

Direct Synthesis of Zinc and Nickel(II) Complexes with 1,4-Diazabicyclo[2.2.2]octane

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The peculiarities of the formation of zinc and nickel(II) complexes by interaction of metal powder or metal oxide with ammonium salts (halides, nitrate, thiocyanate) were investigated in non-aqueous solutions (methanol, acetonitrile, N,N-dimethylformamide=DMF, dimethylsulfoxide=DMSO) in presence of 1,4-diazabicyclo[2.2.2]octane. The stoichiometry of the complexes was found to depend on the initial reagent ratio Ni/ZnO:NH₄X and Ni/ZnO:Ten. The compounds of compositions Zn(HTen)(H₂O)(NO₃)₃ and Ni(HTen)(Ten)Cl₃ were characterized by X-ray crystallography. Both complexes contain five-coordinate metal atoms. The zinc compound possesses monomeric molecular structure whilst the nickel complex is polymeric.

Introduction

A number of zinc and nickel(II) complexes with different bioactive amino ligands have recently been synthesized and characterized by X-ray diffraction [1–4]. Following up these investigations we have studied the interaction in the systems: ZnO-*n*NH₄X-*m*Ten-Solv, where Ten = 1,4-diazabicyclo[2.2.2]octane, or triethylenediamine; X = Cl, Br, I, NO₃ and NCS; Solv = CH₃OH, CH₃CN, DMF and DMSO; *n* = 2–4, *m* = 1–3. The present paper describes the synthesis of zinc and nickel(II) complexes with Ten, the details of the preparation and the structural features of Zn(HTen)(H₂O)(NO₃)₃ and Ni(HTen)(Ten)Cl₃.

Experimental

Synthesis and analytical data

All chemicals were commercial products of reagent grade, used without further purification; all experiments were carried out in air.

[Zn(HTen)(H₂O)(NO₃)₃]: 0.81 g (0.01 mol) of zinc oxide, 2.4 g (0.03 mol) of ammonium nitrate and 1.12 g (0.01 mol) of triethylenediamine were placed into the reactor and then 20 ml of DMSO was added. The reaction

mixture was heated to 90–100°C and stirred for 10 min to completely dissolve the oxide. The crystalline complex was formed by precipitation with isopropanol. Yield: 3.4 g (89 %).

[Ni(HTen)(Ten)Cl₃]_∞: 0.58 g (0.01 mol) of nickel metal, 1.61 g (0.03 mol) of ammonium chloride and 2.24 g (0.02 mol) of triethylenediamine were placed into the reactor and then 20 ml of DMF was added. The reaction mixture was heated to 50–60°C with constant stirring for 6 h. The precipitate was washed with DMF, filtered and dried. Yield: 3.2 g (83 %).

All complexes prepared were characterized by elemental analysis (Table I) and infrared spectroscopy (4,000–400 cm⁻¹, KBr). The identification and investigation methods are analogous to those described previously [5].

Crystal structure determination

Crystallographic measurements were made using an Enraf-Nonius CAD-4 diffractometer (graphite-monochromatized radiation) operating in the $\omega/2\theta$ scan mode. The structures were solved by the heavy atom method and refined in the anisotropic approximation for non-hydrogen atoms and isotropically for hydrogen atoms using SHELXL-93 [6]. Crystal data, details of data collection and structure refinement parameters are summarized in Table II.

Selected interatomic distances and bond angles are presented in Tables III–V. Additional crystal structure data are available from the Cambridge Crystallographic Data Centre [7].

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Table I. Investigated systems and complexes obtained.

