Synthesis and X-ray Crystal Structures of Cobalt and Copper Complexes of 1,3-Bis(benzotriazolyl)propanes

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Two propylene-bridged bis-benzotriazole ligands, **1** and **2**, were used to obtain three novel coordination polymers with cobalt(II), copper(II) and copper(I). The complexes were structurally characterised by X-ray crystallography. The complex $[Co(1)Cl_2]_n$, **3**, possesses a helical zigzag chain structure in which tetrahedral $CoCl_2$ centres are bridged by molecules of **1** having an extended conformation. The complex $[Cu(1)Cl_2]_n$, **4**, exhibits a more complex supramolecular architecture, which extends in two dimensions, with bridging through Cu_2Cl_4 dimeric units in one direction and through the organic ligand in an orthogonal direction. The complex $[Cu(2)Cl]_n$, **6**, has a one-dimensional polymeric structure involving 16-membered M_2L_2 rings bridged by Cu_2Cl_2 units.

Introduction

The use of linear and angular components for the controlled self-assembly of two- and three-dimensional metallosupramolecular species has been the subject of considerable study in recent years.[1] The most commonly employed organic-connecting components are rigid, linear, bridging heterocyclic ligands, such as pyrazine and 4,4′-bipyridine. More recently, flexible ligands have been employed in order to gain access to topologies not available from logical combination of rigid building blocks. The simplest way to introduce flexibility into ligand design is by incorporation of alkyl chain spacer groups. For example, symmetrical ligands containing propylene spacer groups between 4-pyridyl,[2] 8-quinolyloxy,[3] 1-pyrazolyl,[4] 1-triazolyl,[5] and 2-benzimidazolyl[6] donor groups have recently been used for the construction of interesting new supramolecular architectures.

For some years now we have been involved in the synthesis and study of ligands containing less commonly studied heterocyclic ring systems.[7] One such heterocycle is benzotriazole, which is extensively used as a synthetic auxiliary in organic chemistry[8] but has been largely ignored by coordination chemists. The parent heterocycle can coordinate up to three metals in its deprotonated form.[9] Particular emphasis has been placed on copper complexes, due to the importance of benzotriazole as a corrosion inhibitor.[10] We have recently reported the incorporation of benzotriazole groups into a number of chelating ligands[11] and into a bidentate bridging ligand that forms a triple stranded helicate.[12] We now describe complexes of two symmetrical, isomeric ligands, **1** and **2**, which contain benzotriazole groups separated by flexible propylene spacer units (see Figure 1).

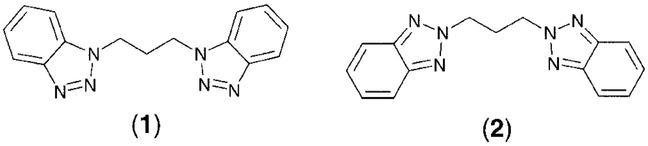

Figure 1. Structural formulae of ligands **1** and **2**

Results and Discussion

The ligands **1** and **2** were prepared by reaction of benzotriazole with 1,3-dibromopropane in the presence of sodium hydroxide in DMSO solution, as described previously by Katritzky et al.[13] This reaction produces a mixture of the symmetrical 1,1′- and 2,2′-isomers **1** and **2**, along with the unsymmetrical 1,2′-isomer. The three isomers were separated by column chromatography on silica gel and recrystallized from absolute ethanol, and their properties were in agreement with those described previously.[13] However, ligand **1** has recently been described by other workers,[14] who reported a ^{1}H NMR spectrum that we believe to be that of isomer **2**. In order to resolve this discrepancy unambiguously, we carried out an X-ray crystal structure determination of the compound we identified as **2**.

