Static–Dynamic Distortions of the Tris(1,2-diaminoethane)copper(II) Cation $[Cu(en)_3]^{2+}$. Crystal Structures of the Salts † $[Cu(en)_3][SO_4]$ at 120 K and of $[Cu(en)_3]Cl_2{\cdot}0.75$ en at 298 K

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The structure of $[Cu(en)_3]Cl_2{\cdot}0.75$ en at room temperature and of $[Cu(en)_3][SO_4]$ at *ca.* 120 K have been determined by *X*-ray analysis using diffractometric data. The crystals of $[Cu(en)_3]Cl_2{\cdot}0.75$ en are monoclinic, space group *C2/c*, with $a = 33.774(6)$, $b = 8.756(2)$, $c = 23.972(5)$ Å, $\beta = 99.96(4)°$, and $Z = 16$. The structure has been refined to a conventional *R* factor of 0.062 over 1 465 independent reflections. It consists of $[Cu(en)_3]^{2+}$ cations, Cl^- anions, and interposing 1,2-diaminoethane (en) molecules. The cell contains two independent $[Cu(en)_3]^{2+}$ cations, one of which shows disorder in the co-ordination polyhedron due to two different positions of the nitrogen atoms. All of these polyhedra can be described as tetragonally elongated octahedra. The crystals of $[Cu(en)_3][SO_4]$ are triclinic, space group $P\bar{1}$, with $a = 8.814(3)$, $b = 8.896(3)$, $c = 9.588(3)$, $\alpha = 90.34(4)$, $\beta = 89.37(4)$, $\gamma = 119.80(4)°$, and $Z = 2$. The structure has been refined to an *R* factor of 0.063 over 1 044 independent reflections. It consists of $[Cu(en)_3]^{2+}$ cations and of $[SO_4]^{2-}$ anions, the cations being compressed octahedra. The nitrogen atoms of the three en molecules, however, have surprisingly high temperature factors in comparison with those found for the room-temperature structure. Single-crystal e.s.r. spectra have shown one and three signals for the chloride and sulphate respectively. In the former compound spin exchange over the whole crystal accounts for the observed *g* values and for the shape of the signals, whereas for the latter a three-domain structure is proposed. The possibility that in each domain elongated chromophores are coupled in an antiferrodistortive manner is discussed.

SEVERAL reports have shown that octahedral copper(II) complexes may undergo dynamical distortions which are attributed to Jahn–Teller or pseudo-Jahn–Teller effects depending on whether the metal ion sits in a high- or a low-symmetry site.[1-15] It has also been shown that by decreasing the temperature such dynamic distortions can be frozen out.[9,14,15] In the case of undiluted complexes the freezing of the distortions is accompanied by at least one first-order phase transition,[16,17] which demonstrates the role of co-operative effects in these systems, the understanding of which requires a detailed analysis. In this context, $K_2Pb[Cu(NO_2)_6]$ [18-21] and $[Cu(en)_3][SO_4]$ [22,23] (where en = 1,2-diaminoethane) are of particular interest. For the former compound, several *X*-ray structural determinations at various temperatures are now available,[24-26] together with e.s.r. studies.[18-21] Although the *X*-ray data show that the room-temperature T_h chromophore [24] becomes tetragonally compressed at lower temperatures [26] and the *g*-value pattern is somewhat similar to that of a compressed octahedral copper(II) complex,[19] it is now becoming clear that the Jahn–Teller-distorted chromophore is elongated octahedral, the apparent compression resulting from antiferrodistortive order, *i.e.* all the elongated octahedra have one pair of short bonds parallel to each other whereas alternate long and short bonds should average in a plane orthogonal to the above parallel short bond.[26,27] Since the low-temperature *g* values of $[Cu(en)_3][SO_4]$,[22,23] which at room temperature has D_3 symmetry,[28] are similar to those of frozen $K_2Pb[Cu(NO_2)_6]$,[19] it appeared to us desirable to collect structural information on the former complex at low temperature. Further, the e.s.r. spectra of $[Cu(en)_3]Cl_2{\cdot}0.75$ en at room temperature were also similar to those of a compressed octahedron,[29] so that we felt that the resolution of the *X*-ray structure of this complex at room temperature would be useful for comparison.

EXPERIMENTAL

Collection and Reduction of the X-*Ray Intensity Data.*—The blue crystals of $[Cu(en)_3]Cl_2{\cdot}0.75$ en are very unstable in air and therefore the crystal chosen for the data collection was sealed under nitrogen in a glass capillary. The data for blue $[Cu(en)_3][SO_4]$, the crystals of which are stable in air, were collected at low temperature using a Leybold–Heraeus cryostat. The sample was cooled by a cold nitrogen stream surrounded by a warm nitrogen stream which prevents water vapour from condensing on the cold surface of the sample. The temperature of the cold gas stream, measured with a thermocouple, was kept constant at *ca.* 120 K.

