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Dipyrazinyl Sulfoxide Complexes of Silver(I), Zinc(II), and Cadmium(II): Ligation Modes and Anion Tuning

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The new ligand dipyrazinyl sulfoxide (also named sulfinyldipyrazine and abbreviated as pyz_2SO) and a series of its metal complexes including $\{[Ag(pyz_2SO)](NO_3)\cdot CH_3CN\}_\infty$ (**1**), $\{[Ag(pyz_2SO)](PF_6)\}_\infty$ (**2**), $[Ag_3(pyz_2SO)_2(ClO_4)_3]_\infty$ (**3**), $[Ag(pyz_2SO)(CF_3CO_2)]_\infty$ (**4**), $\{[Zn(pyz_2SO)(H_2O)_4](NO_3)_2\cdot H_2O\}_\infty$ (**5**), $\{[Zn(pyz_2SO)(H_2O)_2](ClO_4)_2\}_\infty$ (**6**), and $\{[Cd(pyz_2SO)_2(H_2O)](ClO_4)_2\cdot H_2O\}_\infty$ (**7**) have been synthesized and characterized by single-crystal X-ray analysis. The counteranions in these complexes prefer to be embraced by a pair of π-acidic heterocyclic rings via anion$-\pi$ interactions, which consequently affect the process of supramolecular assembly. Seven distinct ligation modes of pyz_2SO involving various bonding combinations of the sulfoxide oxygen and/or pyrazinyl nitrogen atoms (labeled **A**−**G**) are observed. Diverse coordination motifs such as (4,4) network, ladder-type, necklace-like, linear, and zigzag-chain structures are found in **1**−**7**. Interestingly, the sulfoxide group of the pyz_2SO ligand exhibits unusual dipolar sulfinyl···sulfinyl and S=O···π(pyrazinyl) intermolecular interactions in the supramolecular assemblies of neat pyz_2SO, **1**, and **3**−**5**.

Introduction

The study of metal complexes bearing sulfoxide ligands has undergone phenomenal development since the early 1960s.[1] By virtue of its coordination sites at the sulfur and/or oxygen atoms, the C−S(O)−C fragment (with C_s local symmetry) in various symmetrical and unsymmetrical dialkyl sulfoxide ligands exhibits diverse coordination geometries in accordance with different electronic and steric demands.[2,3] Recent interest in chiral sulfoxide ligands stemmed from stereochemical consequences arising from the configuration of the R−S*-(O)−R′ group.[4] A wide range of such studies focused on their biological activity[4b−e] and synthetic applications in asymmetric synthesis,[5a−d] as well as their behavior as intermediates in homogeneous catalytic processes[5e−k] or versatile precursors in inorganic synthesis.[6] However, the use of sulfoxide as an efficient ligand to construct coordination networks remains almost unexplored. So far several well-characterized complexes of diphenyl sulfoxide (L) have been reported, such as $HgCl_2(L)$,[7] $[Et_4N][PtCl_3(L)]$,[8] and $K[PtCl_3(L)]\cdot Me_2CO$.[9]

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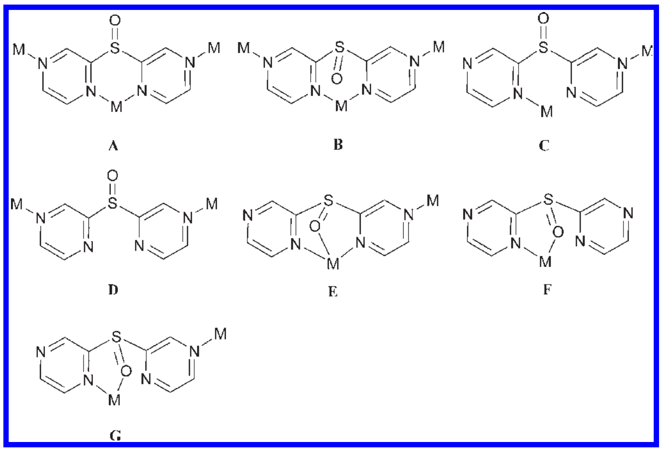
Scheme 1. Ligation Modes of Dipyrazinyl Sulfoxide (pyz_2SO) in This Study



