}_3\text{CO}_2)]\text{ClO}_4$  (Simmons, Clearfield, Fitzgerald, Tyagi & Hathaway, 1983; Simmons, Seff, Clifford & Hathaway, 1983).

According to this model, the molecular geometry of  $[\text{Cu}(\text{phen})_2(\text{CH}_3\text{CO}_2)]\text{ClO}_4$  is a statistical mean weighted according to the relative thermal populations of two minima, which, at a given temperature, is a function of  $\Delta E$ . The observed distortions from  $C_2$  symmetry, as measured by

$$\begin{aligned} \delta^\circ = & \{[\text{Cu}(1)-\text{N}(27)] - [\text{Cu}(1)-\text{N}(13)]\} \\ & + \{[\text{Cu}(1)-\text{N}(16)] - [\text{Cu}(1)-\text{N}(2)]\} \\ & + \{[\text{Cu}(1)-\text{O}(31)] - [\text{Cu}(1)-\text{O}(30)]\}, \end{aligned}$$

should increase with decreasing temperatures, a result of depopulating the higher-energy well. The increase in the  $\delta^\circ$  values from 0.25 (1) (298 K) to 0.44 (1) Å (173 K) is consistent with the model. Because of the marked temperature dependence of its molecular geometry, the  $\Delta E$  value for  $[\text{Cu}(\text{phen})_2(\text{CH}_3\text{CO}_2)]\text{ClO}_4$  should be relatively small, of the order of  $kT$  or less. In fact, a preliminary calculation of  $\Delta E$  using a methodology that incorporates temperature-variable crystallographic data with Boltzmann statistics (Simmons, Clearfield, Fitzgerald, Tyagi & Hathaway, 1983), gives a value of only 125 (15)  $\text{cm}^{-1}$  (Simmons & Hathaway, 1984), compared with the value of 74  $\text{cm}^{-1}$  accurately determined for the more symmetric  $[\text{Cu}(\text{bpy})_2(\text{ONO})]\text{NO}_3$  complex (Simmons, Clearfield, Santarsiero & Hathaway, 1984). With this value for  $\Delta E$ , the relative thermal populations of the two minima are 64 and 36% at 298 K, which together with the large differences in corresponding Cu-O bonds between conformers explains the large anisotropic thermal motions observed for the acetato O atoms at room temperature. (Conversely, small and nearly isotropic

thermal motions are observed for the coordinated phen N atoms because of the small differences in Cu-N bonds between conformers.) The  $\Delta E$  values are quite sensitive to variations in crystal-packing forces, as demonstrated by the significant structural differences between  $[\text{Cu}(\text{phen})_2(\text{CH}_3\text{CO}_2)]\text{ClO}_4$  and  $[\text{Cu}(\text{phen})_2(\text{CH}_3\text{CO}_2)]\text{BF}_4$  (see above). The unusual crystallographic properties and temperature-variable ESR spectra of  $[\text{Cu}(\text{phen})_2(\text{CH}_3\text{CO}_2)]\text{ClO}_4$  strongly suggest that it consists of two interconverting asymmetric structures (a 'dynamic pseudo-Jahn-Teller effect') associated with two energetically non-equivalent and thermally accessible energy minima.

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