Unit-cell parameters for both complexes were determined by carefully measuring the setting angles (θ, ω, and χ) of 25 reflections on a Philips PW 1100 diffractometer. Several crystals of each complex were examined and in every case all the reflections found by automatic peak hunting were consistent with a single lattice. Details of the crystal data and data collection for the two compounds are given in Table 1. For both structures the reflections were collected to $2\theta = 40°$ since beyond this limit practically no reflection could be observed. The small number of observed reflections for the chloride derivative is due to the continuous, although slow, decomposition and to the presence of some disorder in the structure. The phase transition experienced [22,23,30,31] by $[Cu(en)_3][SO_4]$ at 180 K was found to correspond to a change from the room-temperature trigonal unit cell [28] to a triclinic cell. This transition is evidenced from a crystallographic point of view by the non-equivalence of the reflections of the trigonal Laue group and by the disappearance of the systematic extinctions of the $P\bar{3}1c$ space group.

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† Tris(1,2-diaminoethane)copper(II) sulphate and tris(1,2-diaminoethane)copper(II) chloride–1,2-diaminoethane (4/3).

TABLE 1

Crystal data and data collection details

	$[Cu(en)_3]Cl_2 \cdot 0.75$ en	$[Cu(en)_3][SO_4]$
Molecular formula	$C_{7.5}H_{30}Cl_2CuN_{7.5}$	$C_6H_{24}CuN_6O_4S$
M	359.82	339.90
a/Å	33.744(6)	8.814(3)
b/Å	8.756(2)	8.896(3)
c/Å	23.972(5)	9.588(3)
α/°	90	90.34(4)
β/°	99.96(4)	89.37(4)
γ/°	90	119.80(4)
D_m/g cm^{-3}	1.38	1.75
D_c/g cm^{-3}	1.377	1.740
U/Å^3	6 982.2	652.3
Z	16	2
Space group	$C2/c$	$P\bar{1}$
μ(Mo-K_α)/cm^{-1}	15.60	19.24
Dimensions (mm)	0.8 × 0.4 × 0.2	0.3 × 0.3 × 0.2
Scan speed/° s^{-1}	0.08 in a range of 0.7° in θ	0.08 in a range of 1.0° in θ
Background time/s	8.75 on each side of the peak	12.5 on each side of the peak
Standards	3 every 100 min	3 every 120 min
Max. deviation of standards (%)	20	5
Total data	3 645	1 242
Data used	1 465 ($I \geqslant 3\sigma$)	1 044 ($I \geqslant 3\sigma$)

Other details applicable to both complexes: colour, blue; diffractometer, Philips PW 1100; λ(Mo-K_α) = 0.710 7 Å; monochromator, graphite crystal; take-off angle, 3°; method, $\omega - 2\theta$ scan; 2θ limit, $6 \leqslant 2\theta \leqslant 40°$.

After correction for background, the standard deviation $\sigma(I)$ of the intensity, I, of each reflection was calculated as described elsewhere,[32] using a value of the instability factor, k, of 0.03 for both complexes. The observed intensities were corrected for Lorentz and polarization effects. An absorption correction based upon numerical methods was applied for both complexes.[33] The transmission factors are in the range 0.54—0.74 and 0.58—0.70 respectively for the chloride and sulphate derivatives. Atomic scattering factors for Cu, Cl, S, O, N, and C and those for H atoms were taken from refs. 34 and 35, respectively. Corrections for anomalous-dispersion effects for copper and chlorine atoms were applied in the refinement.[36]

Solution and Refinement of the Structures.—$[Cu(en)_3]Cl_2 \cdot 0.75$ en. The structure of $[Cu(en)_3]Cl_2 \cdot 0.75$ en was solved by direct methods using the MULTAN program which clearly showed the two copper and four independent chlorine atoms, together with some nitrogen and carbon atoms. Two successive F_o Fourier syntheses showed all non-hydrogen atoms, including the atoms of two independent en solvent molecules. One of these molecules lies near to a centre of symmetry, therefore its maximum occupancy is 0.5. Also close to this centre of symmetry are three independent maxima of electron density which, together with the maxima obtained by the inversion operation, give rise to several dispositions of the en molecule. In order to obtain an occupancy of 0.5, since the heights of these maxima are approximately equal, a population parameter of $\frac{2}{3}$ was assigned to each maximum. Furthermore, owing to the impossibility of distinguishing between carbon and nitrogen atoms, all the maxima were considered as due to carbon atoms.

