Synthesis and Characterization of Imidazolate-bridged Copper(II) Complexes of Triangular Skeleton

Hisashi Ōkawa,* Masahiro Mikuriya, and Sigeo Kida

Department of Chemistry, Faculty of Science, Kyushu University 33, Higashi-ku, Fukuoka 812

(Received February 16, 1983)

New polynuclear copper(II) complexes of the composition [CuL(im)]X (L=*N,N,N',N'*-tetramethylethylenediamine (tmen), bip, phen; X=ClO_4, PF_6, BF_4; im=imidazolate ion) have been prepared. Cryomagnetic measurements have indicated that the complexes involve a trianglar-trinuclear skeleton and an antiferromagnetic spin-exchange interaction operates between copper(II) ions; exchange integrals being evaluated at -37—-45 cm^{-1}. Based on the Dreiding model consideration of the complexes and the crystal structure of $[Cu(tmen)(imH)_2](ClO_4)_2$, a trinuclear structure of the triangular skeleton with imidazolate bridges, Cu-Im-Cu-Im-Cu-Im-┐, was supposed for the complexes.
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Bovine erythrocyte superoxide dismutase (BESOD) is known to involve an imidazolate-bridged copper(II)–zinc(II) unit at the active site.[1] Cryomagnetic investigation of the copper-substituted enzyme Cu_4-BESOD revealed that an antiferromagnetic spin-exchange interaction operates within each Cu^{2+}–Im–Cu^{2+} unit, the exchange integral being evaluated at -26 cm^{-1}.[2] Therefore, imidazolate-bridged polynuclear copper(II) complexes are of current interest.

So far binuclear and tetranuclear copper(II) complexes with imidazolate bridge have been prepared and characterized. Syntheses of the complexes were achieved (1) by the use of polynucleating ligands containing imidazolate group,[3-6] (2) by the use of biimidazolate or bibenzimidazolate as bridging group,[7] (3) by the reaction of a tridentate or tetradentate ligand, copper(II) ion and imidazole (or 2-methylimidazole) in the 2:2:1 mole ratio,[4,6,8-11] and (4) by the reaction of a binucleating macrocycle, copper(II) ion and imidazole in the 1:2:1 mole ratio.[12,13] Haddad and Hendrickson also prepared and characterized the imidazolate-bridged complexes $[Cu_2(bip)_4(im)](PF_6)_3$ and $[Cu_2(phen)_4(im)](ClO_4)_3$.[7]

In this study we have synthesized new imidazolate-bridged trinuclear copper(II) complexes of the composition CuL(im)X (L=*N,N,N',N'*-tetramethylethylenediamine (tmen), bip, phen; X=ClO_4, PF_6, BF_4; im=imidazolate ion). The triangular structure has been characterized on the basis of cryomagnetic properties, Dreiding model consideration, and the crystal structure of $[Cu(tmen)(imH)_2](ClO_4)_2$.

Experimental

Syntheses. *[CuL(im)]X (L=tmen, bip, phen; X=ClO_4, PF_6, BF_4)*: The synthetic methods for the complexes are nearly the same and exemplified by $[Cu(tmen)(im)]ClO_4$. Copper(II) acetate monohydrate (2.0 g) and tmen (1.2 g) were dissolved in a methanol–water mixture (1:1, 100 cm^3) and warmed at 60 °C. To this was added an aqueous solution of NaOH (0.4 g) and $NaClO_4$ (1.4 g) with stirring to give a di-μ-hydroxo complex $[Cu_2(tmen)_2(OH)_2](ClO_4)_2$. Imidazole was added to this mixture with stirring and warming. When the most part of the di-μ-hydroxo complex was dissolved, the reaction mixture was quickly filtered to separate insoluble materials and the filtrate was allowed to stand overnight. The crystals thus obtained were filtered, washed with methanol and dried *in vacuo*.

$[Cu(phen)(im)]ClO_4$ was practically insoluble in water and in methanol. In order to avoid the contamination of $[Cu_2(phen)_2(OH)_2](ClO_4)_2$, it was prepared by adding a small excess of imidazole to the di-μ-hydroxo complex and the product was throughly washed with hot water.

$[Cu(tmen)(imH)_2](ClO_4)_2$. Copper(II) perchlorate hexahydrate (3.7 g), tmen (1.2 g), and imidazole (1.5 g) were dissolved in hot water (30 cm^3), and the resulting purple solution was filtered and left stand overnight to give bluish purple crystals.

