ORIGINAL RESEARCH

A 2D network silver coordination polymer with the multimodal ligand 2-pyrazyl methyl ketazine

Abdurrahman Sengul · Ozgur Kurt ·
Orhan Buyukgungor

Abstract A two-dimensional coordination polymer $\{Ag(\textbf{PMK})(OTf)\cdot MeCN\}_n$ (**1**) based on multi-modal bridging ligand, namely N,N'-bis[1-(pyrazin-2-yl)ethylidene]-hydrazine or 2-pyrazyl methyl ketazine (**PMK**), and AgOTf salt has been synthesized and characterized by ESI-MS, ^{1}H-NMR, ATR-IR, and single crystal X-ray diffraction. The **PMK** shows distinct binding sites, both chelating and monodentate, and bridging modes in **1** where each silver(I) centre is five coordinate, and bound to one bidentate pyrazylketimine and a monodentate pyrazine through the peripheral N atom from another ligand, and also a bridging pyrazine through the peripheral N atom of the adjacent chelating unit from another ligand, and to triflate anion to feature one-dimensional infinite chain. The triflate anions have effectively increased the 1D coordination polymers to a 2D network via H-bonding interactions. These 2D planes are stacked together building up channels (1D tube) in which the acetonitrile solvent molecules reside and form very weak contacts with the triflates and the pyrazylketimine units via C–H···O and C–H···N, respectively. In addition, the fluorescent spectrum of **1** in the solid state exhibits two emission maxima at 496 and 522 nm. The ESI-MS, IR, and ^{1}H-NMR confirm the structure.

A. Sengul (✉) · O. Kurt
Department of Chemistry, Faculty of Arts and Sciences,
Zonguldak Karaelmas University, 67100 Zonguldak, Turkey
e-mail: sengul@karaelmas.edu.tr

O. Buyukgungor
Department of Physics, Faculty of Arts and Sciences, Ondokuz
Mayis University, Kurupelit, 55139 Samsun, Turkey
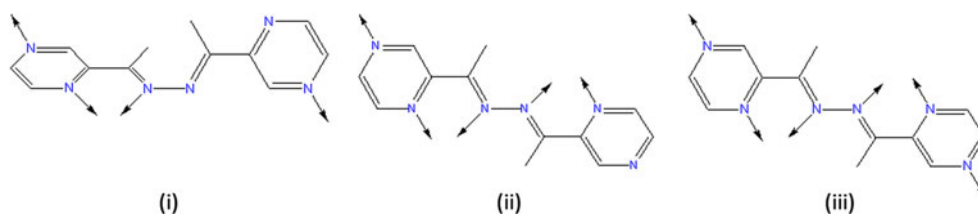
Introduction

During the past decades, pronounced interest has been focused on the construction of polymeric coordination complexes owing to their structural topologies and interesting catalytic, electronic, magnetic, and spectroscopic properties [1]. The building-block methodology is the most useful and flexible strategy for the crystal engineering design of novel extended networks. The construction of coordination networks relies upon utilizing the specific geometries of both metal ions and ligands [2]. In this context, multi-modal bridging ligands have recently gained considerable interest since they contain distinct binding sites, both chelating and monodentate, and bridging modes [2–4]. An assembly process containing multidentate ligands is usually very complicated and is influenced by various factors such as solvent system, templates, counter ions, valences and the geometrical preference for the metal ions [5, 6]. Therefore, it is difficult to design and synthesize supramolecular architectures with predicted structures and properties when the number of donor atoms in the ligands is more than two. This has been exemplified by the novel organic–inorganic composite coordination polymers generated from **PMK** having additional pyrazine nitrogen atoms in comparison to pyridylketimine ligand and Ag(I) salts [3, 4]. Depending on the anions, the ligand shows distinct coordination modes as illustrated in Fig. 1. It has also been demonstrated that changes in the counter ion can have influence upon the solid state structures of a series of compounds, often with surprising results [3].

