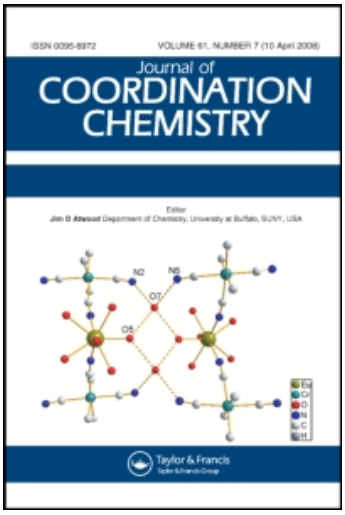

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Synthesis, Crystal Structure and Properties of Novel Zinc(II) and Cobalt(II) Chain Complexes with 3,5-dimethylpyrazole and Thiocyanate

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SYNTHESIS, CRYSTAL STRUCTURE AND PROPERTIES OF NOVEL ZINC(II) AND COBALT(II) CHAIN COMPLEXES WITH 3,5-DIMETHYLPYRAZOLE AND THIOCYANATE

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This paper presents the synthesis, crystal structure and properties of new zinc(II) and cobalt(II) 1-D chain complexes with 3,5-dimethylpyrazole and thiocyanate, $[M(pz^*)_2(NCS)_2]\cdot H_2O$ ($M = Zn, Co$; $pz^* = 3,5$-dimethylpyrazole). The structures of both complexes were determined by X-ray diffraction methods and showed very similar crystallographic character. The M(II) ion in each complex is coordinated to two pyrazole nitrogen atoms and two nitrogen atoms of NCS^- to form a distorted tetrahedron. In the cell of each complex are four complex molecules and four H_2O molecules. Adjacent complex molecules are connected by hydrogen bonds to form 1-D chain. Each sulfur atom in the complex is connected by a weak coordination bond with an M(II) ion of an adjacent chain to form a sawtooth-type double 1-D chain structure. The bond distances Zn-S and Co-S are 3.919 Å and 3.853 Å, respectively.

Keywords: 1-D complexes; Zinc(II) complex; Cobalt(II) complex; Carbonic anhydrase; Inhibitor; Thiocyanate

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INTRODUCTION

Carbonic anhydrase (CA) is found in both plants and animals, and its only known biological function is to catalyze the interconversion of CO_2 and HCO_3^- (1) [1]. The active site environment, as determined by X-ray diffraction, is known for human carbonic anhydrase C(HCAC).

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons HCO_3^- + H^+ \quad (1)$$

The zinc(II) ion is bound to three histidine imidazole groups, in a distorted tetrahedral array, with the fourth site occupied by either a water molecule or a hydroxide ligand, depending on pH [2, 3]. The water or hydroxide can be replaced by inhibitors. Many inorganic ions such as X^-, SCN^-, $N_3{}^-$, CN^-, CNO^-, ClO^- and NO_3^- have some inhibiting ability for CA. The inhibiting ability of SCN^- is most striking among them. Recently, many papers reported mimicing of CA with multi-nitrogen ligands such as imidazole, pyrazole, 1,4,7-triazacylononane, and hydrotris(pyrazolyl)borate ligands [4–15]. In the mimics of CA, Zn(II) was usually substituted by Co(II) because of poor spectroscopic properties. The ligands used in the model complexes are almost always hydrotris(pyrazolyl)borate ligands with sterically hindered substitutents. Steric effects on metal complexes are particularly profound in these systems due to the orientation of substituents in 3- or 5-positions of pyrazole, which enclose the bound metal ion in a highly protected pocket. The simple hydrotris(pyrazolyl)borate (Tp) and hydrotris(3,5-dimethylpyrazolyl)borate (Tp^*) ligands are known to form stable and inert full sandwich complexes $[M^{II}Tp_2]$ or $[M^{II}Tp_2^*]$ easily. The mononuclear fragments $[TpM^{II}X]$ or $[Tp^* M^{II}X]$ are difficult to isolate. In the course of our studies on the synthesis of mononuclear complexes $[Tp^*M^{II}X]$ and reactivity of $[M^{II}Tp_2^*]$ related to the model complexes of CA with simple substituted ligands, novel zinc(II) and cobalt(II) complexes with 3,5-dimethylpyrazole and thiocyanate $[M(pz^*)_2(NCS)_2] \cdot H_2O$ ($M = Zn$, Co; $pz^* =$ pyrazole) were obtained and structurally characterized.

