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The first dinuclear orotate complex: Syntheses, spectral, thermal and structural characterization of supramolecular orotate complexes of nickel(II) and copper(II) with 2-hydroxyethylpyridine

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ABSTRACT

Two novel orotate complexes, mononuclear $[Ni(HOr)(H_2O)_2(etpy)]$ -H₂O (1) and dinuclear $[Cu(\mu-HOr)(etpy)]_2$ (2) (etpy = 2-hydroxyethylpyridine, HOr^{2–} = dianionic orotate), have been prepared and characterized by elemental analyses, spectroscopic (IR, UV–vis), thermal, magnetic and single crystal X-ray diffraction studies. The mononuclear Ni(II) complex crystallizes in the triclinic space group $P\overline{1}$ and the dinuclear copper(II) complex crystallizes in the monoclinic space group $P2_1/c$. The mononuclear complex consists of individual units in which nickel(II) lies on the inversion center and has octahedral coordination by bidentate HOr^{2–}, bidentate etpy and two aqua ligands. The dinuclear copper(II) complex composed of a double-orotate bridge and bidentate etpy ligands. Each HOr^{2–} ligand simultaneously exhibits chelating bidentate and bridging coordination modes. HOr^{2–} is tricoordinated to one copper atom through N3 atom of pyrimidine ring, one oxygen atom of the carboxylate group. The structural units are joined into the framework by the hydrogen bonds in 1 and 2.

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1. Introduction

Orotic acid has a great importance in the field of biological activity, that is meaning vitamin B13 (Scheme 1) [1–5]. Mono- and dianion of orotic acid are potential polydentate ligands. The coordination may occur through the heterocyclic nitrogens of the pyrimidine ring, the exocyclic carbonyl oxygens, and the carboxylic group. The orotato anion may exhibit versatile coordinating modes such as monodentate [6-12], bidentate [13-33], bridging ligand [34-39] and counter anion [40-43]. To our knowledge, so far the only one structural characterization of polymeric copper-orotate complex has been reported [34] and X-ray crystal structures of a few mononuclear copper(II) orotate complexes have appeared in the literature [8,15,23,28,32,44,45]. Although orotic acid has been studied extensively, both structurally and spectroscopically for many years [10–12], the dinuclear complexes of this ligand have not been reported. In the polymeric orotate complex, $[Cu(HOr)(H_2O)_2]_n$ [34] the carboxylate group acts as a bridge between two metal atoms using its two oxygen atoms of carboxylate group. By contrast, in polymeric Co(III) and Ni(II) complexes [30], metal ions are coordinated to one orotato ligand at the N3 ring nitrogen and the adjacent carboxylate oxygen and to another orotato anion at the exocyclic carbonyl oxygen. In the $[Cu(HOr)(NH_3)_2]$ [15] and [Cu(HOr)(phen)] [23] complexes, orotate is coordinated to the copper ion through nitrogen atom of pyrimidine ring and oxygen atom of carboxylate group as a chelate manner. The primary coordination spheres about copper(II) were square-planer and they were extended to octahedral coordination by exocyclic ketooxygens or other oxygen atom of carboxylate group of the symmetry related complex units.

Following of our work on [24–28,39,42–45], we now are reporting on the preparation, spectral, thermal and structural characterization of orotate complexes of nickel(II) and copper(II) with 2-hydroxyethylpyridine (Scheme 1b).

2. Experimental

2.1. Preparation of the complexes

A solution of etpy (0.44 g, 4 mmol) in ethanol (5 mL) was added dropwise upon stirring to a solution of $[Ni(HOr)(H_2O)_4]$ ·H₂O [20] (0.61 g, 2 mmol) and $[Cu(HOr)(H_2O)_4]$ ·H₂O [24] (0.62 g, 2 mmol) in distilled water (30 mL). The solution was heated to 60 °C in a temperature-controlled bath and stirred for 5 h at 60 °C. Then the reaction mixture was cooled to room temperature. The formed

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Scheme 1. Structures of the ligands: (a) Orotic acid (1,2,3,6-tetrahydro-2,6-dioxo-4-pyrimidinecarboxylic acid, H₃Or). (b) 2-Hydroxyethylpyridine, etpy.

light-blue for Ni(II) complex and violet for Cu(II) complex crystals were filtered and washed with 10 ml of water and ethanol and dried in air. Found: C 35.84, H 4.39, N 10.73. Calcd. for $C_{12}H_{17}N_3O_8$. Ni: C 36.96, H 4.39, N 10.78% and found: C 42.51, H 3.32, N, 12.74. Calcd. for $C_{24}H_{22}N_6O_{10}Cu_2$: C 42.29, H 3.25, N 12.33%.

