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Helical and zigzag coordination polymeric chains derived from di-3-pyridyl ketone and silver(I) salts

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Abstract

A series of silver(I) complexes $[AgL(X)]_\infty$ ($X=BF_4$, ClO_4, NO_3, CF_3SO_3, PF_6; L = di-3-pyridyl ketone) have been characterized by X-ray crystallography. Argentophilic interaction, π–π stacking, Ag···X interaction, C–H···X (X = F, O) and C–H···O=C hydrogen bonding contribute to different extents in the construction of helical or zigzag infinite chains.

Keywords: Silver; Di-3-pyridyl ketone; Di-3-pyridinylmethanone; Coordination polymer; Helical chain

1. Introduction

During the past 15 years, rapid development in the construction of supramolecular architectures based on metal centers and organic building blocks has continuously produced coordination polymers with interesting compositions and diverse topologies, along with their potential applications in the fields of host–guest chemistry, catalysis, electrical conductivity, and magnetic materials [1–7]. In the development of both solution-based supramolecules and solid-state infinite polymers and networks, the coordination motif has been recognized as an effective ingredient in the design and self-assembly of a wide variety of supramolecular aggregates [1,8]. It is noteworthy that anions also play very important roles in supramolecular assembly [9–11] and crystal engineering [12]. As is well known, di-2-pyridyl ketone is an extraordinary ligand within the family of basic building blocks for the construction of metal–organic complexes with intriguing architectures and potential applications as catalysts and advanced materials [13–17]. In contrast, the ligand behavior of its positional isomer di-3-pyridyl ketone (di-3-pyridinylmethanone) remains unexplored to this date (Scheme 1).

Here we report our studies on five silver(I) complexes generated from di-3-pyridyl ketone (L) together with various monoanions, namely $[AgL(BF_4)]_\infty$ (**1**), $[AgL(ClO_4)]_\infty$ (**2**), $[AgL(NO_3)]_\infty$ (**3**), $[AgL(CF_3SO_3)]_\infty$ (**4**), $[AgL(PF_6)]_\infty$ (**5**), which were shown by X-ray analysis to exhibit two kinds of polymeric chains in the solid state.

2. Experimental

2.1. Materials and general methods

Diethyl ether was purchased from Aldrich and further refluxed over sodium and benzophenone. All other chemicals were purchased from Aldrich and used without further purification.

Elemental analyses of C, H and N were performed by the MEDAC LTD Vrunel Science Center, United Kingdom. IR spectra were recorded with a Nicolet Impact 420 FT-IR spectrometer using KBr pellets. ^1H NMR spectra were measured at 300 Hz with a Bruker-300 spectrometer using $CDCl_3$ as solvent. Mass spectrometry was conducted on a ThermoFinnigan MAT 95 XL spectrometer.

2.2. Synthesis

2.2.1. Synthesis of di-3-pyridyl ketone (L)

Under the protection of N_2, 3-bromopyridine (1.58 g, 10 mmol) in 10 ml anhydrous diethyl ether was added

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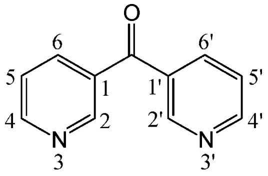

Scheme 1. Structure and atom labeling of di-3-pyridyl ketone.

slowly into 6.3 ml (10 mmol) *n*-butyllithium (15% in hexane) in 15 ml anhydrous diethyl ether at −78 °C. The resulting solution was kept at −78 °C for 30 min, and then 1.37 g (10 mmol) methyl nicotinate in 15 ml anhydrous diethyl ether was added slowly within 20 min with vigorous stirring. After stirring at −78 °C for another 30 min, the solution was allowed to warm slowly to −20 °C over 3 h, after which it was further quenched with 15 ml HCl solution in water and methanol (water/methanol/conc. HCl = 5:5:1). The mixture was extracted with dichloromethane, and the combined organic extract was dried over anhydrous sodium sulfate and finally concentrated in vacuo to give an orange–yellow solid. Purification by chromatography on silica-*gel* using ethyl acetate/hexane as the eluent gave 1.4 g L as a white solid in 76% yield, m.p. 115.8–116.3 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.01 (d, $J=1.5$ Hz, 2H), 8.85 (dd, $J_1=1.2$, $J_2=4.8$ Hz, 2H), 8.14 (dt, $J_1=7.8$, $J_2=1.8$ Hz, 2H), 7.49 (dd, $J_1=4.8$, $J_2=7.8$ Hz, 2H), IR (KBr): 1651s, 1581s, 1473w, 1416s, 1333m, 1294s, 1193w, 1143w, 1113w, 1083w, 1018w, 931m, 845w, 812w, 729s, 696m, 667w, 621w, 567w cm^{-1}; MS *m/z*: 184.06 ($[MH]^+$, 100% relative abundance); Anal. for $C_{11}H_8N_2O$: Calcd. C 71.73, H 4.38, N 15.20; Found C 71.69, H 4.34, N 15.19.