System	Results of analysis [%] (exp/calc)						Compound
	Zn	NCS	N	C	H		
ZnO-2NH ₄ Cl-Ten-DMF/DMSO	26.2	27.8	11.3	28.2	4.5	Zn(Ten)Cl ₂	(I)
ZnO-3NH ₄ Cl-Ten-DMF/DMSO	26.31	28.54	11.79	29.00	4.88	Zn(HTen)(Ten)Cl ₃	(II)
	16.6	26.8	14.4	36.8	6.5		
ZnO-4NH ₄ Cl-2Ten-DMF	16.46	26.78	14.11	36.29	6.36	Zn(HTen) ₂ Cl ₄	(III)
	15.1	32.1	13.7	33.0	6.1		
Ni-NH ₄ Cl-Ten-Solv	15.08	32.71	12.93	33.24	6.06	Ni(HTen)(Ten)Cl ₃	(IV)
	15.6	27.2	14.1	36.9	6.2		
ZnO-2NH ₄ Br-Ten-DMF/DMSO	15.04	27.25	14.36	36.22	6.47	Zn(Ten)Br ₂	(V)
	19.5	46.9	8.4	21.6	3.5		
ZnO-2NH ₄ Br-2Ten-DMF/DMSO	19.38	47.38	8.31	21.36	3.59	Zn(Ten) _{1.5} Br ₂	(VI)
	16.1	40.4	10.9	27.8	4.7		
ZnO-4NH ₄ I-2Ten-DMF	16.62	40.62	10.68	27.47	4.62	Zn(NH ₃)(Ten)I ₂	(VII)
	14.8	57.1	9.2	16.7	3.8		
ZnO-4NH ₄ I-2Ten-DMSO	14.58	56.60	9.37	16.07	3.38	Zn(Ten)I ₂	(VIII)
	14.9	58.6	6.3	15.9	2.7		
Ni-2NH ₄ NCS-2Ten-DMSO	15.16	58.84	6.50	16.71	2.81	Ni(Ten) ₂ (NH ₃) ₂ (NCS) ₂ ·4DMSO	(IX)
	8.8	16.5	15.9	36.4	7.7		
Ni-3NH ₄ NCS-Ten-DMF	8.27	16.37	15.79	37.22	7.68	Ni(HTen)(NCS) ₃ ·3DMF	(X)
	10.5	31.1	20.0	39.2	6.1		
Ni-4NH ₄ NCS-Ten-DMSO	10.38	30.82	19.82	38.23	6.07	Ni(HTen) ₂ (NCS) ₄ ·2DMSO	(XI)
	9.1	34.7	16.5	35.6	5.8		
ZnO-3NH ₄ NO ₃ -Ten-DMF/DMSO	8.71	34.49	16.64	35.65	5.70	Zn(HTen)(NO ₃) ₃ (H ₂ O)	(XII)
	17.9	—	18.2	19.2	4.1		
	17.09	—	18.31	18.83	3.96		

Table II. Crystallographic data.

Compound	Zn(HTen)(H ₂ O)(NO ₃)	Ni(HTen)(Ten)Cl ₃
Formula weight	382.60	390.42
Crystal system	monoclinic	trigonal
Space group	P2 ₁	R32
<i>a</i> (Å)	6.966(1)	10.648(2)
<i>b</i> (Å)	13.723(3)	10.648(2)
<i>c</i> (Å)	6.984(1)	12.227(3)
α(°)	90	90
β(°)	94.89(3)	90
γ(°)	90	120
Volume (Å ³)	665.2(2)	1200.6(4)
Z	2	3
T(K)	293(2)	293(2)
D _{calc} (g cm ⁻³)	1.910	1.620
Irradiation	Mo-Kα	Mo-Kα
Wavelength (Å)	0.71073	0.71073
μ (cm ⁻¹)	19.13	17.08
F(000)	392	612
θ Range (°)	2.93 to 27.03	2.77 to 23.95
Index ranges	-8 ≤ <i>h</i> ≤ 15, -5 ≤ <i>k</i> ≤ 17, -8 ≤ <i>l</i> ≤ 8	0 ≤ <i>h</i> ≤ 6, 0 ≤ <i>k</i> ≤ 10, -13 ≤ <i>l</i> ≤ 13
Reflections collected	2136	269
Independent reflections	2014 (<i>R</i> _{int} = 0.0097)	248 (<i>R</i> _{int} = 0.0142)
Data / restraints / parameters	2010 / 1 / 219	248 / 0 / 33
<i>R</i> 1 [<i>I</i> > 2σ(<i>I</i>)]	0.0200	0.0176
<i>wR</i> 2 [<i>I</i> > 2σ(<i>I</i>)]	0.0537	0.0444
Goodness-of-fit on F ²	1.005	1.167
Absolute struct. parameter	0.003(12)	0.06(3)

Table III. Selected bond lengths (Å) and angles (°) for [Zn(HTen)(H₂O)(NO₃)₃].