The F_o Fourier synthesis showed also that in one of the two $[Cu(en)_3]^{2+}$ ions all the nitrogen atoms occupy two statistically different positions. The disorder of the nitrogen atoms is not accompanied by an analogous disorder of the carbon atoms, for which no double positions were observed. Two octahedra differing in chirality are consistent with the disorder of the bound en moieties. The refinement was performed by the full-matrix least-squares method of Busing and Levy and as adapted by Stewart.[37] The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, in which weights were assigned according to the expression $w = 1/\sigma^2(F_o)$. After some isotropic cycles, anisotropic thermal parameters were assigned to the copper and chlorine atoms. Refinement led to occupancies of the two possible configurations as 0.54 and 0.46. These values were therefore used for the subsequent refinement. The hydrogen atoms of the linked en groups were introduced in calculated positions (C–H 0.95 Å). They were not refined and were assigned an isotropic temperature factor of $B_H = 1 + B$ (atom attached). The final conventional R factor was 0.062, while R', defined as $[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$, was 0.066. A ΔF Fourier synthesis, calculated at the end of the refinement, did not show any remarkable feature. The final values of the positional parameters and their standard deviations are shown in Table 2.

$[Cu(en)_3][SO_4]$. The structure was solved by a Patterson

TABLE 2

Positional parameters (× 10^4) for $[Cu(en)_3]Cl_2 \cdot 0.75$ en with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
Cu(1)	4 339(1)	2 316(3)	969(1)
Cu(2)	1 616(1)	2 095(3)	2 310(1)
Cl(1)	4 297(2)	2 647(7)	2 668(2)
Cl(2)	743(2)	2 907(7)	732(2)
Cl(3)	1 205(2)	2 320(8)	4 005(2)
Cl(4)	2 942(2)	1 591(7)	2 293(3)
N(1)	4 773(4)	3 368(18)	553(6)
N(2)	4 419(5)	4 253(19)	1 451(7)
N(3)	4 358(5)	351(18)	528(6)
N(4)	4 786(5)	920(20)	1 613(7)
N(5)	3 839(6)	1 564(22)	1 324(7)
N(6)	3 802(6)	3 463(22)	334(7)
C(1)	4 820(6)	4 934(27)	738(9)
C(2)	4 802(7)	4 950(25)	1 376(10)
C(3)	4 722(7)	−469(25)	712(9)
C(4)	4 795(7)	−594(28)	1 350(11)
C(5)	3 482(8)	2 334(34)	1 075(11)
C(6)	3 453(8)	2 596(35)	444(11)
N(71) [a]	1 077(11)	4 045(37)	2 088(15)
N(72)	1 298(12)	3 643(45)	2 692(16)
N(81)	1 125(8)	1 077(33)	2 607(12)
N(82)	1 065(11)	1 189(39)	1 988(16)
N(91)	2 032(9)	3 335(36)	1 963(12)
N(92)	1 688(12)	3 609(42)	1 583(15)
N(101)	1 484(9)	1 228(32)	1 568(12)
N(102)	1 932(12)	560(45)	1 778(16)
N(111)	2 092(10)	390(36)	2 772(14)
N(112)	1 701(12)	270(45)	3 002(17)
N(121)	1 796(10)	3 313(37)	3 059(13)
N(122)	2 160(11)	2 852(46)	2 744(15)
C(7)	822(7)	3 535(28)	2 403(10)
C(8)	751(6)	1 896(25)	2 328(8)
C(9)	1 944(6)	3 009(27)	1 291(9)
C(10)	1 842(7)	1 293(27)	1 237(10)
C(11)	2 161(7)	832(30)	3 329(11)
C(12)	2 207(6)	2 546(30)	3 344(9)
N(7) [b]	4 373(5)	1 987(20)	4 108(6)
N(8)	3 531(6)	2 697(25)	3 519(8)
C(14)	4 076(7)	2 842(27)	4 352(8)
C(15)	3 655(8)	2 350(32)	4 136(10)
C(16) [c]	2 329(18)	2 534(142)	5 028(32)
C(17)	2 672(24)	4 031(93)	5 008(31)
C(18)	2 802(24)	939(97)	5 102(30)

[a] The nitrogen atoms of set 1 (as indicated by the last digit) are those having population parameters of 0.54. [b] This atom and the following belong to the two en solvent molecules. [c] The last three atoms have a population parameter of $\frac{2}{3}$.

synthesis which showed the copper and sulphur atoms in positions very close to those found at room temperature.[28] Two F_0 Fourier syntheses showed all non-hydrogen atoms. Three oxygen atoms of the sulphate ion appear to be disordered, occupying two different positions with almost equal occupancy factors, as shown by the height of the F_0 peaks and by the least-squares refinement which gave population parameters close to 0.5 for the six positions. Occupancy factors of 0.5 were subsequently used for these atoms.