2.2.2. Synthesis of $[AgL(BF_4)]_\infty$ (**1**)

$AgBF_4$ (40 mg, 0.2 mmol) and L (37 mg, 0.2 mmol) were dissolved in 5 ml CH_3OH with stirring at room temperature. A white precipitate formed immediately, which was dissolved by the addition of CH_3CN. After filtration, the solution was placed in the dark for a week to give light yellow crystals of **1**. Yield: 73%. Anal. for $C_{11}H_8BF_4N_2OAg$: Calcd. C 34.87, H 2.13, N 7.39; Found C 35.03, H 2.16, N 7.42. IR (KBr): 1653s, 1585s, 1477w, 1419m, 1333m, 1298s, 1196w, 1119s, 1080s, 1034s, 931m, 843w, 814w, 721m, 698m, 671w, 623w, 525w cm^{-1}.

2.2.3. Synthesis of $[AgL(ClO_4)]_\infty$ (**2**)

This complex was obtained as light-yellow crystals in a similar manner as for **1** by the reaction of $AgClO_4$ with L. Yield: 80%. Anal. for $C_{11}H_8ClN_2O_5Ag$: Calcd. C 33.75, H 2.06, N 7.15; Found C 33.80, H 2.05, N 7.17. IR (KBr): 1653s, 1585s, 1477w, 1419m, 1333w, 1298s, 1143s, 1113s, 1088s, 1022w, 933w, 842w, 814w, 729m, 698m, 671w, 627m, 571w cm^{-1}.

2.2.4. Synthesis of $[AgL(NO_3)]_\infty$ (**3**)

$AgNO_3$ (34 mg, 0.2 mmol) and L (37 mg, 0.2 mmol) were dissolved in a mixed solvent of 3 ml CH_3CN and 3 ml CH_3OH with stirring at room temperature. The solution was stirred overnight in the dark, filtered, and allowed to stay in the dark for two weeks to give light-yellow crystals of **3**. Yield: 77%. Anal. for $C_{11}H_8N_3O_4Ag$: Calcd. C 37.31, H 2.28, N 11.86; Found C 37.23, H 2.25, N 11.82. IR (KBr): 1651s, 1583s, 1416s, 1383vs, 1294s, 1193w, 1115w, 1020w, 930w, 841w, 823w, 729m, 698m, 669w, 621w cm^{-1}.

2.2.5. Synthesis of $[AgL(CF_3SO_3)]_\infty$ (**4**)

This complex was synthesized in the same way as for **1** by the reaction of $AgSO_3CF_3$ with L. Yield: 63%. Anal. for $C_{12}H_8F_3N_2O_4SAg$: Calcd. C 32.67, H 1.83, N 6.35; Found C 32.82, H 1.83, N 6.32. IR (KBr): 1653s, 1585s, 1475w, 1417m, 1333m, 1294brs, 1174m, 1117w, 1082w, 1034s, 935m, 843w, 813w, 760w, 729m, 698m, 646m, 575w, 519w cm^{-1}.

2.2.6. Synthesis of $[AgL(PF_6)]_\infty$ (**5**)

This complex was prepared using the same method as for **1** by the reaction of L with $AgPF_6$ in 1:1 molar ratio. Yield: 82%. Anal. for $C_{11}H_8F_6N_2OPAg$: Calcd. C 30.23, H 1.85, N 6.41; Found C 30.26, H 1.88, N 6.30. IR (KBr): 1655s, 1585s, 1477w, 1419s, 1335m, 1298s, 1250w, 1203w, 1117w, 1022w, 937m, 835brs, 731s, 698m, 671w, 621w, 559s cm^{-1}.