Figure 2 shows a perspective view of the structure of this ligand, which is indeed the 2,2′-isomer, in agreement with the NMR assignment of Katritzky et al.[13] The compound crystallizes in the orthorhombic space group $P2_12_12_1$ with

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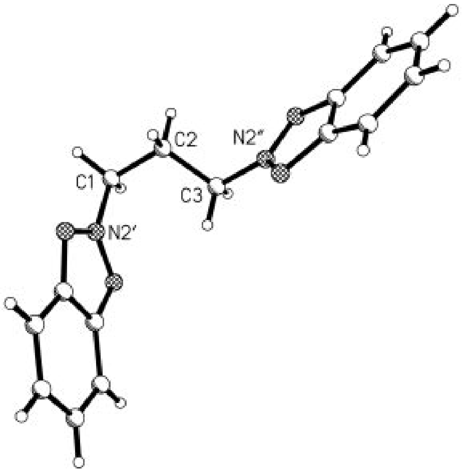

Figure 2. Perspective view of the X-ray molecular crystal structure of ligand **2**

a complete molecule in the asymmetric unit. The bonding geometry of the benzotriazole rings is similar to that in other 2-alkylbenzotriazoles.[13,15] In the solid state it adopts an unsymmetrical conformation about the central propylene spacer group. Specifically, one of the benzotriazole rings exists in a *gauche* conformation [N2′−C1−C2−C3 torsional angle = 59.0(2)°], while the other ring has the expected *anti* conformation [C1−C2−C3−N2″ torsional angle = 172.2(1)°]. This unusual shape undoubtedly results from a complex system of intermolecular forces, comprising face-to-face and edge-to-face aromatic interactions,[16] as well as C−H···N interactions,[17] all of which are now well-known to contribute significantly to the solid-state structures of heteroaromatic compounds.

Having unambiguously established the structures of the ligands, we proceeded to study their coordination chemistry. All three ligands were treated with a variety of first row transition metal salts. Complexes of the unsymmetrical 1,2′-isomer failed to assemble into any crystalline product. However, reactions of **1** and **2** with both cobalt(II) chloride and copper(II) chloride furnished single crystals suitable for X-ray structure determination.

Reaction of cobalt(II) chloride with **1** formed $[Co(1)Cl_2]_n$, **3**, which is a one-dimensional coordination polymer. Figure 3 shows a perspective view of a section of the extended structure with selected atom labelling. The complex crystallizes in the orthorhombic space group *Pnna*, with half the ligand and half a $CoCl_2$ in the asymmetric unit. Thus, the distorted tetrahedral cobalt atom and the central carbon of the propylene group (C2) each lie on different two-fold rotation axes. The resulting polymer chains extend into a helical zigzag pattern, in which the bridging ligand adopts the most extended possible form, with *anti* conformations of the propylene spacer [N1−C1−C2−C1B torsional angle = 179.6(2)°] and coordination by the less sterically hindered N3 nitrogen atoms, as was observed for the $CuCl_2$ complex of the related ligand with a methylene spacer group.[11] As a result, the ligand bridges the cobalt atoms, which are separated by 12.462(1) Å. The polymer chains stack on each other by face-to-face interactions between the benzotriazole groups in such a way that each chain stacks with four other chains.

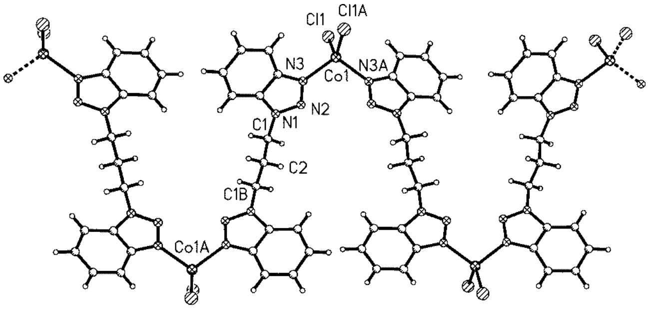

Figure 3. Perspective view, with selected atom labelling, of the one-dimensional coordination polymer $[Co(1)Cl_2]_n$, **3**; selected bond lengths (Å) and angles (°): Co1−N3 2.011(2); Co-Cl1 2.2235(6); N3−Co1−N3A 108.2(1); N3−Co1−Cl1 104.33(5); N3−Co1−Cl1A 112.02(5)

An analogous reaction of **1** with copper(II) chloride led to a complex, $[Cu(1)Cl_2]_n$, **4**, with a more complex supramolecular architecture. The compound crystallizes in the monoclinic space group $P2_1/n$ with a dichlorocopper(II) unit and a whole bridging ligand in the asymmetric unit. Figure 4 shows a perspective view of the contents of the asymmetric unit and the symmetry-related connecting atoms. The benzotriazole rings are both coordinated through the N3 nitrogen atoms in preference to the more sterically congested N2 nitrogen atoms. Within complex **4** the bridging ligand exists in a more compact conformation than was observed in **3**. In particular, the propylene bridge folds into a *gauche-gauche* conformation [N1″−C1−C2−C3 torsional angle = 57.2(3)° and C1−C2−C3−N1′ torsional angle = 68.0(3)°], which is similar to that observed in a zinc(II) thiocyanate complex of the same ligand.[14] As a consequence, copper atoms bridged by ligand **1** are separated by only 9.157(1) Å, much less than the metal−metal separation in **3**.

