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1. Introduction

Angle isomerism, as exemplified in a five-coordinate, dimeric copper(II) Schiff base complex. Observation of Ostwald ripening*

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The 1:1 condensate of benzil and 2-hydrazinopyridine is the ligand (LH; H: a dissociable proton) here. Its reaction with CuCl₂·2H₂O in methanol at room temperature in equimolar proportion affords a mixture of two types of dark green (with metallic luster) single crystals—hexagonal (**1a**) and rectangular (**1b**). They are separated mechanically. The yield of **1a** is higher. X-ray crystallography shows that **1a** and **1b** are penta-coordinate, dichloro-bridged dimers of the type Cu₂L₂Cl₂ with very similar centrosymmetric structures. All the bonding parameters except for two mutually dependent bond angles in the N₂OCl₂ coordination sphere of Cu(II) are the same. Correspondingly, two different minima are located in DFT calculations on **1a** and **1b**. Energetically **1b** is more stable than **1a** in the gas phase by 3–4 kcal mol⁻¹. Their X-band EPR spectra in the solid state at 77 K, which are axial, reveal that $(d_{x^2-y^2})^1$ is the ground state in **1a** $(g_{||} > g_{\perp})$ and $(d_{z^2})^1$ in **1b** $(g_{||} < g_{\perp})$. In keeping with Ostwald ripening, the energetically less stable isomer **1a** crystallizes first. As the crystallization time is allowed to be longer, more of **1b** is formed. The transformation of **1a** to **1b** in methanol solution is found to follow the kinetics of a zero order reaction. The reverse transformation is not possible.

The concept of "isomer" was introduced in chemistry by Berzelius in 1831.¹ In Greek, it means "equal parts". It all started with the observations that despite having the same elemental composition, silver cyanate (AgOCN) and silver fulminate (AgCNO) possess different physicochemical properties.¹ Berzelius argued that the connectivities of the atoms in these two compounds are different. This remarkable idea paved the way for the concept of structure in chemical compounds. It is noteworthy that present day's ball and stick model of a molecule emerges only from Bader's theory of atoms-in-molecules (AIM),² since from X-ray crystallography one can know³ only about the shape of a molecule. Isomers, as now understood, are molecules with the same chemical formula but different structures.

Inorganic complexes are different from organic molecules in many ways. They usually contain a central atom which is surrounded by other neutral molecules or ions. It was Werner who first recognized this type of structure for coordination compounds.^{4,5} Prior to Werner, it was assumed that there can be only associative bonds. For example, he showed that in CoCl₃·6NH₃, there is an octahedral Co atom with six ammonia molecules bound at the apices and the three chloride ions are free from any type of bonding. Since six ammonia molecules are attached to the central Co³⁺, the coordination number of cobalt in CoCl₃·6NH₃ is six. Ammonia is a "ligand" here and the chloride anion is not. In CoCl₃·4NH₃, two of the three chloride anions behave as ligands giving rise to "cis" and "trans" isomers (geometric), maintaining six coordination for the metal. The number of isomers of an inorganic complex depends on the coordination number of the central atom and the nature of the ligands. Coordination chemistry now is rife with varieties of isomerism.⁶ Herein, we describe a hitherto undiscovered type of isomers in some five-coordinate $copper(\pi)$ complexes. In five-coordinate complexes, the most characteristic isomerism is the adoption of square pyramidal (SP) and trigonal bipyramidal (TBP) geometries. For example, the CuCl₅³⁻ ion in (piperazinium)₂CuC1₆·CH₃OH is square pyramidal⁷ but in $[Cr(NH_3)_6][CuCl_5]$ it is trigonal bipyramidal.⁸ In our pair of five-coordinate complexes, all the bonding parameters except for two angles are the same in their X-ray crystal structures, a feature which we call "angle isomerism". Additionally, we point out the relevance of Ostwald ripening in the formation of our isomers.