EXPERIMENTAL

Preparation of the Complexes

The Zn(II) and Co(II) complexes $[Zn(pz^*)_2(NCS)_2] \cdot H_2O$ (**1**) and $[Co(pz^*)_2(NCS)_2] \cdot H_2O$ (**2**) were prepared by three different methods.

Method A

A solution of $Zn(ClO_4)_2 \cdot 6H_2O$ (0.2 mmol, 74.8 mg) or $Co(ClO_4)_2 \cdot 6H_2O$ (0.2 mmol, 73.2 mg) in 5 cm^3 of MeOH was added to 10 cm^3 of a methanolic solution of KTp* (0.2 mmol, 67.3 mg) (KTp*: potassium hydrotris(3,5-dimethylpyrazolyl)borate). The mixture was stirred for 10 hours at room temperature. An aqueous solution (1 cm^3) of KSCN (0.6 mmol, 58.3 mg) was added to the mixture and stirred for another 10 hours, and the precipitates were filtered off. The colorless (**1**) or purple (**2**) crystals suitable for X-ray structure analysis were obtained by slow evaporation of the filtrate. The yields were found to be 79% (**1**) and 73% (**2**) based on the metal salts, respectively. *Anal*., calc. for $C_{12}H_{18}N_6OS_2Zn$ (%): C, 36.79; H, 4.63; N, 21.45. Found: C, 37.02; H, 4.72; N, 21.48. *Anal*., calc. for $C_{12}H_{18}CoN_6OS_2$ (%): C, 37.40; H, 4.71; N, 21.81. Found: C, 37.53; H, 4.56; N, 21.73.

Method B

$Zn(ClO_4)_2 \cdot 6H_2O$ (0.2 mmol, 74.8 mg) or $Co(ClO_4)_2 \cdot 6H_2O$ (0.2 mmol, 73.2 mg) was mixed with KSCN then reacted with KTp* (0.2 mmol, 67.3 mg) in methanol for 10 hours. **1** and **2** were obtained in 57% (**1**) and 48% (**2**) yields. Satisfactory analyses were obtained.

Method C

$ZnCl_2 \cdot 6H_2O$ (0.2 mmol, 27.3 mg) or $Co(ClO_4)_2 \cdot 6H_2O$ (0.2 mmol, 73.2 mg) were reacted with Hpz* and KSCN at 1 : 2 : 2 molar ratio in methanol for 10 hours and the precipitates filtered off. The colorless (**1**) or purple (**2**) crystals suitable for X-ray structure analysis were obtained by slow evaporation of the filtrate. Yield: 89% (**1**) and 82% (**2**), respectively. Satisfactory analyses were obtained.

Physical Measurements

Analyses for C, H and N were carried out on a Perkin-Elmer instrument at the Institute of Elemental Organic Chemistry, Nankai University. Infrared spectra using KBr pellets were recorded on a Shimadzu IR-408 spectrophotometer in the range $4000 \sim 600\ cm^{-1}$. Electronic spectroscopy in MeOH was performed on a Shimadzu UV-2401 PC UV-VIS recording spectrophotometer in the range $200 \sim 1000$ nm. Cyclic voltammetry was performed with a BAS-100B electrochemical analyzer using 0.1 mol dm^{-3}

TABLE I Crystal data and structure refinement details for complexes $[M(pz^*)_2(NCS)_2] \cdot H_2O$