2.2. Materials and measurements

All chemicals used were analytical reagent and were commercially available. IR spectra were obtained with a Bruker Tensor 27 FT-IR spectrometer using KBr pellets in the 4000–400 cm⁻¹ range. Elemental analyses for C, H and N were performed using a Vario EL III CHNS elemental analyzer. Magnetic susceptibility measurements at room temperature were performed using a Sherwood Scientific MXI model Gouy magnetic balance. The UV–vis spectra were obtained for the aqueous solution of the complex (10^{-3} M) with a Unicam UV2 spectrometer in the range 900–190 nm. Diamond TG/DTA thermal analyzer were used to record simultaneous TG, DTG and DTA curves in the static air atmosphere at a heating rate of 10 K min⁻¹ in the temperature range 50–600 °C using platinum crucibles.

2.3. Crystallographic analysis

Data collection was performed on a STOE IPDS II image plate detector using MoK_{α} radiation ($\lambda = 0.71073$ Å). Details of crystal data, data collection, structure solution and refinement are given in Table 1. Data collections: Stoe X-AREA [46]. Cell refinement: Stoe X-AREA [46]. Data reduction: Stoe X-RED [46]. The structures were solved by direct-methods using SIR97 [47] and anisotropic displacement parameters were applied to non-hydrogen atoms in a full-matrix least-squares refinement based on F^2 using SHELXL-97 [48]. Molecular drawings were obtained using ORTEP III [49].

3. Results and discussion

3.1. UV-vis spectra and magnetic susceptibility

The electronic spectrum of **1** in H₂O exhibits two absorption bands at 634 and 884 nm and the corresponding ε values are 12 and 10 L mol⁻¹ cm⁻¹, respectively. These values were assigned to v_2 : ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}$ and v_1 : ${}^{3}A_{2g} \rightarrow {}^{3}T_{2g}$ d-d transitions. The \varDelta_0 values for **1** was calculated as 11,300 cm⁻¹ since $\varDelta_0 = v_1$ for d⁸ complexes [50]. The UV-vis spectrum of **2** in H₂O displays broad absorption band at 730 nm ($\varepsilon = 19 \text{ L mol}^{-1} \text{ cm}^{-1}$). These values were assigned to $a_1 \rightarrow b_1$.

Complexes **1** and **2** exhibit magnetic moment values of 2.41 and 2.10 BM which corresponds to two and one unpaired electrons, respectively. However, this magnetic moment value is lower than the spin only value for two unpaired electrons in Cu(II) complex and indicates to antiferromagnetic effect.

Table 1

Crystal data and structure refinement for 1 and 2

	1	2
Empirical formula	C ₁₂ H ₁₇ N ₃ O ₈ Ni	$C_{24}H_{22}N_6O_{10}Cu_2$
Formula weight (g mol ⁻¹)	389.97	681.56
Crystal dimensions (mm)	$0.35 \times 0.46 \times 0.57$	$0.34 \times 0.47 \times 0.64$
Crystal system, space group	Triclinic, P1	Monoclinic P2 ₁ /c
Color	Light-blue	Violet
Unit cell dimensions		
a (Å)	6.8688(5)	8.1099(9)
b (Å)	9.7596(8)	8.7365(16)
c (Å)	12.5138(10)	18.0608(17)
α (°)	106.227(6)	
β (°)	99.553(6)	98.919(8)
γ (°)	103.510(6)	
Volume (Å ³)	758.77(10)	1264.2(3)
Ζ	2	2
Absorption coefficient (mm ⁻¹)	1.75	1.75
Data collection	STOE IPDS 2 diffractomer (ω scan)	
Temperature (K)	296(2)	296(2)
T _{min} , T _{max}	0.5801, 0.7135	0.3429, 0.5898
θ Range (°)	1.75, 27.95	2.28-27.94
Index ranges		
h	$-8 \rightarrow 9$	$-10 \rightarrow 10$
k	$-12 \rightarrow 12$	$-11 \rightarrow 11$
1	$-16 \rightarrow 16$	–23 → 23
Reflections collected	14,682	17923
Independent reflections	2984	2482
Reflections with $I > 2\sigma(I)$	2784	2302
Absorption correction	Integration	Integration
Largest diff. peak and hole (eA ³)	0.39, -0.18	0.50, -0.37
Final R indices $I > 2\sigma(I)$	$R_1 = 0.022,$	$R_1 = 0.025,$
	$WR_2 = 0.058$	$WR_2 = 0.066$
R indices (all data)	$R_{\rm int} = 0.033$	$R_{\rm int} = 0.039$
Goodness-of-fit on F ²	1.07	1.07