A refinement performed using isotropic temperature factors for all the atoms showed surprisingly high temperature factors for the atoms of the three en moieties. The mean value of the isotropic B factors relative to the six nitrogen atoms was 3.0 Å^2 which is much higher than the value of 0.9 Å^2 for the copper atom. Furthermore, the mean value for the N atoms was of the same order of magnitude as the mean value of B_{ii} found (3.6 Å^2) for the same atoms at room temperature, which was also considered to be rather high.[28] An isotropic refinement led to very elongated thermal ellipsoids for the nitrogen atoms (see Figure 4). The hydrogen atoms were introduced in calculated positions (C–H 0.95 Å) with an isotropic temperature factor of $B_H = B$ (atom attached) + 1. These atoms were not refined. A final anisotropic refinement gave an R value of 0.063, while R' was 0.080. A final ΔF Fourier synthesis did not show any remarkable feature except for diffuse zones of electron density close to the sulphur atom, of relatively low magnitude (<1 e Å^{-3}). This is probably due to the existence of different statistical orientations of the sulphate ion. The final values of the parameters and their standard deviations are shown in Table 3. A list of the structure-factor amplitudes and of thermal parameters for both complexes is available as Supplementary Publication No. SUP 22528 (22 pp.).*

TABLE 3

Positional parameters ($\times 10^4$) for $[Cu(en)_3][SO_4]$ with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
Cu	6 640(2)	3 332(2)	2 555(2)
N(1)	6 820(15)	5 548(16)	1 224(13)
N(2)	6 968(14)	1 425(16)	3 730(13)
N(3)	8 570(15)	3 317(16)	1 291(12)
N(4)	8 545(17)	5 539(16)	3 764(12)
N(5)	4 578(14)	3 055(16)	3 636(11)
N(6)	4 522(16)	1 332(15)	1 217(13)
C(1)	2 908(19)	1 240(19)	1 709(15)
C(2)	8 405(18)	7 066(18)	1 676(14)
C(3)	2 999(19)	1 390(19)	3 238(15)
C(4)	8 324(19)	7 110(19)	1 739(15)
C(5)	8 742(21)	1 806(21)	1 659(17)
C(6)	8 677(22)	1 612(22)	3 226(18)
S	3 328(5)	6 682(5)	2 467(4)
O(1)	4 948(14)	8 067(15)	1 984(14)
O(2) *	2 038(29)	6 950(31)	3 080(26)
O(3)	1 926(23)	6 989(26)	1 661(23)
O(4)	3 708(25)	5 596(25)	3 709(19)
O(5)	2 674(31)	5 356(30)	1 390(28)
O(6)	2 998(36)	5 051(30)	2 293(31)
O(7)	3 352(34)	7 275(35)	3 855(19)

* This atom and the following atoms have population parameters of 0.5.

E.S.R. Spectra.—Spectra at 4.2—300 K were recorded with a Varian E-9 spectrometer operating at *ca.* 9 GHz and equipped with an Oxford Instruments ESR 9 continuous-flow cryostat.

RESULTS

Description of the Structures.—The structure of $[Cu(en)_3]Cl_2 \cdot 0.75$ en consists of discrete $[Cu(en)_3]^{2+}$ cations, of chloride ions, and of interposed en molecules. The asymmetric unit contains two complex cations, four Cl^- ions, and 1.5 en molecules. The copper atoms are six-co-ordinate being bound to six nitrogen atoms of three en molecules. The six nitrogen atoms of one of the two independent $[Cu(en)_3]^{2+}$ ions are disordered since they occupy two statistically different positions having a population parameter close to 0.5. The two configurations of the nitrogen atoms around copper are shown in Figure 1. The carbon atoms linked to the nitrogen atoms do not show any disorder and they remain in the same positions for the two configurations. The other independent $[Cu(en)_3]^{2+}$ cation does not show any disorder (Figure 2). Distances and angles in the complex cations are shown in Table 4.

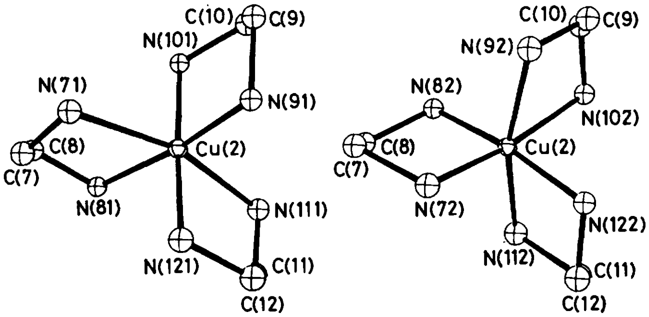

FIGURE 1 Perspective view of the two disordered $[Cu(en)_3]^{2+}$ cations in $[Cu(en)_3]Cl_2 \cdot 0.75$ en

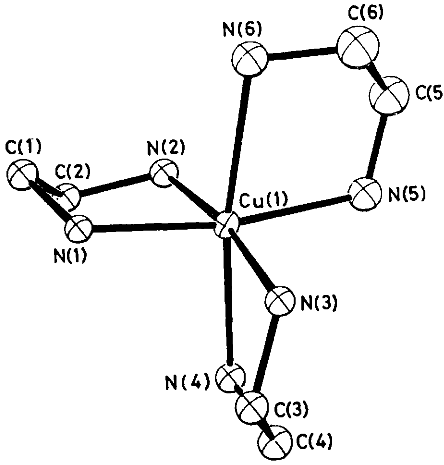

FIGURE 2 Perspective view of the non-disordered $[Cu(en)_3]^{2+}$ cation in $[Cu(en)_3]Cl_2 \cdot 0.75$ en