In the present context, we report the ligand behavior of a new diheterocyclic sulfoxide ligand that contains a pair of pyrazinyl rings, namely, sulfinyldipyrazine or dipyrazinyl sulfoxide (pyz_2SO), wherein one or both nitrogen ligation site(s) at each heteroaromatic ring may exhibit diverse coordination modes to generate supramolecular networks. Furthermore, the π-acidic pyrazinyl rings could in principle engage in anion−π(pyrazinyl) interaction[10] for supramolecular assembly. We herein report the synthesis of the multidentate *N,O*-ligand pyz_2SO and a series of its group 11 and 12 metal complexes, namely, $\{[Ag(pyz_2SO)](NO_3)\cdot CH_3CN\}_\infty$ (**1**), $\{[Ag(pyz_2SO)](PF_6)\}_\infty$ (**2**), $[Ag_3(pyz_2SO)_2(ClO_4)_3]_\infty$ (**3**), $[Ag(pyz_2SO)(CF_3CO_2)]_\infty$ (**4**), $\{[Zn(pyz_2SO)(H_2O)_4](NO_3)_2\cdot H_2O\}_\infty$ (**5**), $\{[Zn(pyz_2SO)(H_2O)_2](ClO_4)_2\}_\infty$ (**6**), and $\{[Cd(pyz_2SO)_2(H_2O)](ClO_4)_2\cdot H_2O\}_\infty$ (**7**), which were characterized by X-ray diffraction, IR spectroscopy, and elemental analysis. Through the subtle tuning of anions and metal ions, pyz_2SO has been shown to exhibit versatile ligation modes (**A**−**G**, Scheme 1), thus leading to diverse extended structural motifs. Consequently, several high-dimensional supramolecular architectures stabilized by sulfinyl···π(pyrazinyl) and anion···π(pyrazinyl) interactions, as well as interesting dipolar sulfinyl···sulfinyl interaction, have been obtained.

Experimental Section

Materials and Methods. All organic reagents were purchased from Aldrich and used without further purification. The silver(I) salts, $Zn(NO_3)_2\cdot 6H_2O$, $Zn(ClO_4)_2\cdot 6H_2O$, and $Cd(ClO_4)_2\cdot 6H_2O$ were obtained from commercial sources. Elemental analyses of C, H, and N were performed by the MEDAC Ltd. Brunel Science Centre, United Kingdom. IR spectra were recorded by a Nicolet Impact 420 FT-IR spectrometer using KBr pellets. ^1H NMR spectra were taken with a 300 MHz Bruker spectrometer.

Caution! *In view of the explosive nature of perchlorate complexes, small amounts of them should be used and handed with extreme care.*

Synthesis of Dipyrazinyl Sulfoxide (pyz_2SO). A solution of 3-chlorobenzoperoxoic acid (72% *m*-CPMA, 748 mg, 3.22 mmol) in 15 mL of CH_2Cl_2 was added to a 10 mL CH_2Cl_2 solution of bis-2-pyrazinylsulfide (624 mg, 3.28 mmol) cooled to 0 °C. After stirring for 1.5 h at 0 °C, the organic phase was treated with 40 mL of saturated $Na_2S_2O_3$ solution, saturated $NaHCO_3$ solution (40 mL), and brine (20 mL) and dried over $MgSO_4$. The combined organic extract was concentrated to give a white solid. The product was further purified by column chromatography on silica gel using ethyl acetate/CH_2Cl_2 (3:2) as eluent. Dipyrazinyl sulfoxide (pyz_2SO) was obtained as a white powder (439 mg). Yield: 65%, mp 117−121 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 9.42 (s, 2H), 8.77−8.78 (d, J = 3 Hz, 2H), 8.55−8.57 (d, J = 6 Hz, 2H). Anal. Calcd (Found) for $C_8H_6N_4SO$: C, 46.59 (46.61); H, 2.93 (3.14); N, 27.16 (27.05). IR (KBr) ν/cm^{-1}: 1066 (vs), 1021(s), (S═O).