	$[Zn(pz^*)_2(NCS)_2] \cdot H_2O$ (**1**)	$[Co(pz^*)_2(NCS)_2] \cdot H_2O$ (**2**)
Empirical formula	$C_{12}H_{18}N_6OS_2Zn$	$C_{12}H_{18}CoN_6OS_2$
Crystal size (mm)	$0.03 \times 0.2 \times 0.4$	$0.45 \times 0.30 \times 0.30$
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	7.9592(9)	7.994(2)
b (Å)	27.173(3)	27.013(5)
c (Å)	8.8746(10)	8.8919(2)
β (°)	106.048(2)	106.34(3)
V (Å^3)	1844.6(4) Å^3	1848.2(7) Å^3
Z	4	4
ρ(calcd) (g cm^{-3})	1.411	1.385
F(000)	808	796
μ(Mo Kα), (mm^{-1})	1.56	1.163
θ Range	$1.50 < \theta < 26.56$	$2.50 < \theta < 25.01$
Limiting indices	$-9 \le h \le 8,\ -34 \le k \le 32,\ -9 \le l \le 11$	$-9 \le h \le 9,\ 0 \le k \le 32,\ 0 \le l \le 10$
Total reflections	8703	3256
Independent reflections	3806	3048
Data/restraints/parameters	3806/0/207	3048/0/199
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Weighting scheme	$w^{-1} = [\sigma^2(Fo^2) + (0.0883P)^2 + 0.0000P]$, $P = (Fo^2 + 2Fc^2)/3$	$w^{-1} = [\sigma^2(Fo^2) + (0.1157P)^2 + 0.0000P]$ $P = (Fo^2 + 2Fc^2)/3$
Final indices ($I > 2\sigma(I)$)	0.038, 0.104	0.062, 0.154
R indices (all data)	0.063, 0.118	0.143, 0.169
Goodness-of-fit on F^2	0.970	1.031
Largest difference peak and hole (e Å^{-3})	0.357, −0.261	0.448, −0.488

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $[Zn(pz^*)_2(NCS)_2] \cdot H_2O$ (**1**). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	*x/a*	*y/b*	*z/c*	*U(eq)*
Zn(1)	5821(1)	6277(1)	3557(1)	49(1)
S(1)	3814(2)	7572(1)	6038(1)	81(1)
S(2)	1423(2)	5867(1)	−968(1)	83(1)
N(3)	6511(3)	5760(1)	5200(3)	49(1)
N(1)	7750(3)	6485(1)	2681(3)	48(1)
O(1)	4602(4)	6521(1)	8230(3)	68(1)
N(4)	6358(3)	5825(1)	6674(3)	50(1)
N(2)	7421(3)	6652(1)	1195(3)	53(1)
N(6)	3983(4)	6053(1)	1775(3)	63(1)
C(8)	6946(4)	5435(1)	7577(4)	53(1)
N(5)	5118(4)	6812(1)	4686(3)	71(1)
C(6)	7199(4)	5311(1)	5203(4)	51(1)
C(3)	8827(4)	6852(1)	915(4)	56(1)
C(11)	4570(4)	7134(1)	5227(4)	53(1)
C(12)	2895(4)	5977(1)	636(4)	54(1)
C(7)	7486(4)	5105(1)	6664(4)	58(1)
C(2)	10129(5)	6803(2)	2255(4)	73(1)
C(10)	6933(6)	5428(2)	9257(4)	78(1)
C(1)	9433(4)	6580(1)	3332(4)	61(1)
C(9)	7524(5)	5111(2)	3754(4)	75(1)
C(5)	8759(6)	7066(2)	−664(5)	88(1)
C(4)	10268(6)	6445(2)	5007(5)	107(2)

TABLE III Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $[Co(pz^*)_2(NCS)_2] \cdot H_2O$ (**2**). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	*x/a*	*y/b*	*z/c*	*U(eq)*
Co(1)	794(1)	3714(1)	3546(1)	54(1)
S(2)	−1220(3)	2415(1)	6050(2)	87(1)
C(12)	−446(7)	2859(3)	5227(6)	60(2)
N(6)	46(7)	3193(2)	4687(5)	66(1)
S(1)	−3601(2)	4139(1)	−987(2)	89(1)
C(11)	−2117(7)	4018(3)	644(6)	59(2)
N(5)	−1010(6)	3932(2)	1775(5)	65(1)
C(10)	3762(9)	2935(3)	−666(7)	80(2)
C(8)	3789(7)	3156(3)	881(6)	59(2)
C(7)	5134(7)	3204(3)	2266(6)	70(2)
C(6)	4407(6)	3424(3)	3325(5)	64(2)
C(9)	5232(10)	3537(4)	4995(7)	108(4)
N(4)	2404(6)	3333(2)	1191(4)	58(1)
N(3)	2717(5)	3506(2)	2671(4)	55(1)
C(4)	2533(10)	4877(3)	3756(7)	83(2)
C(1)	2176(7)	4676(3)	5191(6)	68(2)
C(2)	2463(8)	4895(3)	6677(6)	72(2)
C(3)	1941(8)	4559(3)	7578(6)	69(2)
C(5)	1891(11)	4584(3)	9269(6)	87(2)
N(1)	1497(6)	4233(2)	5186(4)	61(2)
N(2)	1332(6)	4162(2)	6665(4)	60(1)
O(11)	−443(5)	3465(2)	8219(4)	73(1)