Elemental analyses of the complexes are given in Table 1.

Measurements. Electronic spectra were recorded on a Shimadzu Multipurpose Spectrophotometer model MSP-1000 by reflection on powder samples. Magnetic susceptibilities were measured by the Faraday method, the apparatus being calibrated by the use of $[Ni(en)_3]S_2O_3$.

X-Ray Crystal Structure Analysis of $[Cu(tmen)(imH)_2](ClO_4)_2$. A crystal with dimensions of 0.02 mm×0.17 mm×0.45 mm

Table 1. Elemental analyses of complexes

Complex	Found(%)			Calcd(%)		
	C	H	N	C	H	N
$[Cu(tmen)(im)]PF_6$	27.22	4.93	14.23	27.59	4.89	14.30
$[Cu(tmen)(im)]ClO_4$	30.70	5.43	16.07	31.22	5.53	16.18
$[Cu(tmen)(im)]BF_4$	32.13	5.70	16.68	32.40	5.74	16.79
$[Cu(bip)(im)]PF_6$	35.78	2.90	12.90	36.16	2.59	12.98
$[Cu(bip)(im)]ClO_4$	40.04	3.03	14.08	40.43	2.87	14.51
$[Cu(bip)(im)]BF_4$	40.73	3.16	14.38	40.80	3.16	14.64
$[Cu(phen)(im)]PF_6$	39.53	2.77	11.80	39.53	2.43	12.29
$[Cu(phen)(im)]ClO_4$	43.07	2.74	13.65	42.97	2.88	13.36
$[Cu(phen)(im)]BF_4 \cdot H_2O$	43.21	3.13	13.54	43.35	3.15	13.48

was used for the X-ray analysis. The unit-cell parameters and intensities were measured on a Rigaku AFC-5 automated four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ=0.71069 Å) at 20±1 °C. The unit-cell parameters were determined by the least-squares refinement based on the 25 reflections in the range of $17<2\theta<29°$.

Crystal Data: $C_{12}H_{24}Cl_2CuN_6O_8$, F.W.=514.81; monoclinic; $P2_1/n$; a=12.920(5), b=16.171(9), and c=10.084(4) Å; β=97.15(3)°; D_m=1.62; D_c=1.64 g cm^{-3}; Z=4.

The intensity data were collected by the 2θ-ω scan technique with a scan rate of 4° min^{-1}. Three standard reflections were monitored every 100 reflections, and their intensities showed a good stability. A total of 4030 reflections with $2\theta<50°$ were collected. The intensity data were corrected for the Lorentz and the polarization effects, but not for absorption. Independent 1838 reflections with $|F_o|>3\sigma(|F_o|)$ were considered as "observed" and were used for the structure analysis.

The structure was solved by the heavy-atom method and refined by the block-diagonal least-squares method. To identify the nitrogen atoms of the imidazole rings which are not coordinated to the copper atom, the two possible atoms of each ring were both labelled nitrogen. Then the atoms with the lower temperature factors were distinctly labelled nitrogen. Hydrogen atoms were located from the difference Fourier map and included in the refinement. In the least-squares refinement the weighting scheme,[14] $w=(15.56+|F_o|+0.0078|F_o|^2)^{-1}$, was employed. The final R values were R=0.097 and R_w=0.126.

Table 2. Fractional positional parameters ($\times 10^4$) and thermal parameters of non-hydrogen atoms with their estimated standard deviations in parentheses

Atom	x	y	z	B_{eq}/Å^2
Cu	1187(1)	2387(1)	3773(2)	2.8
Cl(1)	1059(3)	3695(2)	6960(4)	3.9
Cl(2)	1851(3)	920(3)	303(4)	4.1
O(1)	1060(13)	3107(7)	5926(12)	7.0
O(2)	1619(12)	4404(8)	6605(13)	6.9
O(3)	1555(15)	3312(13)	8135(14)	9.8
O(4)	88(12)	3904(11)	7143(25)	11.6
O(5)	1487(13)	1515(9)	1158(15)	7.8
O(6)	2539(14)	414(11)	1168(14)	9.5
O(7)	1039(12)	427(11)	−323(19)	9.3
O(8)	2336(20)	1332(16)	−619(17)	15.1
N(1)	579(10)	3277(7)	2473(11)	3.5
N(2)	−332(9)	1915(9)	3597(11)	4.0
N(3)	2634(9)	2837(8)	3801(11)	3.7
N(4)	4003(10)	3634(9)	4117(13)	4.6
N(5)	1761(11)	1413(8)	4870(10)	4.2
N(6)	2317(10)	635(8)	6559(12)	3.9
C(1)	376(15)	4061(11)	3146(18)	5.3
C(2)	1229(16)	3486(13)	1383(17)	5.9
C(3)	−401(14)	2898(11)	1777(17)	4.8
C(4)	−1004(12)	2525(10)	2766(17)	4.7
C(5)	−390(16)	1115(11)	2962(18)	5.2
C(6)	−744(14)	1833(17)	4914(16)	6.8
C(7)	3448(12)	2449(12)	3253(14)	4.7
C(8)	4272(14)	2948(11)	3422(14)	4.5
C(9)	2990(12)	3545(9)	4328(13)	3.3
C(10)	2210(16)	718(12)	4429(15)	5.5
C(11)	2549(16)	247(9)	5457(16)	4.8
C(12)	1867(12)	1353(10)	6196(13)	3.7