Zn-O(1)	2.068(2)	Zn-O(4)	2.074(2)
Zn-O(7)	2.059(2)	Zn-O(10)	2.083(3)
Zn-N(4)	2.179(2)	N(1)-O(1)	1.272(4)
N(1)-O(2)	1.224(4)	N(1)-O(3)	1.238(3)
N(2)-O(4)	1.287(3)	N(2)-O(5)	1.231(4)
N(2)-O(6)	1.216(4)	N(3)-O(7)	1.290(3)
N(3)-O(8)	1.216(4)	N(3)-O(9)	1.227(3)
O(1)-Zn-O(4)	115.1(1)	Zn-O(1)-N(1)	119.3(2)
O(1)-Zn-O(7)	122.9(1)	Zn-O(4)-N(2)	111.5(2)
O(4)-Zn-O(7)	121.94(9)	Zn-O(7)-N(3)	113.0(2)
O(10)-Zn-O(1)	89.7(2)	C(2)-N(4)-C(4)	107.7(2)
O(10)-Zn-O(4)	87.3(1)	C(2)-N(4)-C(6)	107.9(3)
O(10)-Zn-O(7)	90.5(1)	C(4)-N(4)-C(6)	107.5(2)
N(4)-Zn-O(1)	90.6(1)	C(1)-N(5)-C(3)	109.1(3)
N(4)-Zn-O(4)	90.28(9)	C(1)-N(5)-C(5)	109.1(2)
N(4)-Zn-O(7)	91.4(1)	C(3)-N(5)-C(5)	109.9(3)
O(10)-Zn-N(4)	177.4(1)		

Table IV. Hydrogen bond parameters for [Zn(HTen)(H₂O)(NO₃)₃].

Donor (D)	Acceptor (A)	Distances (Å)			Angle (°)
		D...A	D...H	A...H	D-H...A
N(5)	O(4)	3.005(4)	0.84(5)	2.31(5)	140(4)
	(-1-x, -1/2+y, -1-z)				
O(10)	O(3) (1+x, y, z)	2.815(5)	0.73(6)	2.12(6)	159(7)
O(10)	O(5) (x, y, 1+z)	3.082(5)	0.72(5)	2.44(6)	150(6)

Table V. Selected bond lengths (Å) and angles (°) for [Ni(HTen)(Ten)Cl₃].

Ni-N(1)	2.211(3)	Ni-Cl	2.329(1)
N(1)-C(1)	1.480(3)	N(2)-C(2)	1.483(3)
C(1)-C(2)	1.548(4)		
N(1)-Ni-Cl	90.0	Cl-Ni-Cl(a)*	120.0
N(1)-Ni-Cl	90.0	C(1)-N(1)-C(1a)	107.9(2)
C(1)-N(1)-Ni	111.0(2)	C(2)-N(2)-C(2a)	108.9(2)
N(1)-C(1)-C(2)	110.7(2)	N(2)-C(2)-C(1)	109.0(2)
N(1)-Ni-N(1c)	180.0		

* "a", "c" refer to atoms related by the symmetry operations $-y, x-y, z$ and $y, x, -z$, respectively.

Results and Discussion

It is evident from Table I that the compositions of the synthesized complexes depend generally on the molar ratios of the initial reagents, i. e. Ni/ZnO:NH₄X and Ni/ZnO:Ten. Thus, at

Ni/ZnO:NH₄X > 1:2 the anionic complexes were formed in the case of ammonium chloride for zinc,