(i)   (ii)   (iii)

We have previously reported the single crystal X-ray structure of **PMK** which confirmed the expected ligand structure [7]. In the solid state structure, **PMK** assumes a planar structure and adopts a *trans*-configuration about the central N–N bond, with the methyl groups on the opposite sides, suggesting conjugation throughout the π systems. The crystal structures of complexes $\{[Ag_2(\textbf{PMK})_2][PF_6]_2 \cdot MeCN\}_n$ (**2**), and $[Ag_2(\textbf{PMK})_2](SbF_6)_2 \cdot CH_2Cl_2$ (**3**) $[Ag_5 (\textbf{PMK})_3(NO_3)_3][Ag(NO_3)_3] \cdot 3CHCl_3$ (**4**) reveal that the coordination behavior of the ligand in all complexes are distinctly different from each other featuring specific architectures. First two are aggregates of double-helical architectures in which different connectivity of the helical units led to a quite different network, whereas the latter one is a trinuclear circular helicate formed from three ligands wrapping around the three silver(I) centres. Comparison of these silver(I) complexes was described in detail by Hannon [4]. Herein, we wish to report the synthesis and spectroscopic properties, luminescent and X-ray single crystal structure of the novel coordination polymer $\{Ag_2(\textbf{PMK})(OTf) \cdot CH_3CN\}_n$ (**1**) in comparison to previously reported silver(I) complex salts of **PMK** with different anions, namely PF_6^-, SbF_6^-, and NO_3^-, respectively. In the present case, $CF_3SO_3^-$ was chosen as the counter anion since it can act as a non-coordinating anion or as a labile ligand through the sulfonate group, and also its ability to form hydrogen bonds.

Experimental

Preparation of 1

An acetonitrile solution of **PMK** (0.240 g, 0.10 mmol) was added AgOTf (0.026 g, 0.1 mmol) in acetonitrile (15 ml) under dry nitrogen, and set to reflux for 6 h with vigorous stirring. The yellowish homogenous solution was concentrated under vacuum and left for crystallization by slow ether diffusion at room temperature to afford yellow needles, **1**, suitable for X-ray diffraction. Yield: 82%. Anal. calcd. for $C_{15}H_{15}AgF_3N_7O_3S$: C, 33.47; H, 2.81; N, 18.22%. Found: C, 33.50; H, 2.78; N, 18.31%. IR data (ATR, cm^{-1}) **1**: 3354 (w), 3183 (w), 2924 (vw), 1660 (vw), 1594 (m), 1519 (m), 1478 (m), 1403 (w), 1378 (vw), 1270 (s), 1250 (vs), 1223 (s), 1102 (m), 1029 (vs), 973 (vw),

848 (s), 800 (br, m), 755 (s), 692 (s). ^1H NMR (ppm, 400 MHz, DMSO-d_6): δ 9.38 (m, J = 8.6 Hz, 5H), 8.75 (m, J = 8.6 Hz, 5H), 2.51 (s, 3H), 2.33 (s, 3H). Mass spectrum (ESI) *m/z* (%) 538.3 (5) $[Ag(\textbf{PMK})(OTf) (MeCN)]^+$, 605.8 (25) $[Ag_4(\textbf{PMK})_2(OTf)_2]^{2+}$, 1177.0 (100) $[Ag_5(\textbf{PMK})_5(OTf)_3(MeCN)_4]^{2+}$, 1425.0 (65) $[Ag_6(\textbf{PMK})_6 (OTf)_4(MeCN)_4]^{2+}$, 1694.5 (50) $[Ag_7(\textbf{PMK})_7(OTf)_5(Me CN)_5]^{2+}$ and 1946.5 (60) $[Ag_8(\textbf{PMK})_7(OTf)_6(MeCN)_{11}]^{2+}$.

X-ray crystallography

Diffraction experiments were carried out at 296 K on a Stoe IPDS diffractometer. The structures were solved by direct methods and refined using the programs SHELXS-97 [8] and SHELXL-97 [9]. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods. The hydrogen atoms were placed in geometrically idealized positions and refined as riding atoms. Data collection: X-AREA, cell refinement: X-AREA, data reduction: X-RED32 [10]; program(s) used for molecular graphics: ORTEP-3 for Windows [11]; software used to prepare material for publication: WinGX [12] and Mercury 2.3 [13]. Crystal data and structure refinements are summarized in Table 1. Selected bond lengths and bond angles are given in Table 2.