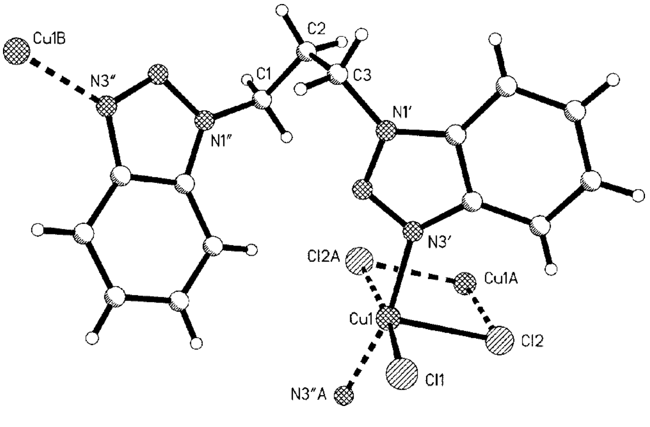

Figure 4. Perspective view showing the contents of the asymmetric unit and the connected atoms (dashed bonds), with selected atom labelling, in the crystal structure of $[Cu(1)Cl_2]_n$, **4**; selected bond lengths (Å) and angles (°): Cu1−N3′ 2.014(2); Cu1−N3″A 2.026(2); Cu1−Cl1 2.2834(8); Cu1−Cl2 2.6442(8); Cu1−Cl2A 2.3238(8); N3′−Cu1−N3″A 166.56(8); N3′−Cu1−Cl1 88.57(6); N3″A−Cu1−Cl1 90.75(6); N3′−Cu1−Cl2A 87.95(6); N3″A−Cu1−Cl2A 90.21(6); Cl1−Cu1−Cl2A 168.94(3); N3′−Cu1−Cl2 96.83(6); N3″A−Cu1−Cl2 96.49(6); Cl1−Cu1−Cl2 100.47(3); Cl2A−Cu1−Cl2 90.36(2); Cu1−Cl2−Cu1A 89.64(2)

The copper atom is five-coordinate, being bonded to two molecules of **1** that are related by a crystallographic glide plane, a terminal chlorine atom and two bridging chlorines that are related by a centre of inversion. The geometry of the copper is square pyramidal with a τ value[18] of 0.088; one of the bridging chlorines occupies the axial site. The terminal chlorine has a bond length of 2.283(1) Å and the two bridging chlorine atoms have bond lengths of 2.324(1) and 2.644(1) Å, giving the Cu_2Cl_2 unit a parallelogram-like shape, which, by virtue of the crystallographic centre of inversion, is strictly planar. The Cu1···Cu1A interatomic distance across the parallelogram is 3.509(1) Å. These distances are within the range of other known di-μ-chlorocopper(II) complexes.[7,10b,19]

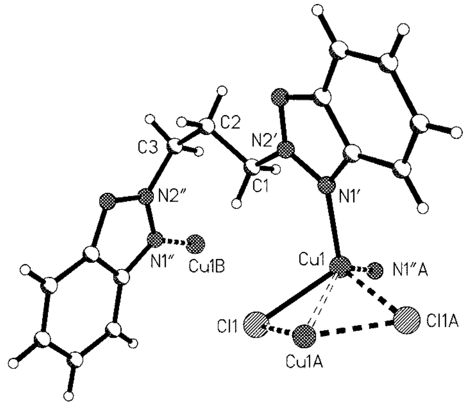

Figure 6. Perspective view showing the contents of the asymmetric unit and the connected atoms (dashed bonds), with selected atom labelling, in the crystal structure of $[Cu(2)Cl]_n$, **6**; selected bond lengths (Å) and angles (°): Cu1−N1′ 2.011(3); Cu1−N1″A 2.015(3); Cu1−Cl1 2.3724(9); Cu1−Cl1A 2.4287(9); N1′−Cu1−N1″A 115.3(1); N1′−Cu1−Cl1 112.29(8); N1″A−Cu1−Cl1 111.19(8); N1′−Cu1−Cl1A 108.30(8); N1″A−Cu1−Cl1A 107.59(8); Cl1−Cu1−Cl1A 101.01(3)