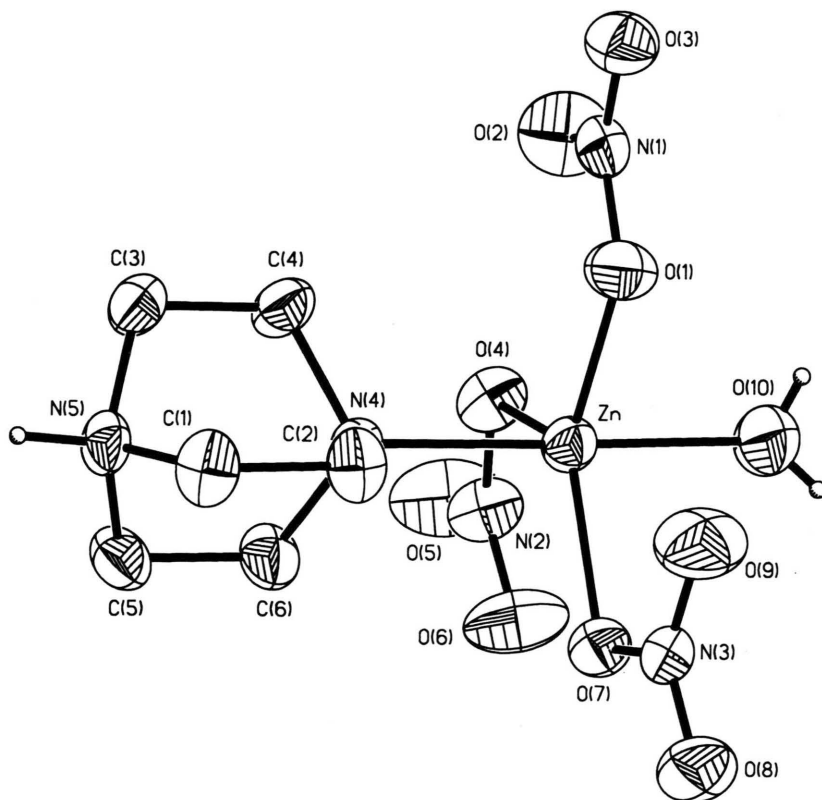


Fig. 1. The molecular structure of [Zn(HTen)(H₂O)(NO₃)₃] (hydrogen atoms are unlabelled for clarity).

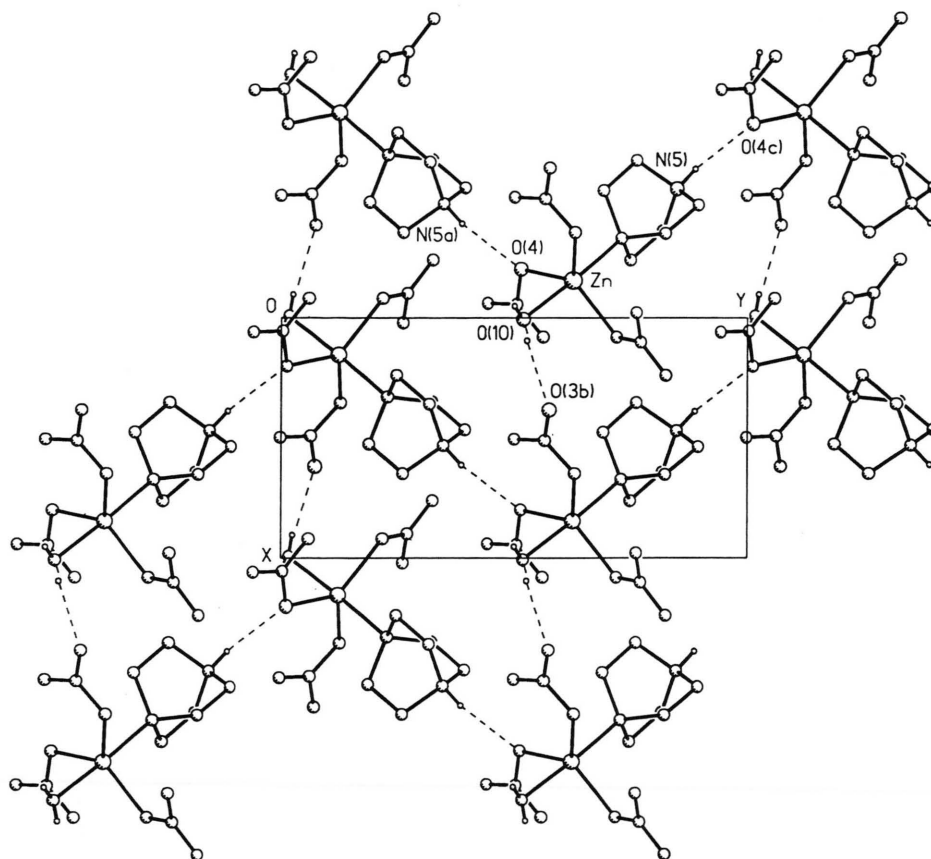


Fig. 2. Projection of the unit cell content for $[\text{Zn}(\text{HTen})(\text{H}_2\text{O})(\text{NO}_3)_3]$ onto the plane xy ("a", "b", "c" refer to atoms related by the symmetry operations $-1-x, 1/2+y, -1-z$; $1+x, y, z$ and $-1-x, -1/2+y, -1-z$, respectively; hydrogen atoms are unlabelled for clarity).