3.2. IR spectra

The most significant frequencies in the IR spectra of the complexes are given in Table 2 and Fig. 1, together with those of H₃Or·H₂O [51], [Cu(HOr)(H₂O)₄]·H₂O [32] and [Ni(HOr)(H₂O)₄]·H₂O [32] for comparison. The strong and broad absorption bands at 3385 and 3372 cm⁻¹ are attributed to the v(OH) vibrations of H₂O or etpy ligand, respectively. The bands at 3111 and 3122 cm⁻¹ are attributed to the NH stretching vibrations in HOr^{2–} ligand. The two weak close bands due to the v(CH) vibrations are found at 2762–2959 cm⁻¹.

A comparison between the carbonyl and carboxyl groups stretching vibration bands of H₃Or and its monodentate, bidentate and tridentate complexes may provide important evidence for the coordination of the orotate ligand. The carbonyl/carboxyl groups appear as three main peaks at 1729 and 1719 [$v_{C=O(acid)} + v_{C(2)=O}$] and 1700 cm⁻¹ [$v_{C(6)=O} + v_{ring}$] in the free orotic acid [51]. Three carbonyl bands were observed at 1701 and 1639 cm⁻¹ for

Table 2	
IR spectral data of complexes ^a (cm ⁻¹)	

Assignment	1	2	$H_3Or \cdot H_2O$
vOH	3385 m	3372 m	3241 sh
vN ₍₁₎ H	3111 m	3122 m	3154 m
N(3)H	-	-	3137 m
CH	2945-2762 w	2959–2802 w	3099 s
OHacid	-	-	2500 m, b
$v_{C=O(acid)} + v_{C(2)=O}$	1634 vs, b	1679 vs	1729, 1719 vs
$v_{C(6)=O} + v_{ring}$		1621 vs	1700 vs
vCOO	1481 m	1462 m	-
M—O, M—N	476 w, 435 w	513 w, 437 w	-

^a Abbreviations: sh, shoulder; w, weak; m, medium; s, strong; vs, very strong; b, broad.



Fig. 1. IR spectra of the complexes.

mono-deprotonated orotate ligand, $[Co(H_2Or)_2(H_2O)_4] \cdot 2 H_2O$ [11], and 1685 and 1645 cm⁻¹ for bis-deprotonated orotate ligand, $[Cu(HOr)(H_2O)_4] \cdot H_2O$ [32], while the bis(bis-deprotonated) orotate

ligands, $(chaH)_2[Cu(HOr)_2(cha)]\cdot 2H_2O$ (chaH = cyclohexylamine) [45], give two equally strong bands at 1654 and 1605 cm⁻¹. In the IR spectra of **1** and **2**, carbonyl/carboxyl stretching is



Fig. 2. TG, DTG and DTA curves of 1.



Fig. 4. The chemical structures of the complexes.

overlapped with the water bending and stretching vibration of C=N of the pyridine ring and are broadened very strong absorption at 1634 cm⁻¹ for **1** and 1679 and 1621 cm⁻¹ for **2**. The $v(OH_{acid})$ band at *ca*. 2500 cm⁻¹ in the free orotic acid completely disappeared and a new carboxylate band (vCOO) appeared at 1481 (**1**) and 1462 (**2**) cm⁻¹, indicating that the carboxylate group participates in the coordination with the metal ions by deprotonation.