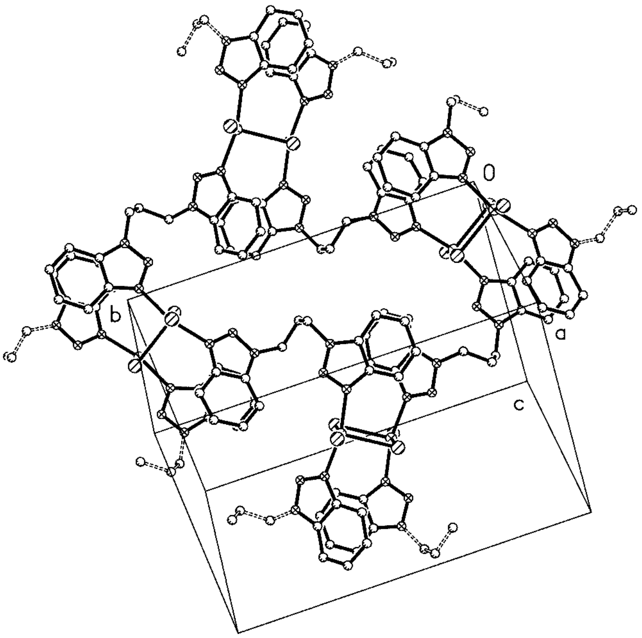

Figure 5. Perspective view of a section of the extended two-dimensional polymeric structure of **4**; the unit cell is indicated

The bridging nature of the heterocyclic ligand serves to extend the structure in one dimension. Further bridging by the chlorine atoms results in an orthogonal extension of the structure that produces a complicated two-dimensional network. Large 44-membered fused metallacyclic ring-systems exist within this network as M_6L_4 units, one of which is shown in Figure 5. A stabilising influence within this structure appears to come from π−π stacking between the benzotriazole rings separated by the Cu_2Cl_2 units. These rings lie perpendicular to the Cu_2Cl_2 plane and are separated by approximately 3.5 Å, although they are offset such that the centroids of the benzo rings are separated by ca. 4.18 Å.

Reaction of **2** with cobalt(II) chloride gave a $[Co(2)Cl_2]_n$ complex, **5**, as a light blue solid, which failed to produce any crystals suitable for X-ray crystallography. In contrast, reaction of **2** with copper(II) chloride in methanol gave, quite unexpectedly, a copper(I) species as lemon-coloured crystals. This surprising result proved to be quite reproducible, although the identity of the metal reductant remains undetermined. The resulting polymeric $[Cu(2)Cl]_n$ complex, **6**, crystallizes in the monoclinic space group *C2*/*c*, with a copper(I) chloride unit and a whole bridging ligand in the asymmetric unit. Figure 6 shows a perspective view of the contents of the asymmetric unit and the symmetry-related connecting atoms.

Within the complex the ligand adopts a conformation quite similar to that found in the structure of the free ligand **2**, in which one benzotriazole group adopts a *gauche* conformation to the propylene linker [C1−C2−C3−N2″ torsional angle = 64.9(4)°] and the other group an *anti* conformation [N2′−C1−C2−C3 torsional angle = 177.8(3)°].