The atomic scattering factors and the anomalous dispersion corrections were taken from the International Tables for X-ray Crystallography.[15] All the calculations were carried out on the FACOM M-200 computer in the Computer Center of Kyushu University by the use of a local version[16] of the UNICS-III[17] and the ORTEP[18] programs. The final positional and thermal parameters with their estimated standard deviations are given in Table 2. The anisotropic thermal parameters of the nonhydrogen atoms, the coordinates and isotropic temperature factors of hydrogen atoms, and the F_o-F_c tables have been deposited as a Document No. 8330 at the Office of the Editor.

Results and Discussion

All the complexes except for [Cu(phen)(im)]BF_4 were isolated as anhydrous purple crystals, while [Cu(phen)(im)]BF_4 crystallized as blue-colored monohydrate. Deprotonation of imidazole nitrogen in these complexes was evidenced by no N–H stretching mode in the region 3200—3500 cm^{-1}.

Reflectance spectra of the complexes show a d-d band at about 17,000 cm^{-1}. Judging from the fact that the d-d frequency of [Cu(tmen)(im)]ClO_4 (17,300 cm^{-1}) is nearly the same as that (17,500 cm^{-1}) of [Cu(tmen)(imH)$_2$]$(ClO_4)_2$ which possesses a nearly coplanar [CuN_4] chromophore as will be shown later, all the complexes (except for [Cu(phen)(im)]$BF_4\cdot H_2O$ are assumed to have a planar configuration with four nitrogen donor atoms. This suggests that the complexes contain imidazolate group acting as a bridge.

Magnetic moments of the complexes fall in the range 1.59—1.65 BM lower than the spin-only value 1.73 BM. This again implies that the complexes are of polynuclear structure bridged by imidazolate group. In order to obtain further informations on the structure of the complexes, magnetic susceptibilities were measured in the temperature range from liquid nitrogen temperature to room temperature. Magnetic susceptibility of each complex (except for [Cu(phen)(im)]-$BF_4\cdot H_2O$) increases with lowering of temperature, while magnetic moment decreases with lowering of temperature and reaches to 1.2—1.3 BM near liquid nitrogen temperature. This behavior suggests that the complexes involve odd, probably three, copper(II) ions within each molecule.

Since a cyclic-polynuclear structure is more likely than a linear-chain structure for the present complexes, it was attempted to explain the magnetism in terms of the susceptibility equation for triangular-trinuclear copper(II) system. Based on the Heisenberg model, magnetic susceptibility expression for the triangular copper(II) system (Fig. 1) is given by

$$\chi_A = \frac{Ng^2\beta^2}{12kT}\frac{5+\exp(-3J/kT)}{1+\exp(-3J/kT)} + N\alpha,$$

on the assumption of equal exchange integrals ($J_{12}=J_{23}=J_{31}=J$). Each symbol in the equation has its conventional meaning. Magnetic susceptibilities of the complexes except for [Cu(phen)(im)]$BF_4\cdot H_2O$ were satisfactorily explained by the use of the equation as is exemplified by [Cu(tmen)(im)]PF_6 in Fig. 2. Mag-

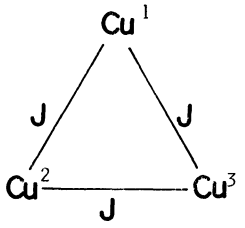

Fig. 1.