Results and discussion

The coordination geometry around the silver(I) is depicted in Fig. S1 in which each silver(I) centre is five coordinate, bound to one bidentate pyrazylketimine binding unit from one ligand and two a monodentate pyrazine nitrogen donors from two symmetry related ligands, and to triflate anion. The ligand uses only four of six nitrogen donors to bind silver(I) centres and one terminal $N_{pyrazinyl}$ and one N_{imine} are free, which is distinctly different from the ligation modes of **PMK** in **2**, **3**, and **4** as depicted in Fig. 1. However, it resembles the silver(I) complexes of pyridylmethylketazine ligand (L^1) in a dinuclear triple helical complex $[Ag_2(L^1)_3][PF_6]_2$ [14], where one ligand uses all four donor atoms to coordinate as a *bis*(bidentate) ligand to the two metal centres, whereas the other two ligands use only three donors and coordinate as a bidentate to one metal centre and a monodentate to the other leaving the imine residue free that

acts as a spacer unit between the binding sites. However, with the difference of **PMK** having additional pyrazine nitrogen donors onto pyrazylketimine binding units also coordinates to another silver(I) centre to form a one-dimensional infinite chain (Fig. 2a). The ligand spans three silver(I) ions, but does not wrap around the metal–metal axis. The twisting of the ligand takes place about the N–N bond between the chelating pyrazylketimine unit (which is slightly deviating from planarity, N(3)–C(10)–C(11)–N(4) 6.9(5)°) and the monodentate part [C(11)–N(4)–N(5)–C(5) = −91.8(4)°]. The weak coordination bonds between the silver(I) atoms and $CF_3SO_3^-$ anions [Ag(1)–O(3) 2.666(3) Å] seem to stabilize the heavily distorted tetrahedron of the silver(I) atoms to form a distorted trigonal–bipyramidal AgN_4O environment in **1**. The triflate anions which point out from the 1D chain make weak intermolecular contacts with the adjacent units through C(3)–H(3)⋯O(2) 2.712(4) Å (Table 3) to form a two-dimensional network (Fig. S2). In the 1D chain, the repeating silver(I) ions are separated by 7.276 Å, whereas in the dinuclear units the Ag⋯Ag contact is 8.123 Å. The distance between silver(I) ions in the two parallel chains is 10.031 Å. In this structure, the CH_3CN molecules are stacked in channels (1D tube) and are stabilized by intermolecular contacts to triflate ions and also to methyl groups onto imine moieties of the ligand strand as shown in Fig. 2b. It is very well known from crystal-engineered coordination polymers that the coordinated anions can result switching between different coordination polymer motifs owing to the ability of the anions to form C–H⋯X contacts [4, 15]. The $CF_3SO_3^-$ which seems to have a greater propensity for coordination than NO_3^-, PF_6^-, or SbF_6^- and ability to take part in hydrogen bonding have resulted distinct coordination mode of **PMK** and very different packing motif in **1** featuring a two-dimensional polymer in comparison to silver(I) complexes of **PMK** with different anions in **2**, **3**, and **4**, respectively.

The solid state luminescence spectra of compound **1** and free ligand **PMK** at room temperature are studied. For **PMK**, no emissions were observed in the visible range. Compound **1** exhibits two emission maxima at 496 and 522 nm upon excitation at 257 nm (Fig. S3). The emission can be attributed to the emission of ligand-to-metal charge-