and ammonium thiocyanate for nickel. The molar ratio $\text{ZnO}:\text{NH}_4\text{X}$ influences also the degree of the oxide conversion. The complete dissolving of the zinc oxide proceeds only in three- to fourfold excess of the ammonium salt. An influence of excess Ten on the complex composition is observed only in the cases of chloride and bromide. The composition of the compounds forming in the system $\text{Ni}-\text{NH}_4\text{Cl}-\text{Ten}-\text{Solv}$ depends neither on molar ratios of initial reagents nor on the nature of the solvent.

It should be noted that DMF and DMSO are the most suitable solvents for the synthesis of the zinc and nickel complexes with Ten. Insoluble compounds are formed in methanol and acetonitrile, which prevents the completion of the reactions.

In the infrared spectra of the compounds IX-XI the band of the coordinated thiocyanate group, that lies in the range from 2090 to 2110 cm^{-1} , can be

easily identified. The bands corresponding to $\nu(\text{CO})$ at 1670 and $\nu(\text{SO})$ at 1020 cm^{-1} of the coordinated DMF and DMSO, respectively, can also be assigned [8, 9]. The IR spectra of the other compounds are less informative because the absorptions of the ammonium cations coincide with bands of the coordinated ligand.

Crystal structure of $[\text{Zn}(\text{HTen})(\text{H}_2\text{O})(\text{NO}_3)_3]$

The crystal consists of the monomeric complex units $[\text{Zn}(\text{HTen})(\text{H}_2\text{O})(\text{NO}_3)_3]$ (Fig. 1). The coordination environment of the zinc atom is a distorted trigonal bipyramid (TBP) formed by four oxygen atoms (from 3NO_3 and H_2O) and by a nitrogen atom (from Ten). Except for an elongated axial $\text{Zn}-\text{N}(\text{Ten})$ distance ($2.18\text{ \AA}$), the deviation of the coordination geometry from idealized TBP is insignificant. The differences of the

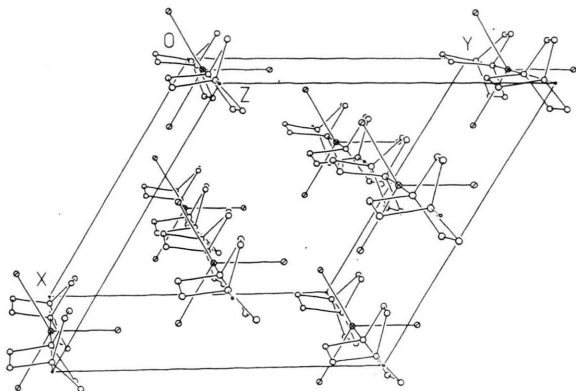


Fig. 3. Perspective view of the unit cell packing for $[\text{Ni}(\text{HTen})(\text{Ten})\text{Cl}_3]$.

equatorial $\text{Zn}-\text{O}(\text{NO}_3)$ bond lengths (on the average 2.07 Å) are not greater than 0.01 Å, and the $\text{O}(\text{NO}_3)-\text{Zn}-\text{O}(\text{NO}_3)$ bond angles vary within 115–123°. The zinc atom is situated in the plane $\text{O}(1)\text{O}(4)\text{O}(7)$, and the axial $\text{N}(\text{Ten})-\text{Zn}-\text{O}(\text{H}_2\text{O})$ angle is 177°. The interatomic distances have intermediate values between those observed in tetrahedral and octahedral structures. For example, in tetrahedral $[\text{Zn}(\text{Me}_2\text{Ea})\text{I}]_4$, where Me_2Ea -deprotonated 2-dimethylaminoethanol, $d(\text{Zn}-\text{N}) \approx 2.10$ and $d(\text{Zn}-\text{O}) \approx 1.95$ Å [4], and in octahedral $[\text{Zn}(\text{En})_2(\text{HEa})\text{I}_2 \cdot 0.5\text{En}]$, where En -ethylenediamine, HEa -monoethanolamine: $d(\text{Zn}-\text{N}) \approx 2.19$, $d(\text{Zn}-\text{O}) \approx 2.23$ Å [3].