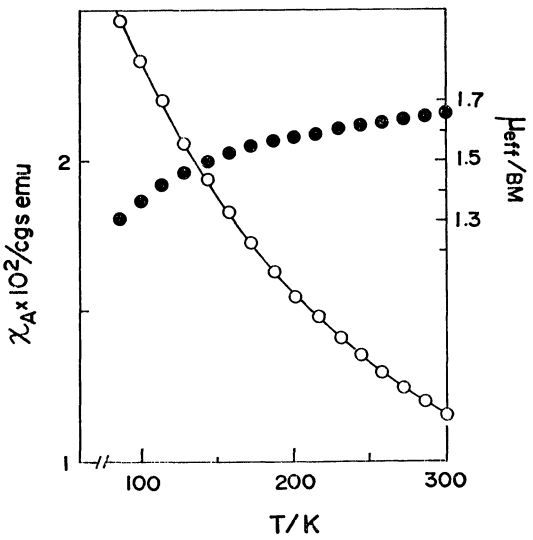

Fig. 2. Temperature variations of magnetic susceptibility and magnetic moment of [Cu(tmen)(im)]PF_6.

Table 3. Magnetic parameters, $-J$, g and $N\alpha$, of complexes

Complex	$-J$/cm^{-1}	g	$N\alpha\times10^6$ / cgs mol^{-1}
[Cu(tmen)(im)]PF_6	37	2.08	40
[Cu(tmen)(im)]ClO_4	45	2.08	60
[Cu(tmen)(im)]BF_4	43	2.08	50
[Cu(bip)(im)]PF_6	40	2.07	45
[Cu(bip)(im)]ClO_4	44	2.08	60
[Cu(bip)(im)]BF_4	45	2.08	50
[Cu(phen)(im)]PF_6	38	2.07	45
[Cu(phen)(im)]ClO_4	37	2.08	60

netic parameters, J, g, and $N\alpha$, obtained by the best fit technique are given in Table 3. The exchange integrals are in the range -37——-45 cm^{-1}, which are moderate or a little larger in absolute value compared with the exchange integrals of the imidazolate-bridged binuclear and tetranuclear copper(II) complexes so far studied.

Magnetic susceptibility of [Cu(phen)(im)]$BF_4\cdot H_2O$ is also subnormal but does not obey the above equation. Judging from its magnetic behavior, this complex is presumed to be composed of even copper(II) ions. However, its structure was not further investigated in this study.

The structure of the present complexes was considered by means of the Dreiding model. The projec-

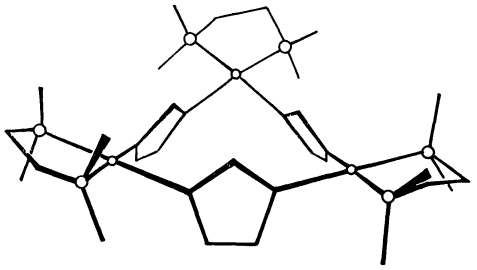

Fig. 3. The projection of Dreiding model for [Cu(tmen)(im)]$^+$.

Table 4. Bond lengths (l/Å) and bond angles (ϕ/°) with their estimated standard deviations in parentheses