Fig. 2 (**a**) Self-assembly of one-dimensional coordination polymer from AgOTf and **PMK**. Hydrogen atoms have been omitted for clarity. (**b**) View of the 2D network structure of the complex {Ag(**PMK**)(OTf)·MeCN}$_n$ (**1**) along the crystallographic a-axis showing the presence of channels encapsulating acetonitrile solvent molecules. Hydrogen atoms have been omitted for clarity
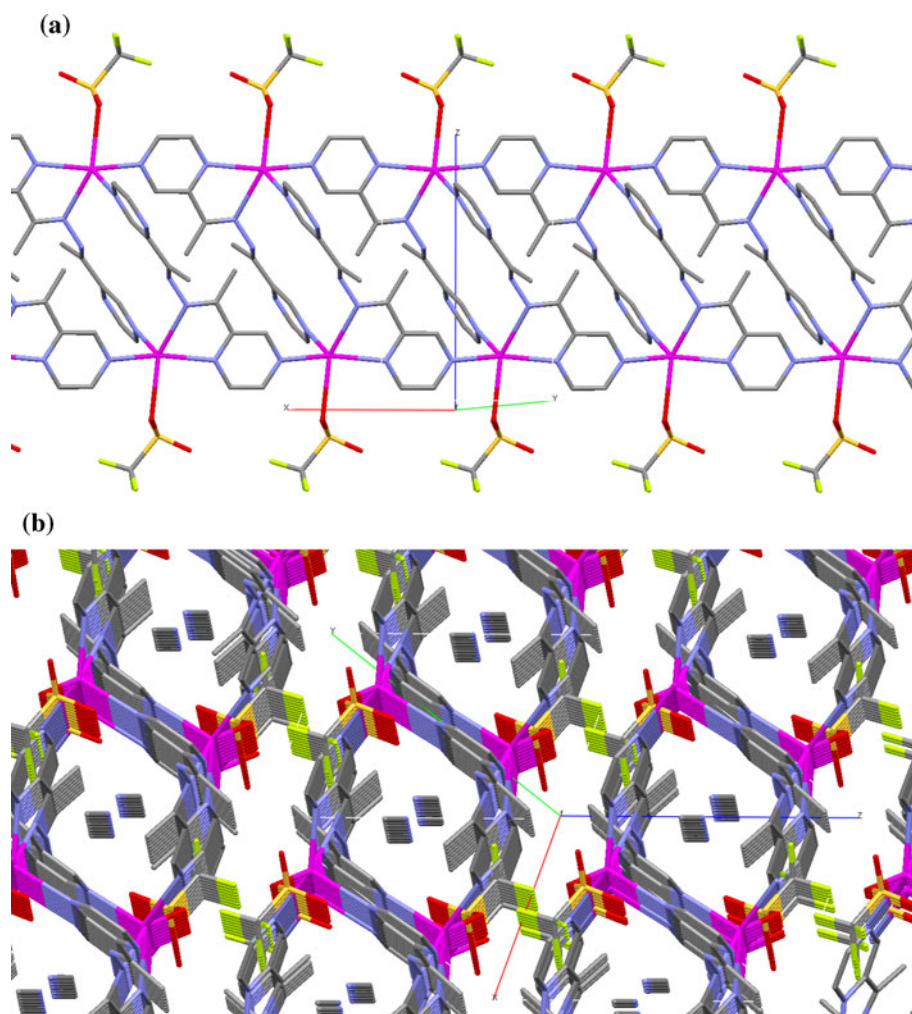
Table 1 Crystal data and structure refinements for the silver coordination polymer (**1**)

Empirical formula	$C_{15}H_{15}AgF_3N_7O_3S$
Formula mass	538.27
Temperature (K)	296(2)
Wavelength	0.71073
Crystal system	Triclinic
Space group	P-1
a (Å)	7.2757(5)
b (Å)	11.9853(11)
c(Å)	12.0905(10)
α (°)	107.697(7)
β (°)	95.298(6)
γ (°)	94.217(7)
V (Å^3)	994.37(15)
Z	2
D_{calc} (Mg m^{-3})	1.798
μ (mm^{-1})	1.18
$F[000]$	536
Crystal size (mm^3)	$0.35 \times 0.23 \times 0.13$
θ (°)	1.8–26.5
Index ranges	$h = -9$ to 9
	$k = -15$ to 15
	$l = -15$ to 15
Reflections collected	3406
Independent reflections	4114
Absorption correction	Integration
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4114/36/274
Goodness-of-fit on F^2	1.05
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.030$
R indices (all data)	$wR_2 = 0.087$
Largest diff. peak and hole	0.62 and -0.67 eÅ^{-3}
CCDC deposition number	CCDC 779996