Two of the three crystallographically independent coordination polyhedra seen in the present structure can be described as elongated. The third polyhedron, which corresponds to one of the two disordered ions, shows three longer and three shorter distances. However, even in this case we feel that the geometry of the polyhedron can be taken as tetragonally elongated, the elongation axis being defined by the pair of longest opposite bonds, *i.e.* Cu–N(92) (2.24 Å) and Cu–N(112) (2.29 Å). The direction cosines of the three elongation axes with respect to the crystallographic axes are reported in Table 5. The unit cell is shown in Figure 3.

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

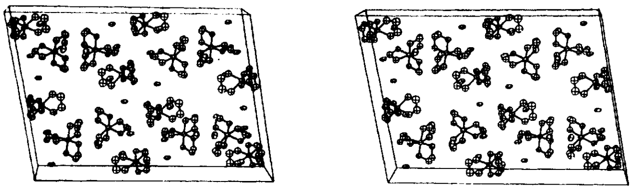

FIGURE 3 Stereoscopic view of [Cu(en)$_3$]Cl$_2$·0.75 en showing the crystal packing. The en solvent molecules have been omitted. The *c* axis is vertical, *a* is horizontal, and *b* points into the paper

The structure of [Cu(en)$_3$][SO$_4$] at low temperature consists of discrete [Cu(en)$_3$]$^{2+}$ cations and [SO$_4$]$^{2-}$ anions. Figure 4 shows a view of the [Cu(en)$_3$]$^{2+}$ cation. The coordination polyhedron can be described as compressed; distances and angles are reported in Table 6. The unit cell is shown in Figure 5. Some short contacts between the oxygen atoms of the [SO$_4$]$^{2-}$ anions and some hydrogen atoms are observed as previously found in the room-temperature structure.[24] It seems therefore that the phase transition [22,23,30] at 180 K is associated with a freezing out of the Jahn–Teller distortion which shows up as a change in chromophore from an almost regular octahedron to a compressed octahedron. The implications of this change in connection with the high thermal parameters and the e.s.r. will be discussed in the next section.

TABLE 4

Selected bond distances (Å) and angles (°) for [Cu(en)$_3$]Cl$_2$·0.75 en with estimated standard deviations in parentheses

(*a*) Distances

Cu(1)–N(1)	2.12(2)	N(4)–C(4)	1.47(3)
Cu(1)–N(2)	2.04(2)	N(5)–C(5)	1.42(3)
Cu(1)–N(3)	2.03(2)	N(6)–C(6)	1.47(4)
Cu(1)–N(4)	2.31(2)	C(1)–C(2)	1.54(3)
Cu(1)–N(5)	2.12(2)	C(3)–C(4)	1.51(3)
Cu(1)–N(6)	2.38(2)	C(5)–C(6)	1.52(4)
Cu(2)–N(71)	2.49(3)	N(71)–C(7)	1.32(5)
Cu(2)–N(81)	2.11(3)	N(81)–C(8)	1.51(3)
Cu(2)–N(91)	2.06(3)	N(91)–C(9)	1.61(4)
Cu(2)–N(101)	1.91(3)	N(101)–C(10)	1.56(4)
Cu(2)–N(111)	2.33(3)	N(111)–C(11)	1.37(4)
Cu(2)–N(121)	2.09(3)	N(121)–C(12)	1.58(4)
Cu(2)–N(72)	2.04(4)	N(72)–C(7)	1.64(4)
Cu(2)–N(82)	2.05(4)	N(82)–C(8)	1.57(5)
Cu(2)–N(92)	2.24(4)	N(92)–C(9)	1.31(5)
Cu(2)–N(102)	2.24(4)	N(102)–C(10)	1.43(5)
Cu(2)–N(112)	2.29(4)	N(112)–C(11)	1.69(5)
Cu(2)–N(122)	2.06(3)	N(122)–C(12)	1.44(4)
N(1)–C(1)	1.44(3)	C(7)–C(8)	1.46(3)
N(2)–C(2)	1.47(3)	C(9)–C(10)	1.54(3)
N(3)–C(3)	1.43(3)	C(11)–C(12)	1.51(4)