2.3. X-Ray crystallography

Crystals mounted inside Lindemann glass capillaries were used for data collection on a Bruker SMART 1000 CCD diffractometer operating at 50 KV and 30 mA using Mo Kα radiation ($\lambda=0.71073$ Å) at 293 K. Data collection and reduction were performed using the SMART and SAINT software [18]. An empirical absorption correction was applied using the SADABS program [19]. All five structures were solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXTL program package [20]. Crystallographic data of complexes **1–5** are listed in Table 1.

3. Results and discussion

The known ligand di-3-pyridyl ketone (L) was synthesized by a procedure similar to that for 2-pyridinyl-3-pyridinylmethanone as reported by Mikhura, et al. [21,22]. Ligand L readily gives rise to silver(I) complexes upon reaction with various silver salts, which can be crystallized by slow evaporation of the solvent. This family of coordination polymers exhibits two structural types in the crystalline state, namely helical and zigzag chain, due to the different linkage modes that L may take. Changing of the reaction ratio between ligand L and the Ag(I) salts does not affect the structure of the polymers and leads to the same product in each case.

Table 1
Crystallographic data of complexes **1**–**5**

Complexes	**1**	**2**	**3**	**4**	**5**
Empirical formula	$C_{11}H_8BF_4N_2OAg$	$C_{11}H_8ClN_2O_5Ag$	$C_{11}H_8N_3O_4Ag$	$C_{12}H_8F_3N_2O_4SAg$	$C_{11}H_8F_6N_2OPAg$
Formula weight	378.87	391.51	354.07	441.13	437.03
Crystal size	0.60×0.45×0.29	0.58×0.46×0.37	0.65×0.51×0.20	0.65×0.54×0.42	0.45×0.38×0.23
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	*Pbca* (No. 61)	$P2/c$ (No. 13)
a (Å)	10.9257(8)	10.8435(7)	11.521(1)	12.2360(6)	8.358(2)
b (Å)	8.3727(6)	8.4137(5)	7.4031(7)	13.5248(7)	6.273(2)
c (Å)	14.243(1)	14.4632(9)	13.856(1)	17.1609(9)	13.643(3)
α (°)	90	90	90	90	90
β (°)	98.685(1)	96.551(1)	97.322(2)	90	106.049(5)
γ (°)	90	90	90	90	90
V (Å^3)	1287.9(2)	1310.9(1)	1172.1(2)	2839.9(3)	687.4(3)
Z	4	4	4	8	2
D_{calc} (g/cm^3)	1.954	1.984	2.006	2.063	2.112
μ(Mo Kα) (mm^{-1})	1.607	1.761	1.734	1.622	1.653
F(000)	736	768	696	1728	424
Reflections collected	6644	6784	5968	14261	3513
Independent reflections (R_{int})	2266 (0.0511)	2310 (0.0293)	2058 (0.0351)	2492 (0.0311)	1220 (0.0377)
Observed reflections [$I>2\sigma(I)$]	1936	1965	1831	2107	1006
Parameters	217	217	172	208	104
Goodness-of-fit	1.198	1.133	1.232	1.149	1.128
R_1 [$I>2\sigma(I)$]^a	0.0612	0.0462	0.0574	0.0389	0.0487
wR_2 (all data)^b	0.1512	0.1195	0.1307	0.0910	0.1336

[a] $R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$.
[b] $wR_2=\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