(a) Copper coordination spheres			
Cu–N(1)	2.037(11)	Cu–N(5)	2.013(13)
Cu–N(2)	2.093(13)	Cu–O(1)	2.487(12)
Cu–N(3)	2.003(12)	Cu–O(5)	3.058(15)
N(1)–Cu–N(2)	85.5(5)	N(2)–Cu–O(5)	88.7(5)
N(1)–Cu–N(3)	92.1(5)	N(3)–Cu–N(5)	89.8(5)
N(1)–Cu–N(5)	173.1(5)	N(3)–Cu–O(1)	88.9(5)
N(1)–Cu–O(1)	99.8(4)	N(3)–Cu–O(5)	87.8(5)
N(1)–Cu–O(5)	81.4(4)	N(5)–Cu–O(1)	86.9(4)
N(2)–Cu–N(3)	176.0(4)	N(5)–Cu–O(5)	92.0(4)
N(2)–Cu–N(5)	92.2(5)	O(1)–Cu–O(5)	176.5(5)
N(2)–Cu–O(1)	94.7(5)		
(b) Tmen moiety			
N(1)–C(1)	1.477(22)	N(2)–C(4)	1.499(20)
N(1)–C(2)	1.502(23)	N(2)–C(5)	1.442(22)
N(1)–C(3)	1.500(21)	N(2)–C(6)	1.496(21)
C(3)–C(4)	1.470(25)		
Cu–N(1)–C(1)	112.8(9)	C(3)–C(4)–N(2)	109.3(13)
Cu–N(1)–C(2)	115.1(10)	Cu–N(2)–C(4)	106.2(9)
Cu–N(1)–C(3)	104.4(9)	Cu–N(2)–C(5)	111.2(11)
C(1)–N(1)–C(2)	106.9(13)	Cu–N(2)–C(6)	113.0(9)
C(1)–N(1)–C(3)	112.2(13)	C(4)–N(2)–C(5)	110.3(12)
C(2)–N(1)–C(3)	105.4(12)	C(4)–N(2)–C(6)	108.0(13)
N(1)–C(3)–C(4)	109.8(13)	C(5)–N(2)–C(6)	108.0(15)
(c) Im moiety			
N(3)–C(7)	1.396(21)	N(4)–C(9)	1.360(20)
C(7)–C(8)	1.330(25)	C(9)–N(3)	1.321(19)
C(8)–N(4)	1.379(23)		
Cu–N(3)–C(7)	125.4(11)	C(7)–C(8)–N(4)	107.8(15)
Cu–N(3)–C(9)	126.7(11)	C(8)–N(4)–C(9)	107.6(13)
C(7)–N(3)–C(9)	107.9(13)	N(4)–C(9)–N(3)	108.8(13)
N(3)–C(7)–C(8)	107.9(15)		
N(5)–C(10)	1.364(23)	N(6)–C(12)	1.329(20)
C(10)–C(11)	1.318(23)	C(12)–N(5)	1.330(16)
C(11)–N(6)	1.343(21)		
Cu–N(5)–C(10)	127.4(9)	C(10)–C(11)–N(6)	107.1(15)
Cu–N(5)–C(12)	126.5(11)	C(11)–N(6)–C(12)	108.4(12)
C(10)–N(5)–C(12)	105.8(13)	N(6)–C(12)–N(5)	109.1(13)
N(5)–C(10)–C(11)	109.5(14)		
(d) ClO_4			
Cl(1)–O(1)	1.411(12)	Cl(1)–O(3)	1.417(16)
Cl(1)–O(2)	1.425(15)	Cl(1)–O(4)	1.334(18)
O(1)–Cl(1)–O(2)	108.0(8)	O(2)–Cl(1)–O(3)	111.8(10)
O(1)–Cl(1)–O(3)	106.3(10)	O(2)–Cl(1)–O(4)	110.3(10)
O(1)–Cl(1)–O(4)	111.1(12)	O(3)–Cl(1)–O(4)	109.3(13)
Cl(2)–O(5)	1.410(16)	Cl(2)–O(7)	1.404(17)
Cl(2)–O(6)	1.425(17)	Cl(2)–O(8)	1.359(23)
O(5)–Cl(2)–O(6)	104.4(9)	O(6)–Cl(2)–O(7)	108.9(11)
O(5)–Cl(2)–O(7)	112.0(10)	O(6)–Cl(2)–O(8)	113.3(13)
O(5)–Cl(2)–O(8)	107.5(13)	O(7)–Cl(2)–O(8)	110.7(12)

tion of the model for $[Cu(tmen)(im)]^+$ is shown as an example in Fig. 3. Two coordination sites around planar copper(II) ion are occupied by tmen and remaining sites by imidazolate nitrogens. Triangular-trinuclear skeleton is built up of three copper atoms at the apices and three imidazolate groups combining these copper atoms. The plane of each imidazolate group is nearly perpendicular (*ca.* 70—80°) to the plane described by the donor atoms and are arranged "*cis*" to each other with respect to nitrogen atoms (see Fig. 3). The alternative configuration in which one of the imidazolate groups is placed "*trans*" to the remaining two is also possible, but this configuration seems unfavorable to that in Fig. 3. This trinuclear skeleton is quite rigid, but this is reasonably constructed without changing bond distances and distorting bond angles from the usual ones. ESR spectra of the complexes in *N,N*-dimethylformamide showed a very broad signal both at room temperature and near liquid nitrogen temperature. This implies that the polynuclear structure of the complexes is considerably stable and is maintained even in *N,N*-dimethylformamide solution. Since such a rigid skeleton can not be formed in the cases of cyclic polynuclear structure larger than triangular structure, the stability of the complexes in *N,N*-dimethylformamide seems to be associated with the triangular-trinuclear skeleton shown in Fig. 3.