(*b*) Angles

N(1)–Cu(1)–N(2)	82.6(6)	N(81)–Cu(2)–N(91)	171.2(11)
N(1)–Cu(1)–N(3)	92.0(6)	N(81)–Cu(2)–N(101)	94.4(12)
N(1)–Cu(1)–N(4)	96.9(6)	N(81)–Cu(2)–N(111)	94.9(11)
N(1)–Cu(1)–N(5)	170.3(7)	N(81)–Cu(2)–N(121)	93.0(12)
N(1)–Cu(1)–N(6)	91.5(6)	N(91)–Cu(2)–N(101)	84.3(12)
N(2)–Cu(1)–N(3)	170.7(6)	N(91)–Cu(2)–N(111)	93.9(12)
N(2)–Cu(1)–N(4)	93.1(6)	N(91)–Cu(2)–N(121)	87.7(12)
N(2)–Cu(1)–N(5)	93.8(7)	N(101)–Cu(2)–N(111)	102.6(12)
N(2)–Cu(1)–N(6)	91.3(6)	N(101)–Cu(2)–N(121)	171.4(13)
N(3)–Cu(1)–N(4)	79.8(6)	N(111)–Cu(2)–N(121)	81.0(12)
N(3)–Cu(1)–N(5)	92.6(7)	N(72)–Cu(2)–N(82)	84.9(15)
N(3)–Cu(1)–N(6)	96.6(6)	N(72)–Cu(2)–N(92)	95.3(15)
N(4)–Cu(1)–N(5)	92.4(7)	N(72)–Cu(2)–N(102)	172.1(15)
N(4)–Cu(1)–N(6)	171.0(6)	N(72)–Cu(2)–N(112)	98.5(15)
N(5)–Cu(1)–N(6)	79.4(7)	N(72)–Cu(2)–N(122)	93.0(15)
N(71)–Cu(2)–N(81)	76.9(11)	N(82)–Cu(2)–N(92)	98.6(14)
N(71)–Cu(2)–N(91)	94.4(12)	N(82)–Cu(2)–N(102)	92.5(14)
N(71)–Cu(2)–N(101)	91.7(12)	N(82)–Cu(2)–N(112)	89.7(14)
N(71)–Cu(2)–N(111)	164.1(12)	N(82)–Cu(2)–N(122)	171.5(15)
N(71)–Cu(2)–N(121)	85.8(12)	N(92)–Cu(2)–N(102)	77.7(14)
N(92)–Cu(2)–N(112)	164.5(15)	Cu(2)–N(81)–C(8)	107.2(17)
N(92)–Cu(2)–N(122)	89.8(14)	Cu(2)–N(91)–C(9)	106.8(17)
N(102)–Cu(2)–N(112)	88.9(15)	Cu(2)–N(101)–C(10)	112.5(18)
N(102)–Cu(2)–N(122)	90.6(15)	Cu(2)–N(111)–C(11)	105.6(21)
N(112)–Cu(2)–N(122)	82.5(14)	Cu(2)–N(121)–C(12)	104.8(19)
Cu(1)–N(1)–C(1)	108.5(13)	Cu(2)–N(72)–C(7)	109.0(21)
Cu(1)–N(2)–C(2)	108.0(13)	Cu(2)–N(82)–C(8)	107.6(20)
Cu(1)–N(3)–C(3)	111.7(12)	Cu(2)–N(92)–C(9)	110.4(23)
Cu(1)–N(4)–C(4)	104.5(12)	Cu(2)–N(102)–C(10)	101.4(23)
Cu(1)–N(5)–C(5)	111.2(16)	Cu(2)–N(112)–C(11)	97.0(21)
Cu(1)–N(6)–C(6)	102.4(14)	Cu(2)–N(122)–C(12)	112.2(24)
Cu(2)–N(71)–C(7)	99.9(20)		

TABLE 5

The direction cosines of the elongation axes of the three crystallographically independent CuN$_6$ chromophores in [Cu(en)$_3$]Cl$_2$·0.75 en with respect to the *a**, *b*, and *c* axes

Axis	*a**	*b*	*c*
1	−0.659	0.517	−0.545
2	0.718	−0.690	0.094
3	−0.071	−0.585	0.808

E.S.R. Data.—The polycrystalline powder spectra of [Cu(en)$_3$]Cl$_2$·0.75 en at room temperature yield three *g* values: $g_1 = 2.16$, $g_2 = 2.12$, and $g_3 = 2.07$.[29] Single-crystal e.s.r. spectra show only one signal for every orientation in the static magnetic field; g_2 is observed parallel to *b* while g_1 bisects, within 5° of experimental error, the *ac** positive quadrant.

The polycrystalline powder spectra of [Cu(en)$_3$][SO$_4$] were recorded in the range 4.2—180 K. The *g* values, determined at 77 K, are:[22] $g_1 = 2.159$, $g_2 = 2.134$, and $g_3 = 2.053$. Below this temperature the spectra show some sharpening and a variation of g_1 and g_3, from 2.16 to 2.17 and from 2.05 to 2.04 respectively. Approaching the liquid-helium temperature, a sudden change in the linewidth occurs: at 4.2 K, the e.s.r. spectra are broader than at higher temperatures (Figure 6). This effect might be due to diminished spin-exchange interactions which become of the same order of the microwave quantum.