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2. Results and discussion

The ligand involved here is the 1:1 Schiff base of benzil and 2-hydrazinopyridine (LH where H is a dissociable proton). It has been first reported by Chiswell et al. in 1964.9 It can exist in two forms-keto and enol. In its X-ray crystal structure, reported very recently by Hu et al.,¹⁰ the keto form is observed. This is commensurate with our DFT calculations. At the BP86/ LanL2DZ level, the keto form is found to be more stable than the enol form by 27.96 kcal mol⁻¹ and at the B3LYP/6-311++G(2d,p) level, by 21.39 kcal mol⁻¹. Crucial bond distances in the tautomers of LH are given in Table 1. The bond distances calculated for a particular tautomer at two different levels of DFT are comparable. As expected, the N-N bond is much shorter in the enol form than in the keto form as it assumes the character of a double bond in the enol form. Similarly, the C-O bond is much longer in the enol form than in the keto form as its bond order is two in the keto form but one in the enol form. The copper(n)complex CuLCl has been reported by Chiswell et al.⁹ And the use of LH as a very sensitive colorimetric detector for the Cu²⁺ ion has been described by Hu *et al.*¹⁰ where the related copper(π) complex in solution is CuL₂. It is argued qualitatively that LH prefers to bind to a metal in the anionic enolate form as a tridentate N,N,O donor ligand.9,10 But to date, there has been no X-ray crystal structure available for any of its metal complexes (Chart 1).

We have found that LH reacts with $CuCl_2 \cdot 2H_2O$ in methanol at room temperature in equimolar proportion to yield a mixture of two types of single crystals (Fig. 1) – hexagonal (1a) and rectangular (1b) which are dark green with metallic sheen. On crushing, they become red powder. This, we believe, is an optical phenomenon. The colour of their solutions is deep red. The two types of crystals were separated mechanically. They both were analysed as CuLCl. Their FTIR spectra in KBr, devoid of an N–H peak, are essentially similar. It is clear from their electronic spectra that these two are different species. The ligand is light yellow in colour in methanol showing strong absorptions at

Table 1	Selected	bond	distances	(in Å)	in	the	two	tautomers o	f LH ^a	
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	Keto fori	n		Enol for	m
Bond	X-ray ^b	BP86	B3LYP	BP86	B3LYP
C-O C(Ph)-C(Ph) C(Ph)-N(NH) N-N	1.239 1.496 1.301 1.328	1.277 1.503 1.338 1.362	1.221 1.495 1.295 1.328	$1.403 \\ 1.401 \\ 1.413 \\ 1.320$	1.359 1.366 1.391 1.260

 $[^]a$ The basis set used in conjunction with the BP86 functional is LanL2DZ and that with the B3LYP functional is 6-311++G(2d,p). b From ref. 10.



Chart 1 Tautomers of the ligand LH.



Fig. 1 Morphology of the single crystals of 1a (a) and 1b (b).



Fig. 2 Electronic spectra of LH (black), **1a** (blue) and **1b** (red) in methanol. The intensity ε for **1a** and **1b** shown is per copper.

333 and 234 nm together with a shoulder at 257 nm (Fig. 2). The band at 333 nm ($\varepsilon = 34,300 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) has been assigned to the n $\rightarrow \pi^*$ transition of the carbonyl group by Bahgat¹¹ from DFT calculations. This band upon complexation shifts to a longer wavelength at 506 nm in **1a** and **1b** giving rise to their intense red colour in solution (Fig. 2). The ε of this band in **1b** is 25 300 dm³ mol⁻¹ cm⁻¹. It is 90% of that in **1a**. Interestingly, the other strong band observed at 294 nm in the copper(n) complexes has an ε of 15 600 dm³ mol⁻¹ cm⁻¹ in **1b** which is also 90% of that in **1a**.

The crystal structure of **1a** is shown in Fig. 3. The X-ray structure of **1b** is similar.

Both are centrosymmetric dimers, $Cu_2L_2Cl_2$, with equivalent connectivities but have slightly different geometries. Selected crystallographic data are given in Table 2 and the dimensions are compared in Table 3. LH binds the copper atoms in the anionic mode and behaves as a tridentate (N,N,O) ligand. Bond lengths from the metal to the three donor atoms in the ligand are very similar in **1a** and **1b**. A slight difference is observed in the metal-chlorine bonds with Cu(1)–Cl(1) being 2.266(1) and 2.242(1) Å in the equatorial plane. The metal atom is 0.168(1) Å from the plane in **1a** and 0.295(1) Å in **1b**. The Cu···Cu distances in **1a** and **1b** are 3.269(1) and 3.344(1) Å, respectively. In the two complexes, the bonds of the ligand fragment listed in Table 1 are found to be closer to the enol form of LH. For example, experimental N–N bond lengths in **1a** and **1b** are



Fig. 3 The centrosymmetric structure of **1a** with ellipsoids at 50% probability.