In the isostructural complexes **1**, **2** and **3**, the bidentate bridging ligand L and silver atom are linked alternatively to form an infinite helical chain (Fig. 1). In each complex, five kinds of weak interactions are involved in cross-linking such chains into a three-dimensional network: argentophilic interaction [23], π–π stacking [24], Ag⋯X interaction [25], C–H⋯X (X=F in **1**, X=O in **2** and **3**) hydrogen bonding and C–H⋯O=C hydrogen bonding [26]. Among these, the weak C–H⋯O=C hydrogen bonds (H⋯O 2.433 Å, C–H⋯O 154.9°) occur between L ligands belonging to adjacent chains, leading to 10-membered rings that bind the chains together to form a two-dimensional network (Fig. 2a). In the (1 0 0) plane, the chains are also linked together by argentophilic and π–π stacking interactions (Fig. 2b), as well as Ag⋯X interaction and C–H⋯X hydrogen bonding (X=F in **1**, X=O in **2** and **3**). The intervening space between adjacent repeating pitches of the helical structure is filled by the corresponding counter anions. This suggests that the spring-like chains in complexes **1** and **2** are in a more relaxed state than that in **3**, since the steric bulk of BF_4^- or ClO_4^- is much larger than that of NO_3^-. Concerning the non-bonded distance between Ag1 and Ag1B as shown in Fig. 1, the values are 8.373 Å, 8.414 Å and 7.403 Å for complexes **1**, **2** and **3**, respectively.

Complexes **4** and **5** comprise the same kind of infinite zigzag polymeric chain (Fig. 3), whose conformation is

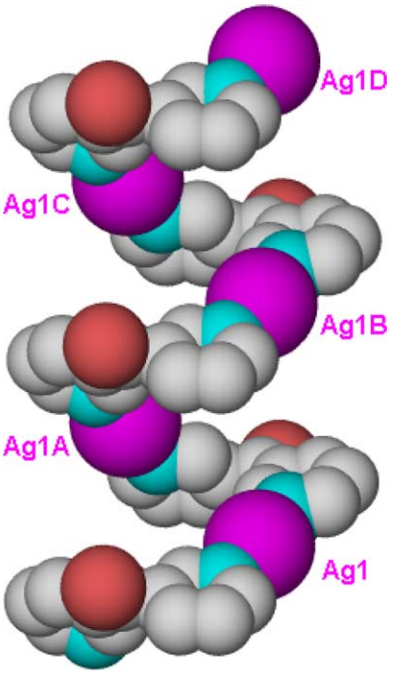

Fig. 1. Helical structure in complexes **1**–**3**. Hydrogen atoms are omitted for clarity. Color code: purple: silver; light gray: carbon; turquoise: nitrogen; red: oxygen.

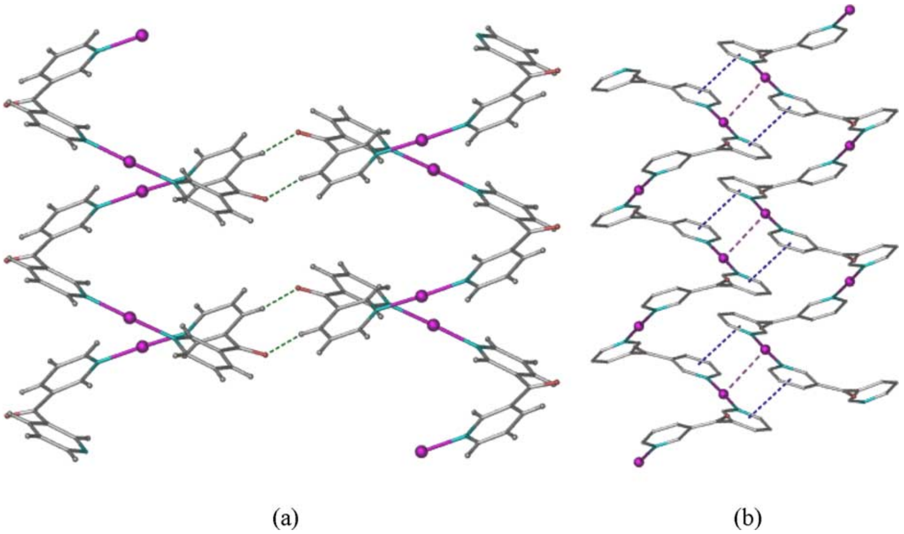

Fig. 2. (a) Cross-linkage of adjacent chains through hydrogen bonding in complex **3**, viewed along the [111] direction. (b) Assembly of the adjacent chains by argentophilic interaction and π–π stacking interaction, viewed along the [100] direction. Color code: purple: silver; light gray: carbon; turquoise: nitrogen; red: oxygen.