The coordinated nitrato groups are planar and their geometrical parameters are normal (Table III) [10].

The geometrical parameters of Ten ($d(\text{C}-\text{C}) \approx 1.52$, $d(\text{C}-\text{N}) \approx 1.48$ Å, $\angle \text{CNC} \approx 109^\circ$) are close to values found earlier [1–3]. The NCCN fragments can be considered as planar.

For the crystal packing H-bonding is likely to be important. There are three shortened intermolec-

ular van der Waals contacts between amine nitrogen atoms, oxygen atoms of nitrato groups, and H_2O molecules (Fig. 2; Table IV). The values of the $\text{N}\cdots\text{O}$ and $\text{O}\cdots\text{O}$ distances suggest weak hydrogen bonding [10]. The interactions $\text{N}(5)\cdots\text{O}(4) \langle -1-x, -0.5+y, -1-z \rangle$ and $\text{O}(10)\cdots\text{O}(3) \langle 1+x, y, z \rangle$ link the molecules into layers oriented parallel to the xy plane, and the most weak H-bond $\text{O}(10)\cdots\text{O}(5) \langle x, y, 1+z \rangle$ connects these layers along the z direction.

Crystal structure of $[\text{Ni}(\text{HTen})(\text{Ten})\text{Cl}_3]_\infty$

The crystal is formed by polymeric chains $[\cdots\text{H}\cdots\text{Ten}-\text{NiCl}_3-\text{Ten}\cdots\text{H}\cdots]_\infty$ oriented along the z axis (Fig. 3). Geometrical parameters of the $\text{N}\cdots\text{H}\cdots\text{N}$ interaction: $d(\text{N}(2)\cdots\text{N}(2a)) = 2.66$, $d(\text{N}(2)\cdots\text{H}) = d(\text{N}(2a)\cdots\text{H}) = 1.33$ Å, $\angle \text{N}(2)\text{HN}(2a) = 180^\circ$ are evidence of strong symmetrical hydrogen bonds [10].

The structure is highly symmetrical (Fig. 4; Table V). The nearest coordination environment of the nickel atom formed three Cl atoms and two N atoms of triethylenediamine has almost ideal TBP geometry. The only deviation from regularity is a difference in equatorial and axial bonds lengths (2.33 and 2.21 Å, respectively). The equatorial $\text{Ni}-\text{Cl}$ bonds have values characteristic of five-coordinate complexes of nickel [11]. The axial $\text{Ni}-\text{N}$ distances are elongated owing to the presence of strong hydrogen bonds. In a similar nickel compound containing no H-bonds [12] the nickel-nitrogen distance is shorter (2.14 Å).

The NCCN fragments of Ten possess the *gauche* conformation with a dihedral angle between the $\text{N}(1)\text{N}(2)\text{C}(1)$ and $\text{N}(1)\text{N}(2)\text{C}(2)$ planes equal to 8° .

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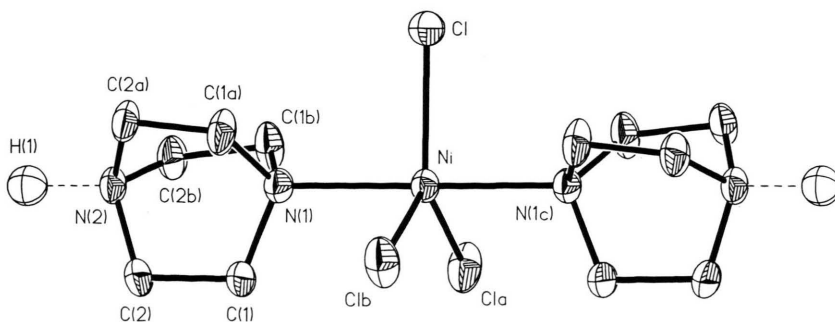


Fig. 4. The nearest coordination environment of nickel in $[\text{Ni}(\text{HTen})(\text{Ten})\text{Cl}_3]$ ("a", "b", "c" refer to atoms related by the symmetry operations $-y, x-y, z$; $-x+y, -x, z$ and $y, x, -z$, respectively; methyl hydrogen atoms are unlabelled for clarity).

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