TABLE IV Selected bond lengths (Å) and angles (°) for $[M(Pz^*)_2(NCS)_2] \cdot H_2O$

	$[Zn(pz^*)_2(NCS)_2] \cdot H_2O$	$[Co(pz^*)_2(NCS)_2] \cdot H_2O$
M(1)—N(1)	1.986(2)	1.990(5)
M(1)—N(3)	1.990(2)	1.991(4)
M(1)—N(5)	1.934(3)	1.907(5)
M(1)—N(6)	1.932(3)	1.929(6)
N(1)—M(1)—N(3)	113.68(11)	113.42(19)
N(1)—M(1)—N(5)	110.76(13)	112.5(2)
N(1)—M(1)—N(6)	105.19(11)	101.1(2)
N(3)—M(1)—N(5)	102.23(11)	104.47(18)
N(3)—M(1)—N(6)	111.73(12)	112.9(2)
N(5)—M(1)—N(6)	113.52(15)	112.8(2)

acetonitrile solutions of $[n\text{-}Bu_4N]ClO_4$ at room temperature. A three-electrode cell was employed with a platinum working electrode, a platinum wire auxiliary electrode and a saturated calomel reference electrode. The solution was deaerated by an argon stream prior to all measurements, and was kept under argon during the measurements. All formal potentials were taken as the average of the anodic and cathodic peak potentials ($E_{1/2}$) and refer to the saturated calomel electrode (SCE). Ferrocene was added after each run as an internal standard, and the ferrocenium-ferrocene couple was observed at 0.400 V at a scan rate of $100\,mV\,s^{-1}$.

X-ray Structure Analysis

Intensity data for single crystals of the complexes were collected on a Bruker SMART 1000 CCD detector for **1** and an Enraf-Nonius CAD-4 diffractometer for **2**, respectively. The structures were solved by direct methods using the program SHELXS 97 [16a] and subsequent difference Fourier techniques, and refined anisotropically by full-matrix least-squares on F^2 using SHELXL 97 [16b]. Crystal data and structure refinement details are summarized in Table I. Selected interatomic bond lengths and angles are given in Table II.

RESULTS AND DISCUSSION

Synthesis of the Complexes

The composition of complexes was determined to be $[M(pz^*)_2(NCS)_2] \cdot H_2O$ by single-crystal X-ray diffraction. KTp^* is decomposed when excess inhibitor is added. The reason for this may be due to the strong coordination ability and Lewis acidity of $M(ClO_4)_2 \cdot 6H_2O$ [17]. Similar

phenomenan were observed in other hydrotris(pyrazolyl)borate and hydrotris(pyrazolyl)methane complexes [18, 19].

We have prepared the complexes $[M(pz^*)_2(NCS)_2] \cdot H_2O$ by using three different methods. Small stereoscopic ligands KTp^* easily form full sandwich complexes $[MTp^*_2]$. The full sandwich complexes $[MTp^*_2]$ as well as other substituted $[M(II)Tp_2^{R1,R2}]$ complexes have been considered to be stable and inert. However, reactivity of $[M(II)Tp_2^{R1,R2}]$ is observed in previous reports [15, 20]. In method A, $[MTp^*_2]$ is the major product in the first step and is then decomposed by addition of excess KSCN. Although the amount of KSCN used in method B is one-third of that in method A, the major product is still the title compound. The lower yield, compared with method A, is partly because of the formation of $[Tp^*M(NCS)]$. The analogues $[Tp^{ph}M(NCS)]$ (M = Zn and Co) have been isolated in our laboratory [21]. The reactivity of $[MTp^*_2]$ under suitable conditions has been discussed elsewhere [15, 22].