affected by the different electron donor ability of the counter anion. As observed in their crystal structures, the two-coordinated silver atom in **5** takes a strictly linear conformation, whereas in **4** the N–Ag–N bond angle is 165.5°. In complex **4**, besides being coordinated by the N atoms from two independent L ligands, the silver atom also has weak interactions with O atoms from both ligand L and trifluoromethanesulfonate anions at distances between 2.747 and 3.139 Å. Furthermore, Ag···π interaction [27] with a Ag-centroid distance of 3.378 Å accounts for stacking of the zigzag chains into a two-dimensional network (Fig. 4a), which are further consolidated by Ag···O weak interactions and C–H···O (trifluoromethanesulfonate) hydrogen bonding. In complex **5**, Ag···π interaction with a Ag-centroid distance of 3.794 Å, together with π–π interaction with a centroid–centroid distance of 3.739 Å (Fig. 4b), bind the zigzag chains into a two-dimensional network. The highly symmetric PF_6^- anion in **5** acts as

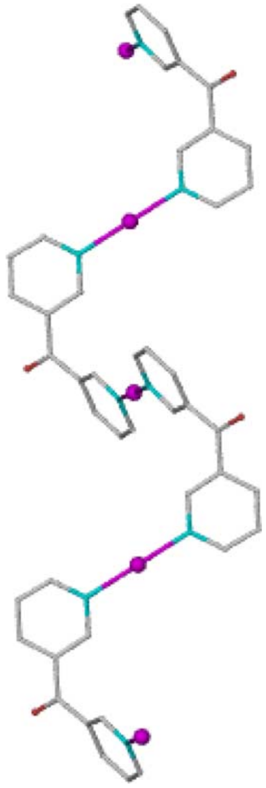

Fig. 3. The zigzag chain in complexes **4** and **5**. Hydrogen atoms are omitted for clarity. Color code: purple: silver; light gray: carbon; turquoise: nitrogen; red: oxygen.

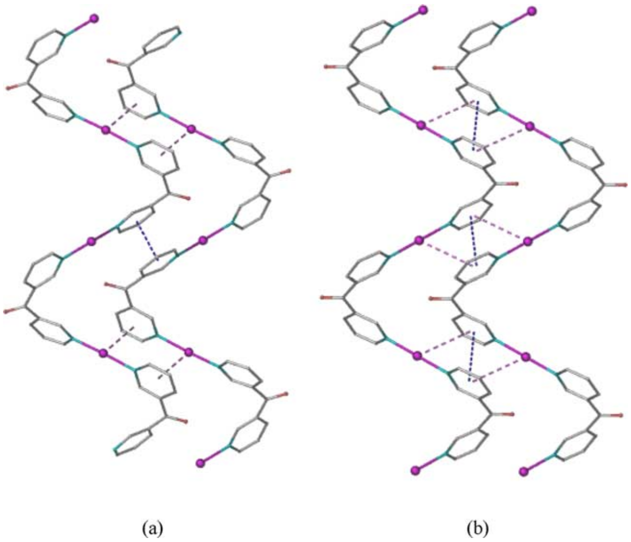

Fig. 4. (a) The Ag···π interactions in complex **4**, which link the infinite chains into a two-dimensional network. (b) The Ag···π and π–π interactions in complex **5**, which link the infinite chains into a two-dimensional network. Hydrogen atoms are omitted for clarity. Color code: purple: silver; light gray: carbon; turquoise: nitrogen; red: oxygen.

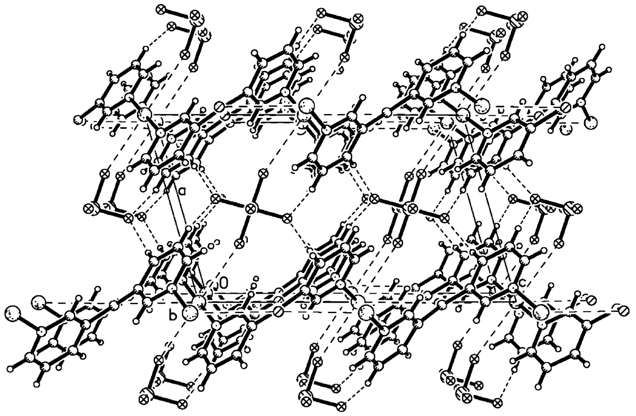

Fig. 5. Three-dimensional network in complex **5** linked by PF_6^- counter anions, viewed along the *b* direction.

the dominent factor in the conglomeration of the layers through C–H···F hydrogen bonding (H···F 2.471 Å and 2.494 Å) [28] and Ag···F weak interaction (3.110 Å) [29] (Fig. 5).