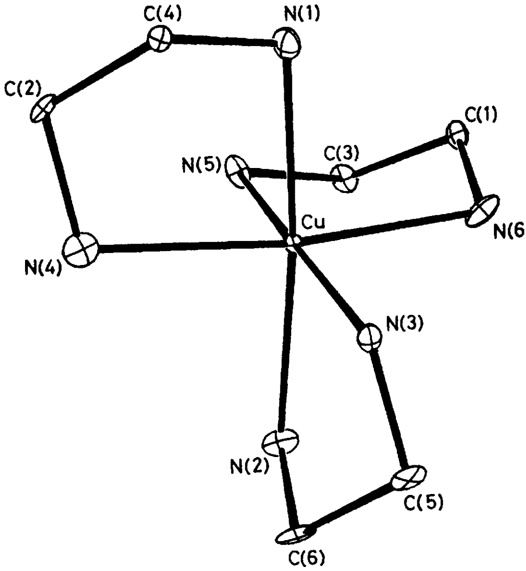

FIGURE 4 Perspective view of the [Cu(en)$_3$]$^{2+}$ cation in [Cu(en)$_3$][SO$_4$]

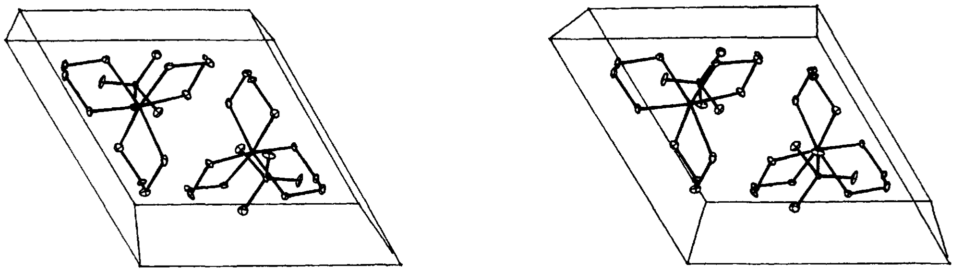

FIGURE 5 Stereoscopic view of $[Cu(en)_3][SO_4]$ showing the crystal packing. The *b* axis is vertical, *a* is horizontal, and *c* points into the paper

A detailed analysis of the single-crystal e.s.r. spectra of $[Cu(en)_3][SO_4]$ at liquid-nitrogen temperature has been published elsewhere.[22, 23]

TABLE 6

Selected bond distances (Å) and angles (°) for $[Cu(en)_3][SO_4]$ with estimated standard deviations in parentheses

(*a*) Distances

Cu–N(1)	2.23(1)	N(6)–C(1)	1.47(2)
Cu–N(2)	2.22(2)	C(1)–C(3)	1.47(2)
Cu–N(3)	2.05(1)	C(2)–C(4)	1.52(2)
Cu–N(4)	2.23(1)	C(5)–C(6)	1.51(2)
Cu–N(5)	2.06(1)	S–O(1)	1.42(2)
Cu–N(6)	2.18(1)	S–O(2)	1.41(3)
N(1)–C(4)	1.45(2)	S–O(3)	1.58(2)
N(2)–C(6)	1.51(2)	S–O(4)	1.66(2)
N(3)–C(5)	1.47(3)	S–O(5)	1.46(3)
N(4)–C(2)	1.48(2)	S–O(6)	1.34(3)
N(5)–C(3)	1.49(2)	S–O(7)	1.43(2)

(*b*) Angles

N(1)–Cu–N(2)	169.8(4)	Cu–N(3)–C(5)	109.9(9)
N(1)–Cu–N(3)	91.2(5)	Cu–N(4)–C(2)	106.4(9)
N(1)–Cu–N(4)	79.8(4)	Cu–N(5)–C(3)	108.1(10)
N(1)–Cu–N(5)	94.0(6)	Cu–N(6)–C(1)	106.2(9)
N(1)–Cu–N(6)	95.4(5)	O(1)–S–O(2)	122.8(12)
N(2)–Cu–N(3)	82.7(5)	O(1)–S–O(4)	109.5(9)
N(2)–Cu–N(4)	92.4(5)	O(1)–S–O(5)	106.8(11)
N(2)–Cu–N(5)	92.7(5)	O(2)–S–O(4)	102.0(14)
N(2)–Cu–N(6)	93.1(5)	O(2)–S–O(5)	114.4(14)
N(3)–Cu–N(4)	93.0(5)	O(4)–S–O(5)	98.4(14)
N(3)–Cu–N(5)	173.7(6)	O(1)–S–O(3)	102.9(9)
N(3)–Cu–N(6)	94.1(5)	O(1)–S–O(6)	118.6(14)
N(4)–Cu–N(5)	91.5(5)	O(1)–S–O(7)	99.5(10)
N(4)–Cu–N(6)	171.5(7)	O(3)–S–O(6)	110.9(15)
N(5)–Cu–N(6)	81.8(5)	O(3)–S–O(7)	104.6(17)
Cu–N(1)–C(4)	107.6(10)	O(6)–S–O(7)	118.4(18)
Cu–N(2)–C(6)	103.7(9)		

DISCUSSION

The three independent cations and the relative disorder found in the lattice of $[Cu(en)_3]Cl_2 \cdot 0.75$ en can be considered as originating from the freezing out of dynamic Jahn–Teller distortions. However, this picture cannot be immediately reconciled with the required presence of three mutually orthogonal distortions,[38] since in the present case the elongation axes of the two distorted chromophores form an angle of 53°. The three distorted octahedra are not equivalent, although all the differences in bond distances and angles fall within 3σ and therefore may not be significant.