Table 2 Some crystallographic data for complexes 1a and 1b

	1a	1b
Colour	Dark green with metallic luster	Same as 1a
Formula	$C_{38}H_{28}N_6Cu_2Cl_2O_2$	$C_{38}H_{28}N_6Cu_2Cl_2O_2$
Μ	798.64	798.64
Space group	Monoclinic, C2/c	Triclinic, <i>P</i> Ī
Cell dimensions (Å, °)		
a	21.798(3)	7.1801(6)
b	9.7924(9)	10.2796(7)
С	17.180(3)	12.3788(8)
β	111.803(18)	95.428(6)
$U(\text{\AA}^3)$	3404.9(8)	846.66(11)
$Z, d_{\text{calc}} (\text{g cm}^{-3})$	4, 1.558	1, 1.566
$\mu (\text{mm}^{-\Upsilon})$	1.451	1.459
F(000)	1624	406
Unique reflections	4801	4734
Observed reflections	3459	4115
$[I > 2\sigma(I)]$		
Parameters	226	226
$R_1, WR_2 [I > 2\sigma(I)]$	0.0619, 0.1515	0.0356, 0.0858
R_1 , w R_2 (all data)	0.0788, 0.1635	0.0432, 0.0899
Largest peak/hole (e Å ⁻³)	1.460 / -1.556	0.400/-0.669

1.304 Å and 1.298 Å, respectively. On the other hand, this bond in the enol form of LH is calculated to be 1.260 Å at the B3LYP/ 6-311++G(2d,p) level and found to be 1.328 Å in the X-ray crystal structure of LH which, as pointed out above, is essentially the keto form of LH.

The angles around the metal are very similar in the two structures, within 3° as shown in Table 3, apart from Cl(1)–Cu(1)–N(18) being 155.94(9) and 171.57(5)° and Cl(1)\$1–Cu(1)–N(18) being 111.19(9) and 92.65(5)° in **1a** and **1b**, respectively. Interestingly, the sum of these two angles remains the same (155.94° + 111.19° = 267.13° and 171.57° + 92.65° = 264.22°). This indicates that the angle Cl(1)–Cu(1)–Cl(1)\$1 remains the same in **1a** and **1b** (within 3°; 92.86(3)° and 95.75(2)°). Since all the bonding parameters except for two mutually dependent angles are the same, we call the relation between **1a** and **1b** as angle isomerism. In a much broader sense, they are manifestations of polymorphism which is "the ability of a compound to crystallize in more than one crystal structure".¹² The most enigmatic example of polymorphism is

Table 3 Experimental (X-ray) and calculated (by DFT using the BP86 functional and the LanL2DZ basis set) dimensions (Å, °) in the metal coordination spheres of **1a** and **1b**^a

	1a		1b		
	X-ray	DFT	X-ray	DFT	
Cu(1)-Cl(1)	2.266(1)	2.379	2.242(1)	2.397	
Cu(1)-Cl(1)\$1	2.575(1)	2.619	2.614(1)	2.567	
Cu(1) - N(18)	1.938(2)	2.011	1.955(2)	2.011	
Cu(1)-N(11)	1.996(3)	2.014	1.983(2)	2.005	
Cu(1)-O(21)	1.996(2)	2.038	1.988(1)	2.043	
Cl(1)-Cu(1)-Cl(1)\$1	92.86(3)	93.89	95.75(2)	94.47	
Cl(1) - Cu(1) - N(11)	99.71(8)	98.25	100.84(5)	98.11	
Cl(1)–Cu(1)–N(18)	155.94(9)	164.06	171.57(5)	153.86	
Cl(1)-Cu(1)-O(21)	97.20(6)	99.69	97.70(4)	98.33	
Cl(1)\$1-Cu(1)-N(11)	96.41(9)	97.05	95.96(Š)	97.77	
Cl(1)\$1-Cu(1)-N(18)	111.19(9)	102.04	92.65(5)	111.67	
Cl(1)\$1-Cu(1)-O(21)	94.90(8)	96.27	94.05(Š)	94.77	
N(11)-Cu(1)-N(18)	79.07(10)	79.28	78.97(7)	79.46	
N(11)-Cu(1)-O(21)	159.11(9)	156.81	157.90(6)	158.43	
N(18)–Cu(1)–O(21)	80.48(9)	79.43	80.93(6)	79.61	
Cu–Ćl(1)–Cu	87.14(3)	86.11	84.26(2)	85.53	