Though the coordination mode of ligand L in complexes **1**–**5** remains invariant, its linking direction in complexes **4** and **5** is different from that in **1**–**3**, resulting in two kinds of infinite chains (Fig. 6). In accordance with this, together with the subtle effect of the counter anions, the torsion angles of the two pyridyl rings with respect to the carbonyl group of ligand L are different in these complexes, as shown in Table 2. Within each infinite chain, the silver atoms of complex **5** are strictly co-linear, while the Ag···Ag···Ag angle involving three consecutive, non-bond silver atoms takes the value 75.1°, 74.6°, 70.0°, and 166.7° for complexes **1**–**4**, respectively, which clearly differentiate the two kinds of chains.

In 1994, Sommerer et al. reported a silver complex of di-2-pyridyl ketone, $[Ag(C_{11}H_8N_2O)(NO_3)]_\infty$, which comprises an infinite helical chain,[30] and in 2000 Chen *et al.* reported a series of related helical complexes $[Ag(C_{11}H_8N_2O)(X)]_\infty$ ($X = NO_2$, ClO_3, PF_6, ClO_4) [31]. The present studies on complexes **1**–**5** show that both positional isomers of dipyridyl ketone exhibit analogous coordination behavior toward silver(I) with the carbonyl group remaining intact.

The IR spectra of the present series of complexes indicate that the coordination of ligand L with silver(I) salts affect the vibration of ligand L only to a minor extent. As to the $\nu(C{=}O)$ mode, ligand L exhibits a sharp and strong peak at 1651 cm^{-1} and complexes **1**–**5** show the same peak at 1653, 1653, 1651, 1653 and 1655 cm^{-1}, respectively.

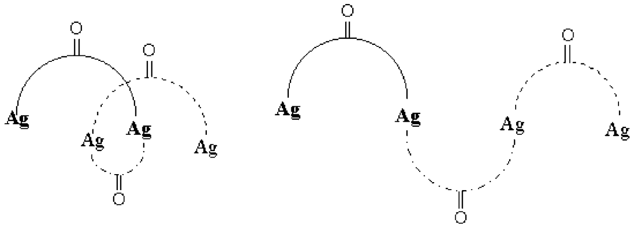

Fig. 6. Different linking directions of consecutive L ligand leading to a helical chain (left, for **1**–**3**) and a zigzag chain (right, for **4** and **5**).

Table 2
Atom labeling of ligand L and torsion angles of the two pyridyl rings with respect to the carbonyl group in complexes **1**–**5**.

Complex	Torsion angle (°)	
	C2–C1–C=O	C2′–C1′–C=O
1	−165.0(8)	−130.3(9)
2	−163.4(6)	−130.8(7)
3	−166.1(6)	−135.5(7)
4	−159.4(4)	−132.1(4)
5	147.0(4)	147.0(4)

In summary, five silver(I) complexes of di-3-pyridyl ketone (L) have been successfully synthesized and their structures characterized by X-ray diffraction. Two kinds of infinite chains resulting from *N*,*N*′-bridging of ligand L have been observed in these complexes. Weak argentophilic interactions are manifested in complexes **1**–**3** that comprise helical chains, while Ag···π interaction exists in complexes **4** and **5** exhibiting zigzag chains. The structural differences within this series of complexes illustrate the significance of the anion effect [9–12], as well as the interplay among various kinds of weak interactions, on the construction of supramolecular metal–organic complexes.

4. Supplementary material

Crystallographic data of complexes **1**–**5** are available in the Supplementary Information. CCDC 258514–258518 for complexes **1**–**5**, respectively.

Acknowledgements

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