Calculated weights $w = 1/\left[\sigma^2\left(F_0^2\right) + (00534P)^2 + 0.199P\right]$, where $P = \left(F_0^2 + 2F_c^2\right)/3$

Table 2 Selected bond lengths (Å) and angles (°) for **1**

N(4)–N(5) 1.385(3)	O(3)–Ag(1)^{iii}–N(1) 84.96(10)
N(4)–C(11) 1.276(4)	O(3)–Ag(1)^{iii}–N(2) 105.06(10)
N(5)–C(5) 1.265(4)	O(3)–Ag(1)^{iii}–N(3) 90.74(10)
Ag(1)–N(1) 2.335(3)	O(3)–Ag(1)–N(4)^{iii} 155.16(10)
Ag(1)–N(2) 2.402(3)	N(1)–Ag(1)–N(2) 96.05(9)
Ag(1)–N(3) 2.329(2)	N(1)–Ag(1)–N(3) 148.57(9)
Ag(1)–N(4)^{iii} 2.503(3)	N(1)–Ag(1)–N(4)^{iii} 107.15(9)
Ag(1)–O(3) 2.666(3)	N(2)–Ag(1)–N(3) 115.07(9)
S(1)–O(1) 1.392(4)	N(2)–Ag(1)–N(4)^{iii} 95.34(9)
S(1)–O(2) 1.418(4)	N(3)–Ag(1)–N(4)^{iii} 67.48(8)
S(1)–O(3) 1.409(3)	Ag(1)^{iii}–O(3)–S(1) 127.0(2)
N(1)–C(7) 1.339(4)	C(2)–N(6)–C(3) 115.8(3)
C(7)–C(10)^i 1.393(4)	N(3)–C(9)–C(8)^{ii} 122.0(3)
N(2)–C(1) 1.327(4)	C(9)–N(3)–C(10) 117.0(3)
N(2)–C(4) 1.336(4)	C(2)–N(6)–C(3) 115.8(3)
N(3)–C(9) 1.335(4)	N(3)–C(10)–C(11)^{iii} 118.8(3)
N(3)–C(10) 1.337(3)	N(5)–C(5)–C(6) 125.9(3)
N(6)–C(2) 1.336(5)	N(4)–C(11)–C(10)^{iii} 115.5(3)
C(10)–C(7)^{ii} 1.393(4)	C(10)^{iii}–C(11)–C(12) 119.1(3)
N(7)–C(13) 1.120(7)	O(3)–S(1)–O(1) 117.0(3)
C(9)–C(8)^{ii} 1.381(4)	N(1)–C(7)–C(10)^i 122.2(3)

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

Table 3 Hydrogen-bonding geometries for **1**

D–H⋯A	H⋯A (Å)	D⋯A (Å)	D–H⋯A (°)
C(4)–H(4)⋯O(1)	2.540	3.328(6)	143.00
C(6)–H(6A)⋯N(6)^i	2.440	2.815(6)	103.00
C(6)–H(6B)⋯O(2)^{ii}	2.560	3.385(6)	144.00
C(8)–H(8)⋯O(3)	2.480	3.198(5)	134.00
C(9)–H(9)⋯O(2)	2.460	3.311(5)	152.00
C(12)–H(12A)⋯N(5)	2.400	2.814(5)	105.00
C(12)–H(12A)⋯N(7)	2.610	3.512(6)	157.00
C(14)–H(14C)⋯O(1)^{iii}	2.390	3.241(8)	148.00

Symmetry codes: (i) $1 - x, 2 - y, 1 - z$; (ii) $-x, 2 - y, -z$; (iii) $1 - x, 1 - y, -z$

transfer (LMCT). The bathocromic shift in the emission spectrum of **1** compare to **4** [3] indicates that the luminescent property of the free ligand is significantly affected by the counter anions and binding modes of **PMK** in the silver(I) coordination polymers adopting specific geometries or network patterns in the solid state.