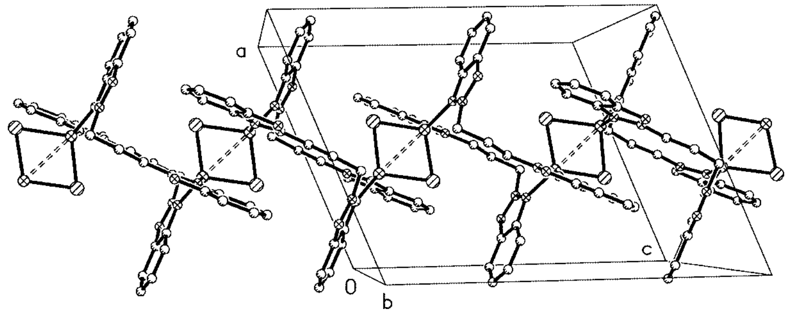

Figure 7. Perspective view of a section of the extended one-dimensional polymeric structure of **6**; the unit cell is indicated

This results in a relatively short intermetallic separation across the ligand bridge [Cu1···Cu1B = 6.010(1) Å]. The copper(I) atom has tetrahedral geometry with coordination to two bridging chlorine atoms, related by a twofold rotation axis, and two nitrogen atoms of different ligands, related by a centre of inversion. The Cu−Cl bond lengths are relatively symmetric [2.372(1) and 2.429(1) Å] and are in the range of other known binuclear Cu_2Cl_2 complexes.[20] The Cu_2Cl_2 unit is nonplanar with a rather short Cu···Cu contact [Cu1···Cu1A = 2.8093(8) Å]. The Cu−N1 distances are also within the range of similar known binuclear Cu_2Cl_2 complexes.[20] Two molecules of ligand **2** bridge two copper atoms, thereby generating a 16-membered M_2L_2 ring structure about a crystallographic centre of inversion. As shown in Figure 7, these rings further extend into a one-dimensional polymeric structure through the chloro bridges. Once again, the extended structure appears to be stabilised by $\pi-\pi$ stacking interactions across the Cu_2Cl_2 units between adjacent benzotriazole systems, whose mean planes are separated by ca. 3.5 Å.

Conclusion

The present study has shown that benzotriazole is a useful heterocyclic ring system for incorporation into bridging ligands. The bidentate ligands **1** and **2**, having flexible propylene linkers, generate one- and two-dimensional coordination polymer networks with copper and cobalt chlorides.

Experimental Section

General Procedures and Ligand Syntheses: NMR spectra were recorded on a Varian Unity 300 spectrometer with a 3 mm probe and operating at 300 MHz and 75 MHz for ^{1}H and ^{13}C, respectively. Melting points were determined using an electrothermal melting point apparatus and are uncorrected. Elemental analyses were performed by the Campbell Microanalytical laboratory at the University of Otago.

The ligands were prepared according to the procedure of Katritzky et al.[13] This gave a mixture of **1** [m.p. 139−139.5 °C (ref.[13] 119−121 °C)], **2** [119−121 °C (ref.[13] 116−118 °C)] and the unsymmetrical 1,2′-disubstituted isomer [80−81 °C (ref.[13] 83−83.5 °C)], which were separated by chromatography on silica gel and recrystallized from ethanol.

Preparation of Complexes

Cobalt(II) Chloride Complex of 1, viz. 3: 1,3-Bis(benzotriazolyl)propane (10 mg, 0.036 mmol) was dissolved in boiling MeOH (1 mL) and added to a solution of $CoCl_2\cdot6H_2O$ (8.5 mg, 0.036 mmol) in MeOH (1 mL). After 20 days blue plate crystals suitable for X-ray crystallography had formed. The crystals were removed and washed with MeOH. Yield: 8.5 mg (58%), m.p. 322 °C. $C_{15}H_{14}Cl_2CoN_6$ (408.15): calcd. C 44.14, H 3.46, N 20.59 %; found: C 44.28, H 3.27, N 20.48 %.

Copper(II) Chloride Complex of 1, viz. 4: $CuCl_2\cdot2H_2O$ (6.0 mg, 0.035 mmol) was dissolved in MeOH (3 mL) and added to a solution of 1,3-bis(benzotriazolyl)propane (10 mg, 0.036 mmol) dissolved in hot MeOH (3 mL). The light green mixture was mixed well and left standing at room temperature. After a few minutes blue crystals began to form and after 1 hour the solution was colourless. The blue block-shaped crystals are stable in air and suitable for X-ray diffraction. Yield: 11.9 mg (82%), m.p. 274 °C. $C_{15}H_{14}Cl_2CuN_6$ (412.76): calcd. C 43.65, H 3.42, N 20.36 %; found: C 43.76, H 3.37, N 20.15 %.