^{*a*} Symmetry operation \$1: 1 - x, 1 - y, 1 - z in **1a** and 2 - x, 1 - y, 1 - z in **1b**. For the atom labeling scheme, see Fig. 3. Note that the optimized structures from DFT showed very small deviations in the last digit between dimensions in the two halves of the molecule, so only dimensions in one half of the molecule are given.

possibly aspirin.^{13,14} Aspirin crystallizes in the space group $P2_1/c$ which gives a wide choice of spatial arrangements in the solid.¹⁵ The polymorphs can have differences in their energies as low as 0.50 kcal mol⁻¹. But isomers can have much larger energy differences between them, as found here.

A further feature should be mentioned here, namely the interaction in the dimer between an *ortho* proton of the pyridine ring of the ligand and O(21)\$1. The dimensions for H···A, D···A, D–H···A (D = donor, A = acceptor O(21)\$1) are 2.79, 3.518 Å, 136° in **1a** and 3.16, 3.604 Å, 111° in **1b**, showing a much larger interaction in the former. While this difference is significant, it seems likely to be a consequence of the angle isomerism rather than the driving force behind it, particularly as the interactions can be considered as weak.

In order to show that they are two distinct species, we have examined the two structures via DFT calculations at BP86/ LanL2DZ and BP86/6-31G(2d,p) levels in quest of two different minima. Spin multiplicity is taken as 3. Single point energies show **1b** to have energy lower than **1a** by 6.37 kcal mol^{-1} using the LanL2DZ basis set and 3.78 kcal mol^{-1} using the larger basis set. Upon geometry optimisation, this difference changes to 3.21 kcal mol⁻¹ at the BP86/LanL2DZ level but the structures do not converge to the same one. The difference comes out to be 4.49 kcal mol⁻¹ at the BP86/6-31G(2d,p)//BP86/LanL2DZ level. The fact that the two optimized structures correspond to true minima has been established by frequency calculations. No imaginary frequency is encountered. Theoretically determined bond parameters are close to the experimental values (Table 3). In particular, the two Cl-Cu-N(18) angles retain the differences, as observed in the X-ray crystal structures.

The X-band EPR spectra of **1a** and **1b** are shown in Fig. 4. They are axial. They reveal that $(d_{x^2-y^2})^1$ is the ground state for



Fig. 4 Solid state X-band EPR spectra of 1a (black) and 1b (blue) at 77 K.

1a $(g_{\parallel} > g_{\perp})$ and $(d_{z^2})^1$ for **1b** $(g_{\parallel} < g_{\perp})$. It is remarkable to find that such a small difference in the structures of the metal coordination spheres in **1a** and **1b** affects the electronic nature of the ground state so dramatically. Very few examples of such effects are known.¹⁶ The A_{\parallel} value in **1a** is unusually small. While the normal mononuclear copper(\mathfrak{n}) complexes show it around 16 mT, it is only 6 mT in **1a**. Such small A_{\parallel} values occur in blue copper proteins.¹⁷ The magnetic moments of **1a** and **1b** correspond to one unpaired electron per copper at room temperature. In keeping with this, no EPR signals at g = 4 are observed for them indicating insignificant coupling between the two unpaired electrons on the metals.¹⁸ Such a situation is indeed expected^{19,20} on the basis of the near 90° values of the Cu–Cl–Cu bridge angles (Table 3). This justifies our consideration of S = 1 (*i.e.* triplet ground state) in our DFT calculations on **1a** and **1b**.