The lack of hyperfine structure in the e.s.r. spectra as well as the observation of a single signal in the single-crystal spectra indicate that intermolecular exchange interactions are operative.[39] The observed *g* values, which are similar to those of $[Cu(en)_3][SO_4]$ at low temperature and which would be typical of compressed octahedral chromophores if they were molecular values,[40] are actually due to the crystal average of the three elongated chromophores revealed by the *X*-ray structure. Owing to the similarity in the *g* values of the exchange-narrowed powder e.s.r. spectra of $[Cu(en)_3]Cl_2 \cdot 0.75$ en and $[Cu(en)_3][SO_4]$ at low temperature, a doubt arises as to whether the compressed-octahedral description of the latter chromophore is adequate. The single-crystal e.s.r. spectra of the two compounds, however, are different since three signals instead of one are observed for the sulphate derivative.[22,23,29] These three signals as well as the orientation of their principal directions would require the presence of three equivalent triclinic cells related by the trigonal axis of the room-temperature structure, whereas no trace of such cells was revealed by the diffractometric data. Furthermore, a comparison of the bond distances in $[Cu(en)_3]Cl_2 \cdot 0.75$ en and $[Cu(en)_3][SO_4]$ shows that the length of the two shortest bonds of the latter compare well with the values of the short bonds of the former, while the lengths of the long bonds of the sulphate are about the average of the long and the short bonds of the chloride. This is in accord with previous suggestions that compressed-octahedral structures of Jahn–Teller-distorted copper(II) chromophores are due to an average of elongated octahedra coupled in an antiferrodistortive order.[41–43]

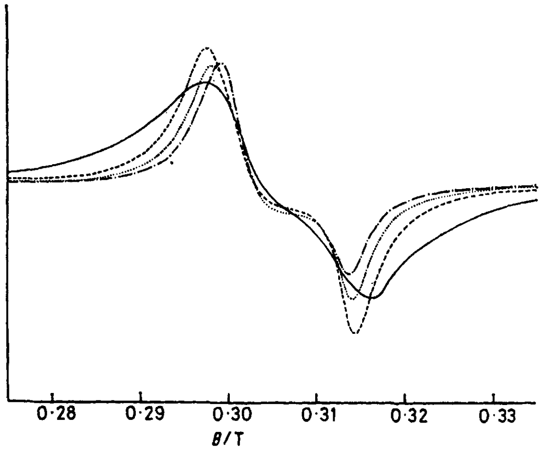

FIGURE 6 Polycrystalline e.s.r. powder spectra of $[Cu(en)_3][SO_4]$ at 65 (— · — · —), 41 (· · · ·), 21 (— — —), and 4.2 K (——)

When rejecting the compressed-octahedral model, it should also be noted that the thermal ellipsoids are anomalously large considering the low temperature of the *X*-ray determination. However, only the thermal ellipsoids of the long bonds should be anomalous in the antiferrodistortive model, whereas no substantial difference is observed in the thermal ellipsoids of all the nitrogen atoms. In order to justify these characteristics of the thermal ellipsoids as well as the observation of the three e.s.r. signals it should be assumed that a large number of domains occur and that within each domain elongated octahedra are coupled in an antiferrodistortive order. Such a model could imply that when a chromophore is frozen out in the distorted form it influences the neighbouring molecules in such a way that an ordered domain is formed extending for a few adjacent cells. Since the three e.s.r. signals seen in the crystal spectra have about the same intensities and the principal *g* values have approximately the same magnitude, the three domains should be equally populated and possibly comprise similarly distorted chromophores. The ensemble of domains should, however, simulate an essentially regular CuN_6 chromophore, as observed in the room-temperature *X*-ray structure, while the low-temperature structure shows a compressed octahedron. Probably, therefore, the three chromophores are not equivalent and the observed *g* values, which would be the average of those of antiferrodistortively coupled octahedra, might be close to each other within experimental error. This analysis is consistent with the characterization of elongated octahedral $[Cu(en)_3][NO_3]_2$ doped into its zinc analogue.[23]

Although it seems feasible that the compressed structure of $[Cu(en)_3]^{2+}$ in the sulphate is actually due to coupled elongated octahedra, a more detailed description of the frozen-out chromophores can hardly arise from the present structural data. Indeed, the disorder of the unit cell and the small relative weight of several possible contributing chromophores may render unsound any further analysis.

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