Structure of Complexes

An ORTEP drawing of both complexes is shown in Figure 1. The M(II) ion in each complex is coordinated to two pyrazole nitrogen atoms and two nitrogen atoms of NCS^- to form a distorted tetrahedron. The average M(II)-N bond lengths are 1.960 for **1** and 1.954 Å for **2**, respectively. The average N-M(II)-N angles are 109.52 (**1**) and 109.55° (**2**), respectively. The unit cell of each complex involves four complex molecules and four H_2O molecules, where each oxygen atom of the H_2O molecules is connected by a hydrogen bond with one nitrogen atom of pz^* to two neighboring complex molecules to form a 1-D chain. In the zinc complex (**1**), The hydrogen bond length $N4-H6A\cdots O1$ and $N2-H5A\cdots O1(x, y, z-1)$ are 2.098 and 2.160 Å for **1**, and 2.077 and 2.152 Å for **2**, respectively. The angles ∠N4H6AO1 and ∠N2H5AO1 $(x, y, z-1)$ are 158.94 and 157.02° for **1** and 158.20 and 154.50° for **2**, respectively. In both complexes, two hydrogen atoms of H_2O molecules are connected by weak hydrogen bonds (O—H···S) with two sulfur atoms of a neighboring chain. The lengths of hydrogen bonds O(1)—H(2)···S(1) and O(1)—H(1D)···S(2) are 2.737 and 2.406 Å and the angles ∠O(1)H(2)S(1) and ∠O(1)H(1D)S(2) are 155.88 and 173.41° for **1**, respectively. The distances O(1)—S(1) and O(1)—S(2) in **2** are 3.346 and 3.391 Å, respectively. Each sulfur atom in both complexes is connected by a weak coordination bond with a zinc(II) or cobalt(II) ion of a neighboring chain to form a sawtooth-type double 1-D chain structure. The distances Zn-S and Co-S are 3.919 Å and 3.853 Å, respectively.