The relative yield of the two isomers 1a and 1b constitutes an interesting phenomenon; it depends on the time allowed for crystallization. When the allowed crystallization time is less, the yield of 1a is found to be more than 1b. When the crystallization is carried out for a longer time, the relative yield of 1a and 1b is reversed. The crystallization time is controlled by varying the volume of the solvent (methanol) used initially to carry out the reaction of LH with CuCl₂·2H₂O. Typically, fixed amounts of the two reagents (maintaining the 1:1 molar proportion) are mixed in methanol which almost instantaneously turns deep red indicating the completion of the reaction. Then, the reaction mixture is left for aerial evaporation. Crystals are deposited when the volume of the reaction mixture reduces to ~ 5 ml. Thus, the more the amount of methanol taken initially, the longer the two species remain in solution. When the synthesis is carried out by taking the amounts of the reagents LH and CuCl₂·2H₂O specified in the Experimental section in 10 ml of methanol, hexagonal crystals (1a) are obtained after 24 h as almost the sole product. In our DFT calculations, we have seen that energetically 1a is less stable than 1b. The time dependent pattern of relative yield of 1a and 1b indicates that the less stable isomer forms first. This observation is in line with the concept of Ostwald ripening. In 1897, Ostwald observed that the solid first formed



Fig. 5 Variation in the concentration of a 3×10^{-5} mol dm⁻³ methanolic solution of **1a** with time *t* as observed by monitoring the absorbance of the solution at 506 nm. Coefficient of determination $r^2 = 0.952$.

on crystallization of a melt or a solution is the least stable polymorph.²¹ This can be justified by intricate thermodynamics.^{22–24} It should be mentioned that Ostwald's law is concerned only with the order of appearance of polymorphs in a single experiment; the appearance of more stable forms later is a result of transition. We have followed the transformation of **1a** to **1b** by monitoring the absorbance at 506 nm with time *t*, spectrophotometrically. Since the absorption maxima of both the isomers occur at the same wavelength with only a 10% difference in the extinction coefficient ε in methanol, we have studied the decrease in the absorbance of a methanolic solution of **1a** in the initial few hours of dissolution to avoid complications. The transformation is found to follow the kinetics of a zero order reaction (Fig. 5).

3. Concluding remarks

Here, we have demonstrated a new type of isomerism where all the bonding parameters except for two mutually dependent bond angles are the same. It is reminiscent of the case of previously reported bond stretch isomerism where all the bonding parameters except for one bond length were presumed to be the same.^{25,26} Anyway, it seems to have been mistaken as no two separate minima could be located clearly on the related potential energy surface. But in **1a** and **1b**, we obtain two distinct minima in our DFT calculations.

We do not understand the reason for the occurrence of angle isomerism in **1a** and **1b**. But a related observation of ours is that replacement of the four phenyl rings in **1a** and **1b** by H atoms leads to the convergence of the two structures to the same structure in DFT calculations where the two relevant Cl–Cu–N(18) angles become 159.2 and 106.7° with the sum of these two angles (265.9°) almost the same as those obtained in the crystal structures of **1a** and **1b**. Thus, the skewness of benzil compared to glyoxal²⁷ may have a role here.

A remarkable result of our present work is the observation of Ostwald ripening in the formation of isomers **1a** and **1b**.

The transformation of **1a** to **1b** follows the kinetics of a zero order reaction. It should be noted that the reverse transformation is not possible. Ostwald's law finds practical application in the area of materials processing.^{28–31} Its present identification is possibly the first in coordination chemistry.

4. Experimental

4.1 Materials and physical measurements

Microanalyses were performed using a Perkin-Elmer 2400II CHNS analyser. Molar conductance was measured using a Syntronics (India) conductivity meter (model 306) in methanol. FTIR spectra (KBr) were recorded on a Shimadzu FTIR-8400S spectrometer and UV-Vis spectra (in CH₃OH) on a Perkin Elmer Lambda 950 spectrophotometer. The 500 MHz NMR spectrum of LH was recorded on a Bruker Avance III 500 spectrometer in CDCl₃. X-band EPR spectra of the copper(II) complexes were recorded on a JEOL JES-FA200 spectrometer and ESI mass spectra (in CH₃CN) on a Waters Qtof Micro YA263 spectrometer. Room temperature magnetic moments were measured using a magnetic susceptibility balance procured from Sherwood Scientific, UK. The diamagnetic correction was evaluated using Pascal's constants.