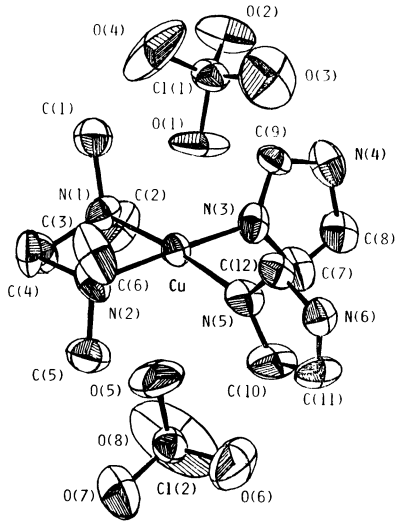

Fig. 4. Crystal structure of $[Cu(tmen)(imH)_2](ClO_4)_2$.

So far all efforts to obtain a single crystal suitable for X-ray analysis have been in vain. In order to obtain an additional support for the triangular-trinuclear structure with the imidazolate bridges for [CuL(im)]X, we have examined the crystal structure of $[Cu(tmen)(imH)_2](ClO_4)_2$ which contains the $[CuN_4]$-chromophore relevant to [Cu(tmen)(im)]X. A perspective drawing of the complex and the numbering system are illustrated in Fig. 4. Bond lengths and angles are listed in Table 4.

The copper atom is coordinated by two amino nitrogen atoms of tmen, N(1) and N(2), and two imidazole nitrogen atoms, N(3) and N(5), at distances 2.037(11), 2.093(13), 2.003(12), and 2.013(13) Å, respectively. These in-plane atoms form an approximate square plane (Table 5). The copper atom is further coordinated by the oxygen atoms of the perchlorate ions, O(1) and O(5), at the distances of 2.487(12) and 3.058(15) Å, respectively. Thus, the coordination geometry may be described as an elongated octahedron. The copper atom lies above the equatorial plane toward the oxygen atom O(1) by 0.09 Å. The tmen moiety forms a five-membered chelate ring with the copper atom. The Cu–N(1)–C(3)–C(4)–N(2) chelate rings has a gauche conformation, C(3) and C(4) being located 0.538 Å below and 0.144 Å above the plane defined by Cu, N(1), and N(2), respectively.

The most striking characteristic in the structure of $[Cu(tmen)(imH)_2](ClO_4)_2$ is that two imidazole rings are nearly perpendicular to the equatorial plane (the rings being inclined by 66.0 and 85.3° to the plane, respectively) and are arranged "*cis*" to each other with respect to the non-coordinating nitrogen atom. It should be noted that the local coordination environment of [CuL(im)]X considered on the basis of the Dreiding model (Fig. 3) is substantially the same as that of $[Cu(tmen)(imH)_2](ClO_4)_2$. Although this is

Table 5. Deviations of the atoms from least-squares planes (l/Å) and dihedral angles between them (ϕ/°)

(I) Plane through N(1), N(2), N(3), N(5)
$-0.2533X+0.5371Y+0.8299Z=4.7546$[a]
[N(1) −0.029, N(2) 0.028, N(3) 0.028, N(5) −0.028, Cu 0.088][b]

(II) Plane through Cu, N(1), N(2)
$-0.2932X+0.5684Y+0.7992Z=4.7857$
[Cu 0.000, N(1) 0.000, N(2) 0.000, C(3) −0.538, C(4) 0.144]

(III) Plane through N(3), C(7), C(8), N(4), C(9)
$0.1893X-0.4558Y+0.8394Z=1.7794$
[N(3) −0.009, C(7) 0.012, C(8) −0.011, N(4) 0.005, C(9) 0.002]

(IV) Plane through N(5), C(10), C(11), N(6), C(12)
$0.8860X+0.4577Y-0.0366Z=2.8939$
[N(5) −0.012, C(10) 0.004, C(11) 0.006, N(6) −0.014, C(12) 0.016]

Dihedral angles between the planes (ϕ/°)
(I) and (III) 66.0 (I) and (IV) 85.3 (III) and (IV) 88.6

a) The equation of the plane is expressed as $LX+MY+NZ=D$, where X, Y, and Z are in Å units referred to the crystallographic axes. b) Deviations (l/Å) of atoms from the planes are listed in square brackets.

not a direct evidence, it may afford a support for the structure of [CuL(im)]X with "*cis*"-arranged imidazolate bridges.

Based on these facts we may conclude that the [CuL(im)]X complexes are imidazolate-bridged trinuclear complexes with a triangular skeleton.

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