3.3. Thermal analysis

The thermal behavior of the nickel(II) and copper(II) complexes was followed up to $600 \,^{\circ}$ C in a static air atmosphere. [Ni(HOr)

 $(H_2O)_2(etpy)]$ · H_2O decomposes in four stages (Fig. 2). The first stage between 80 and 131 °C corresponds to the endothermic dehydration of the complex with a mass loss of 4.65% (calcd. 4.62%). The release of the two aqua ligands takes place in the second stage (132–184 °C). The experimental mass loss of 9.67% agrees well with the calculated mass loss of 9.24%. The decomposition stage in the 185–263 °C range corresponds to removal of CH₂OH radical with an endothermic effect at 242 °C (found: 7.72, calcd. 8.07%). In the last stage, the exothermic degradation of pyridine and HOr^{2–} ligands occurs in the 264–475 °C range with two DTA peaks at 311 and 449 °C, and results in the formation of NiO as an end product.



Fig. 5. Ortep III view of 1 with the atom numbering scheme.

Table 3 Geometric parameters (Å °) for **1**

P				
Ni1—N1 Ni1—N3 Ni1— 04	2.029(1) 2.073(1) 2.053(1)	Ni1— Ni1— Ni1—	05 06 07	2.112(1) 2.107(1) 2.091(1)
N1-Ni1-04 N1-Ni1-N3 04-Ni1-N3 N1-Ni1-07 04-Ni1-07 N3-Ni1-07 N1-Ni1-06 04-Ni1-06 Hydrogen-bond geo	79.73(5) 171.42(5) 93.57(5) 96.34(5) 172.47(5) 90.90(5) 90.08(5) 89.00(5) pometry (Å, °)	N3—I 07—I N1—I 04—I N3—I 07—I 06—I	Ni1—06 Ni1—06 Ni1—05 Ni1—05 Ni1—05 Ni1—05 Ni1—05	95.20(5) 84.57(5) 85.69(5) 97.04(5) 89.86(5) 89.01(5) 171.88(5)
$\begin{array}{l} D & -H & \cdots & A \\ N2 & -H2 & \cdots & O1^{i} \\ O5 & -H5 & \cdots & O3^{ii} \\ O6 & -H6A & \cdots & O2^{iii} \\ O6 & -H6B & \cdots & O7^{iv} \\ O7 & -H7A & \cdots & O8 \\ O7 & -H7A & \cdots & O8 \\ O7 & -H7B & \cdots & O1 \\ O8 & -H8A & \cdots & O2^{v} \\ O8 & -H8B & \cdots & O4^{ii} \end{array}$	D—H 0.87(2) 0.80(2) 0.84(2) 0.85(2) 0.82(2) 0.80(2) 0.79(2) 0.82(2)	H…A 1.88(2) 1.932(6) 2.02(2) 2.12(2) 1.87(2) 1.88(2) 2.05(2) 2.02(2)	DA 2.740(2) 2.728(2) 2.818(2) 2.952(2) 2.684(2) 2.684(2) 2.631(2) 2.838(2) 2.831(2)	D-H···A 173(2) 171(2) 159(2) 167(2) 171(2) 156(2) 172(3) 170(3)

Symmetry codes: (i) -x + 1, -y + 1, -z; (ii) x - 1, y, z; (iii) -x + 2, -y + 1, -z; (iv) -x + 1, -y, -z; (v) x - 1, y - 1, z.

 $[Cu(\mu-HOr)(etpy)]_2$ shows a three stages weight loss (Fig. 3). The first stage between 125 and 190 °C corresponds to the exothermic removal of CH₂OH radical by giving endothermic effect (DTG_{max} = 171 °C, found 9.68, calcd. 9.11%). This type of behavior in the saccharinato complexes with triethanolamine ligand has been reported earlier [52]. The second stage is related to the decomposition of remain etpy ligands with a mass loss of 27.24% (calcd. 27.03). The decomposition of the HOr^{2–} ligands occur in the third stage between 285 and 473 °C with the strong exothermic peak of the DTA curve at 424 °C (found: 40.16, calcd. 40.52%). The final decomposition product CuO was identified by IR spectroscopy (found: 77.08, calcd. 76.66%).