4.2 Synthesis of LH

LH was prepared by modifying the procedure reported by Chiswell et al.9 in the following manner. 2-Hydrazinopyridine (1.09 g, 10 mmol) was added to a solution of benzil (2.10 g, 10 mmol) in ethanol (40 ml). The resulting orange yellow solution was refluxed for 2 h and then it was left in the air. After 16 h, the precipitated light yellow microcrystalline compound was filtered and washed successively with cold ethanol (20 ml) and diethyl ether (25 ml). The compound was dried in air. Yield: 1.8 g (60%). m.p. 138–141 °C (lit. 140 °C).⁹ Anal. calc. for C₁₉H₁₅N₃O: C, 75.73; H, 5.02; N, 13.94 found: C, 75.59; H, 4.99; N, 13.98%. ¹H NMR δ/ppm: 7.73-7.8 (m, 2H), 7.31-7.39 (m, 8H), 7.19-7.25 (m, 8H), 7.02 (t, 1H). FTIR ν /cm⁻¹: 3315m, 3049w, 1631s, 1595s, 1554s, 1492s, 1440s, 1338s, 1292s, 1265s, 1247s, 1176m, 1081m, 1026w, 929w, 896w, 779m, 698m, 673w, 532m, 445w, 408w. UV-Vis $\lambda_{\text{max}}/\text{nm}$ ($\varepsilon_{\text{max}}/\text{dm}^3$ mol⁻¹ cm⁻¹): 234 (29600), 257 (23 000), 333 (34 500). ESI-MS m/z: 302.20 (LH + H⁺, 100%).

4.3 Syntheses of 1a and 1b

A solution of CuCl₂·2H₂O (0.034 g, 0.2 mmol) in methanol (10 ml) was added to a solution of the ligand LH (0.060 g, 0.2 mmol) in methanol (10 ml) and stirred for 3 h at room temperature. The reaction mixture was then left in air for slow evaporation. When the volume reduced to ~5 ml, the deposited dark green crystals were filtered and washed with cold methanol (5 ml) and dried in air. Yield: 0.038 g (48%). Two types of crystals were obtained—hexagonal (1a) and rectangular (1b). They were separated manually. The crystals were suitable for X-ray crystallography. They both were analysed as $C_{38}H_{28}N_6O_2Cu_2Cl_2$. Anal. Calc. for $C_{38}H_{28}N_6O_2Cu_2Cl_2$: C, 57.15; H, 3.53; N, 10.52 found: C, 57.23; H, 3.62; N, 10.45%. FTIR ν/cm^{-1} : 3053w, 1600m, 1556w, 1515m, 1456m, 1440m, 1359s, 1330s, 1215s, 1176s,

1141s, 1093m, 1070w, 1012m, 931m, 844w, 777m, 689m, 599w, 511w. $\Lambda_{\rm M}$ /mho cm² mol⁻¹ (MeOH): hexagonal (1a), 27.4; rectangular (1b), 24.5 (non-electrolyte). UV-Vis $\lambda_{\rm max}$ /nm ($\varepsilon_{\rm max}$ /dm³ mol⁻¹cm⁻¹): rectangular, 506 (25 300), 294 (15 600), 228 (sh); hexagonal, 506 (28 400), 292 (17 700), 230 (sh). $\mu_{\rm eff}/\mu_{\rm B}$ per copper (at 298 K): hexagonal (1a), 1.84; rectangular (1b), 1.89.

4.4 Computation

DFT calculations were performed using GAUSSIAN 09 suite of programs.³² Inputs were given from the X-ray crystal structures.

4.5 X-ray crystallography

Data for **1a** and **1b** were collected with MoK α at 150 K using the Oxford Diffraction X-Calibur CCD system. The crystals were positioned at 50 mm from the CCD and 321 frames were measured with counting times of 10 s. Data analyses were carried out using the CrysAlis program.³³ Both structures were solved by direct methods using the Shelxs97 program.³⁴ The non-hydrogen atoms were refined using anisotropic thermal parameters. The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. Absorption corrections were carried out using the ABSPACK program.³⁵ The two structures were refined using Shelxl97³⁴ on F^2 .

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