Cobalt(II) Chloride Complex of 2, viz. 5: 1,3-Bis(benzotriazol-2-yl)propane (32.4 mg, 0.116 mmol) and $CoCl_2\cdot6H_2O$ (25.2 mg, 0.106 mmol) were stirred and refluxed in MeOH (8 mL) for 16 h, which resulted in a blue solution. The blue solution was evaporated

Table 1. X-ray crystal data and details of data collections and structure refinements

Compound	**2**	**3**	**4**	**6**
Empirical formula	$C_{15}H_{14}N_6$	$C_{15}H_{14}N_6CoCl_2$	$C_{15}H_{14}N_6CuCl_2$	$C_{15}H_{14}N_6CuCl$
Molecular mass	278.32	408.15	412.76	377.31
Crystal system	orthorhombic	orthorhombic	monoclinic	monoclinic
a (Å)	5.8393(6)	14.377(2)	9.692(2)	11.693(1)
b (Å)	5.9826(6)	13.997(2)	15.309(3)	17.876(1)
c (Å)	38.695(4)	8.037(1)	11.093(2)	15.444(1)
β (°)	90	90	91.312(2)	112.131(1)
V (Å^3)	1351.8	1617.2(3)	1645.5(5)	2990.5(4)
Space group	$P2_12_12_1$	Pnna	$P2_1/n$	$C2/c$
Z	4	4	4	8
D_c (mg·m^{-3})	1.368	1.676	1.666	1.647
F (000)	584	828	836	1536
Temperature (K)	168(2)	165(2)	295(2)	165(2)
Crystal form	colourless block	blue plate	blue block	lemon-coloured block
Crystal size (mm)	0.61 × 0.57 × 0.24	0.40 × 0.39 × 0.03	0.34 × 0.14 × 0.14	0.65 × 0.14 × 0.11
μ (mm^{-1})	0.088	1.401	1.661	1.647
$2\theta_{max}$ (°)	52.78	53.12	52.80	50.00
Unique reflections	2752	1680	3297	2638
Completeness (%)	99.5	99.0	97.6	99.8
Parameters	190	110	217	208
R[a] [$I > 2\sigma(I)$][a]	0.0351	0.0304	0.0298	0.0421
wR[b] (all data)	0.0832	0.0776	0.0846	0.1050

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] $wR = (\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2])^{1/2}$.

in vacuo, the resulting solid was redissolved in $CHCl_3$ (2 mL) and the solution was subjected to slow evaporation, which gave a light blue solid. Yield: 39 mg (90%), m.p. 265−266 °C. $C_{15}H_{14}Cl_2CoN_6$ (408.15): calcd. C 44.14, H 3.46, N 20.59 %; found: C 43.89, H 4.07, N 20.29 %.

Copper(I) Chloride Complex of 2, viz. 6: 1,3-Bis(benzotriazol-2-yl)-propane (10 mg, 0.036 mmol) was dissolved in boiling MeOH (1 mL), and $CuCl_2{\cdot}2H_2O$ (6.0 mg, 0.036 mmol) dissolved in MeOH (1 mL) was added. The pale green solution was mixed well. After a few days, lemon-coloured crystals suitable for X-ray crystallography had formed. The crystals were filtered off and washed with MeOH. Yield: 4.9 mg (36%), m.p. 199 °C. $C_{15}H_{14}ClCuN_6$ (377.31): calcd. C 47.64, H 3.73, N 22.22 %; found: C 47.69, H 3.58, N 22.06.

X-ray Crystallography: Crystal data and experimental details of the data collections and structure refinements are listed in Table 1. Data were collected with a Siemens SMART CCD area detector, using graphite monochromatised Mo-K_α radiation (λ = 0.71073 Å). Almost complete spheres of data were collected. The structures were solved by direct methods using SHELXS,[21] and refined on F^2 using all data by full-matrix least-squares procedures with SHELXL-97.[22] Hydrogen atoms were included in calculated positions with isotropic displacement parameters 1.3 times the isotropic equivalent of their carrier atoms. The function minimised was $\Sigma w(F_o^2 - F_c^2)^2$, with $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$, where $P = [\max(F_o,0)^2 + 2F_c^2]/3$. CCDC-207061 (for **3**), -207062 (for **4**), -207063 (for **2**), -207064 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk.

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