The ESI-MS spectrum of **1** (Fig. S4) reveals the presence of number of architectures in solution [14]. The peaks at m/z = 538.3, 605.8, 1177.0, 1425.0, 1694.5 and 1946.5 are observed corresponding to [Ag(**PMK**)(OTf)(MeCN)]$^+$, [Ag$_4$(**PMK**)$_2$(OTf)$_2$]$^{2+}$, [Ag$_5$(**PMK**)$_5$(OTf)$_3$(MeCN)$_4$]$^{2+}$, [Ag$_6$(**PMK**)$_6$(OTf)$_4$(MeCN)$_4$]$^{2+}$, [Ag$_7$(**PMK**)$_7$(OTf)$_5$(MeCN)$_5$]$^{2+}$ and [Ag$_8$(**PMK**)$_7$(OTf)$_6$(MeCN)$_{11}$]$^{2+}$, respectively

showing the supramolecular self-assembly of **PMK** with AgOTf in solution.

The FTIR spectral data for **1** and the free ligand can be easily compared (Fig.S5). The most characteristic bands in **1** are those aroused by the triflate anion. The observed bands at 1270, 1250, 1223, and 1029 cm^{-1} can be assigned to the monodentate coordination modes of the triflate anion [16].

In the present system, the coordination polymer (**1**) constructed by AgCF$_3$SO$_3$ and multimodal ligand (**PMK**) shows that the coordination modes of the ligand along with the coordination geometry around the silver(I) ion, and the

network pattern of the silver coordination polymer are distinctly different than those previously reported which nicely reflects the effect of the coordinated anion on the network formation and the significantly different solid state fluorescence spectrum of **1**.

References

1. Robson R (1996) In: Atwood JL, Eric J, Davies D, MacNicol DD, Lehn JM (eds) Comprehensive supramolecular chemistry. Pergamon Press, Oxford
2. Oxtoby NS, Blake AJ, Champness NR, Wilson C (2003) Dalton Trans 3838–3839
3. Dong YB, Zhao X, Tang B, Wang HY, Huang RQ, Smith MD, Zur-Loye HC (2004) Chem Commun 220–221
4. Pascu M, Tuna F, Kolodziejczyk E, Pascu GI, Clarkson G, Hannon MJ (2004) Dalton Trans 1546–1555
5. Munakata M, Wu LP, Kuroda-Sowa T, Maekawa M, Moriwaki K, Kitagawa S (1997) Inorg Chem 36:5416–5418
6. Carlucci L, Ciani G, Gudenberg DW, Prosperpio DM, Siraoni A (1997) Chem Commun 631–632
7. Sengul A, Karadayi N, Buyukgungor O (2004) Acta Crystallogr C60:507–508
8. Sheldrick GM (1997) SHELXS-97: program for the solution of crystal structures. University of Gottingen, Germany
9. Sheldrick GM (1997) SHELXL-97: program for refinement of crystal structures. University of Gottingen, Germany
10. Stoe & Cie (2002) X-AREA (version 1.18) and X-RED32 (version 1.04). Stoe&Cie, Darmstadt
11. Farrugia LJ (1997) J Appl Crystallogr 30:565–566
12. Farrugia LJ (1999) J Appl Crystallogr 32:837–838
13. Edgington PR, McCabe P, Macrae CF, Pidcock E, Shields GP, Taylor R, Towler M, Van de Streek J (2006) J Appl Crystallogr 39:453–457
14. Hamblin J, Jackson A, Alcock NW, Hannon MJ (2002) J Chem Soc Dalton Trans 1635–1641
15. Hanton LR, Lee K (2000) J Chem Soc Dalton Trans 1161–1166
16. Haynes JS, Rettig SJ, Sams JR, Trotter J, Thompson RC (1988) Inorg Chem 27:1237–1241