The proposed structures of the synthesized complexes which are presented in Fig. 4, are consistent with each other in terms of chemical, thermal and spectroscopic properties.

3.4. Crystal structure of the complexes

3.4.1. [Ni(HOr)(H₂O)₂(etpy)]·H₂O

The molecular structure of [Ni(HOr)(H₂O)₂(etpy)]·H₂O consists of neutral molecules as shown in Fig. 5. Selected bond lengths and angles together with the hydrogen bonding geometry are collected in Table 3. The nickel(II) ion is coordinated by two aqua, one etpy and one HOr²⁻ ligands, exhibiting a distorted octahedral configuration of the NiN₂O₄ type. The etpy molecule acts as a bidentate donor via nitrogen and oxygen atoms, creating a six-membered chelate ring, while the HOr²⁻ also behavior bidentate ligand through nitrogen atom of pyrimidine ring and oxygen atom of carboxylate group. The Ni-Netpy and Ni-Oetpy bonds distances are 2.0729 and 2.1120 Å, while the Ni-N_{HOr} and Ni-O_{HOr} bond distances of 2.0292 and 2.0528 Å are comparable to those reported for the corresponding mononuclear Ni(II) complexes of HOr²⁻ [27,29,30,44]. The Ni-O_{etpy} bond is also much longer than the Ni-Netpy, Ni-NHOr and Ni-OHOr bonds, and these results in formation of an elongated octahedral geometry along the O_{etpy} atom (Table 3). Both the HOr^{2-} and etpy ligands are essentially planar with r.m.s deviations from the best least-squares planes of 0.0122 and 0.0035 Å, respectively. The dihedral angles between



Fig. 6. Part of the crystal structure of **2**, showing the formation of a hydrogen bonded $R_2^2(8)$ ring and π - π interaction (Cg3-Cg3ⁱ). Symmetry codes: (i) 2 - x, 1 - y, -z; (ii) 1 - x, 1 - y, -z; (iii) -1 + x, y, z.

Table 4

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Geometric parameters (Å, °) for 2

Geometric parame	eters (A,) 101 Z			
N1—Cu1	1.948(2)	04-	-Cu1	1.932(1)
N3—Cu1	1.971(2)	05-	-Cu1	1.939(2)
04–Cu1–O5	173.08(7)	04-	-Cu1—N3	94.03(6)
04-Cu1-N1	83.33(6)	05-Cu1-N3		89.08(7)
05-Cu1-N1	92.93(7)	N1-	-Cu1—N3	173.59(7)
Hydrogen-bond g	eometry (Å, °)			
D—H···A	D—H	H···A	$D \cdot \cdot \cdot A$	D—H···A
05—H5…01	0.82(3)	1.73(3)	2.508(2)	158(3)
N2—H2···O2 ⁱ	0.86	2.01	2.820(2)	156

Symmetry codes: (i) 1 - x, 1 - y, -z.



Fig. 7. Ortep III view of 2 with the atom numbering scheme.

the pyrimidine ring of HOr^{2-} and pyridine ring of etpy planes are 65.73° .

The crystal packing of **1** is a composite of intermolecular hydrogen bonding and weak π - π interactions. A packing diagram of [Ni(HOr)(H₂O)₂(etpy)]·H₂O is shown in Fig. 6. The N—H group of HOr²⁻ give intermolecular hydrogen bonds with the carbonyl O1 atom of the neighboring HOr²⁻ ligand (symmetry code: x + 1, -y + 1, -z) and forms R₂²(8) ring. An intermolecular π - π interaction contact occurs between the two symmetry-related pyrimidine rings of the HOr²⁻ ligand [Cg3...Cg3ⁱ 3.5601(9) Å, (i): 2 - x, 1 - y, -z] (Fig. 6). The crystal is mainly stabilized by strong intermolecular H bonds O(6)—H(6A)···O(2), O(7)—H(7A)···O(8), O(7)—H(7B)···O(1), O(8)—H(8A)···O(2) and O(8)—H(8B)···O(4). There are also intramolecular hydrogen bonds between coordine water molecules O7 and crystal water molecules O8, exocyclic O1 atoms of orotate. All of these intermolecular interactions give two-dimensional hydrogen-bonded network results (Table 3).