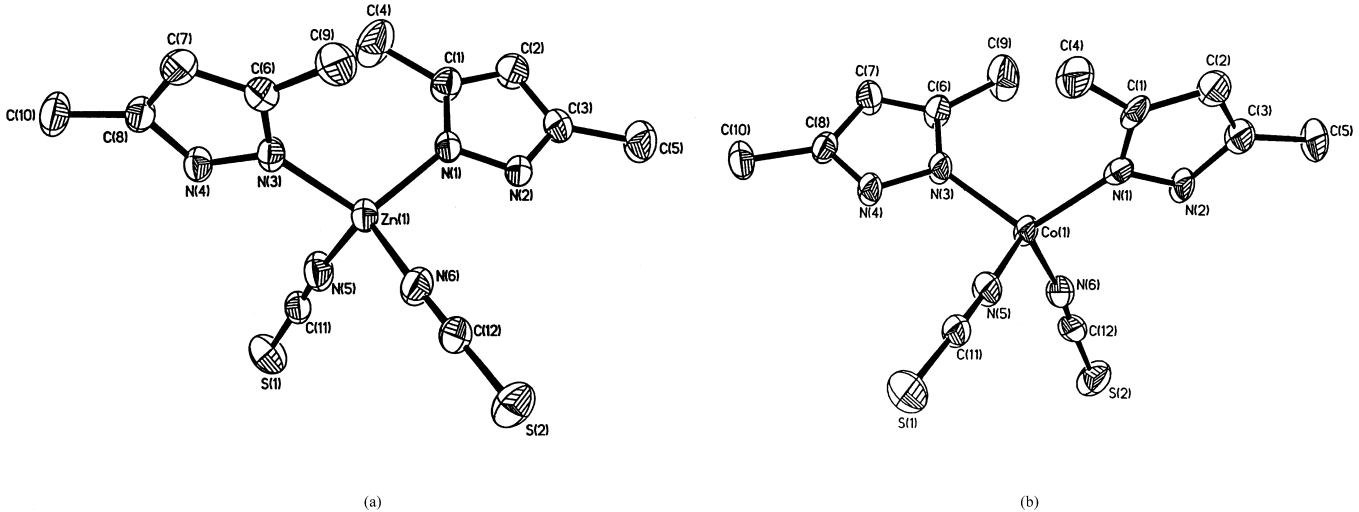

FIGURE 1 ORTEP drawing of the complexes (a) $[Zn(pz^*)_2(NCS)_2] \cdot H_2O$ (**1**) and (b) $[Co(pz^*)_2(NCS)_2] \cdot H_2O$ (**2**).

The intrachain and interchain distances between M – M are 8.875 and 7.793 Å for **1** and 8.919 and 7.933 Å for **2**, respectively.

Spectroscopic and Redox Properties

In the IR of both complexes, the typical $\nu_{s(B\text{-}H)}$ stretch at 2470 cm^{-1} in the free ligand disappears in the complexes, and a strong $\nu_{(N\text{-}H)}$ stretch of pz* appears at 3250 and 2090 cm^{-1}, respectively. The $\nu_{s(C\equiv N)}$ stretch of SCN^- is observed at 2090 and 2085 cm^{-1}, respectively. Other absorptions appear at 1700 ~ 650 cm^{-1}, consistent with pz* but not KTp*. These results are in good agreement with the crystal structure and analytical results.

Two strong bands, 44743 cm^{-1} (6.82×10^4 $M^{-1}cm^{-1}$) and 35907 cm^{-1} (3.40×10^3 $M^{-1}cm^{-1}$) for **1** and 41929 cm^{-1} (1.13×10^4 $M^{-1}cm^{-1}$) and 35651 cm^{-1} (3.6×10^3 $M^{-1}cm^{-1}$) for **2**, are observed in the UV range, and can be assigned to charge-transfer transition of the pz* ligand. In the visible range, two strong bands are observed in the Co(II) complex at 19474 cm^{-1} (4.4×10^2 $M^{-1}cm^{-1}$), 10315 cm^{-1} (1.9×10^2 $M^{-1}cm^{-1}$), respectively. They can be assigned to spin-allowed d-d transition bands of Co(II), $\nu_3(^4T_1(P) \leftarrow {}^4A_2)$ and $\nu_2(^4T_1(F) \leftarrow {}^4A_2)$, respectively. The spin-allowed band $\nu_1(^4T_2 \leftarrow {}^4A_2)$ in the near infrared region was not observed in the scan range (200 – 1000 nm). Ligand-field constants Dq, B' and β were calculated from Lever's transition energy ratio [23] by using observed bands ν_3 and ν_2. The calculated Dq is 571 cm^{-1}, which is smaller than for $[Co(II)(H_2O)_6]^{2+}$ (970 cm^{-1}). B' is 845 cm^{-1}. Compared with the free Co(II) ion (1115 cm^{-1}), the calculated value of $\beta = B_{complex}/B_{free\ ion} = 0.758$, shows some covalent bonding of Co(II) in the complex. The calculated ν_1 is 5706 cm^{-1}.

The cyclic voltammogram of the cobalt complex was scanned in the potential range of −0.8 V to −1.3 V at v = 0.1 V/s; a *quasi*-reversible redox process was detected at $E_{1/2} = -0.260$ V ($\Delta Ep = 181$ mV), assignable to the $Co^{II/III}$ couple. In conclusion, the complexes $[M(pz^*)_2(NCS)_2] \cdot H_2O$ (M = Zn and Co) were prepared by three different methods. Small stereoscopic ligands KTp* easily form stable and inert full sandwich complexes $[MTp^*_2]$. However $[MTp^*_2]$ has some reactivity under suitable conditions and are decomposed by excess KSCN.

Supplementary Material

Supplementary crystallographic data are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk) on request,

quoting the deposition numbers 150227 and 150228. Least-squares plane equations, deviations of atoms (Å) and dihedral angles between planes (°) for **1** and **2** are available from the authors on request.

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