3.4.2. $[Cu_2(HOr)_2(etpy)_2]$ (2)

The molecular view of $[Cu_2(\mu-HOr)_2(etpy)_2]$ with atom numbering scheme is shown in Fig. 7. The selected bond lengths and angles together with the hydrogen bonding geometry are given in Table 4. The compound crystallizes in monoclinic P_1/c space group. Each copper ion in 2 is coordinated by N atom of pyrimidine ring and O atom of carboxylate from the chelating HOr^{2-} ligand, N atom of pyridine ring and O atom of ethanol group forming six-membered chelating etpy molecule in a square–planar arrangement. The other carboxylate O atom further forms a weak bridge to the adjacent Cu ion in the axial direction with a longer Cu—O bond (2.683(2) Å). With this bridging carboxylate oxygen is linking the second [Cu(HOr)(etpy)] unit, square pyramidal coordination geometry is achieved around each copper with the formation of eightmembered ring. Cu…Cu separation of 5.086 Å indicates the very weak interaction between two copper centers.

The bond lengths of Cu–N(1)_{HOr} and Cu–O(4)_{HOr} are 1.948(2)and 1.932(2) Å, respectively. The Cu–N(1)_{HOr} and Cu–O(4)_{HOr} bond distances are similar to the corresponding values found in $[Cu(HOr)(H_2O)_2]_n$ [1.975(2) and 1.948(2)Å] [34], (chaH)_2[Cu (HOr)₂(cha)]·2H₂O [1.980(3), 1.982(3) and 2.013(3), 2.208(3)Å] [45], [Cu(HOr)(H₂O)(bipy)] [1.934(3) and 2.000(2)Å] [28], [Cu (HOr)(TEA)]·H₂O, [1.952(2) and 1.944(2)Å] [27], [Cu(HOr) (ea)₂]·2H₂O [2.004(2) and 1.984(2) Å] [44]. The bridging Cu-O_{acid} bond distance of 2.683(2) Å is significantly longer than the corresponding bond in [Cu(HOr)(H₂O)₂]_n [2.337(2) Å] [34]. In the copper(II) complex the two C-O bond lengths of the carboxylate group of the HOr²⁻ are quite different, 1.224(3) and 1.278(3) Å, with that bridge bonded to Cu(II) being the shorter. The Cu-N_{etpy} and Cu-O_{etpy} bond distances are 1.9705(16) and 1.9387(16)Å. The internal geometries are as expected, with the bond lengths N-C [within range of 1.3440(1) and 1.3524(3) Å]; C-C_{etpy} of pyridine ring [within range of 1.3782(3) and 1.3715(3) Å] corresponding exactly to typical double-bond lengths.

The crystal is mainly stabilized by so many strong intermolecular hydrogen bonds N–H \cdots O. The details of hydrogen bonding geometry are given in Table 4. Each of the HOr^{2–} ligands is doubly H-bonded (DA:AD form) to a corresponding ligand of a neighboring complex unit (Fig. 8). These DA:AD type hydrogen bonds involve



Fig. 8. The hydrogen bonding geometry of 2.

the N2 atom of pyrimidine ring and carbonyl O2 atom $[N(2)-H\cdots O(2)^i; N(2)\cdots O(2) = 2.820(2) \text{ Å}, H\cdots O(2) = 2.01 \text{ Å}, N(2)-H\cdots O(2) = 156^\circ, (i) 1 - x, -y, 1 - z]$ and generate centrosymmetric edge-fussed four $R_2^{-2}(8)$ rings in two-dimensional network. These two-dimensional supramolecular networks have only van der Waals interactions do not have any C-H··· π or $\pi \cdots \pi$ interactions.

4. Conclusion

Although a lot of orotato complexes both mononuclear and polymeric are well known, quite surprisingly, up to now dinuclear metal complexes of the orotate have not been reported. We have successfully synthesized the first dinuclear $[Cu(\mu-HOr)(etpy)]_2$ and mononuclear $[Ni(HOr)(H_2O)_2(etpy)] \cdot H_2O$ orotate complex and characterized.

Supplementary material

Crystallographic data for the structure reported here have been deposited at the CCDC as supplementary data, CCDC No. 645539 for **1** and 645540 for **2**. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. E-mail: deposit@ccdc.-cam.ac.uk.

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