Synthesis of $\{[Ag(pyz_2SO)](NO_3)\cdot CH_3CN\}_\infty$ (1). Dipyrazinyl sulfoxide (21 mg, 0.1 mmol) and $AgNO_3$ (17 mg, 0.1 mmol) were dissolved in a mixed solvent of 2 mL of methanol and 2 mL of acetonitrile with stirring at room temperature. The colorless solution was filtered and then left to stand in air. After five days, colorless block-like crystals of **1** were deposited. Yield: 25.8 mg (62%). Anal. Calcd (Found) for $C_{10}H_9N_6O_4SAg$: C, 28.79 (28.55); H, 2.17 (2.56); N, 20.15 (19.88). IR (KBr) ν/cm^{-1}: 3074(w), 2374(m), 1390(vs), 1405(w), 1164(w), 1060 (vs), 1010(s), 873(w), 833(w), 756(w), 620(w), 555(m).

Synthesis of $\{[Ag(pyz_2SO)](PF_6)\}_\infty$ (2). Dipyrazinyl sulfoxide (21 mg, 0.1 mmol) and $AgPF_6$ (26 mg, 0.1 mmol) were dissolved in a mixed solvent of 2 mL of methanol and 2 mL of acetonitrile with stirring. After filtration, the clear solution was allowed to stand in air for a few days to give yellow crystals of **2**. Yield: 27.5 mg (60%). Anal. Calcd (Found) for $C_8H_6N_4OF_6SPAg$: C, 20.98 (21.40); H, 1.32 (1.30); N, 12.20 (12.04). IR (KBr) ν/cm^{-1}: 3067(w), 2374(m), 1461(w), 1403 (m), 1170(w), 1060(s), 1028(s), 853(vs), 555(m), 490(w).

Synthesis of $[Ag_3(pyz_2SO)_2(ClO_4)_3]_\infty$ (3). Yellow block-like crystals of **3** were obtained using the same method as for **1** and **2**. Dipyrazinyl sulfoxide (21 mg, 0.1 mmol), $AgClO_4\cdot nH_2O$ (30 mg). Yield: 28.3 mg (55%). Anal. Calcd (Found) for $C_{16}H_{12}N_8O_{14}S_2Cl_3Ag_3$: C, 18.58 (18.34); H, 1.17 (1.26); N, 10.86 (10.57). IR (KBr) ν/cm^{-1}: 1445(w), 1397(m), 1099(vs), 1019(m), 859(w), 762(w), 630(m), 561(w).

Synthesis of $[Ag(pyz_2SO)(CF_3CO_2)]_\infty$ (4). Colorless block-like crystals of **4** were deposited using the same method as for **1** after a few days. Dipyrazinyl sulfoxide (21 mg, 0.1 mmol), $AgCF_3CO_2$ (22 mg, 0.1 mmol). Yield: 21.9 mg (51%). Anal. Calcd (Found) for $C_{10}H_6N_4O_3F_3SAg$: C, 28.12 (27.94); H, 1.42 (1.50); N, 13.11 (13.04). IR (KBr) ν/cm^{-1}: 1694(vs), 1468(m), 1397(m), 1209(vs), 1131(vs), 1060(m), 1021(m), 840(m), 807(m), 723(m), 626(w), 548(w), 477(m).

Synthesis of $\{[Zn(pyz_2SO)(H_2O)_4](NO_3)_2\cdot H_2O\}_\infty$ (5). Dipyrazinyl sulfoxide (21 mg, 0.1 mmol) and $Zn(NO_3)_2\cdot 6H_2O$ (30 mg, 0.1 mmol) were dissolved in a mixed solvent of 3 mL of acetonitrile and 1 mL of methanol with stirring at room temperature for 3 h. Slow evaporation of the filtrate gave colorless crystals of **5**. Yield: 26.57 mg (55%). Anal. Calcd (Found) for $C_8H_{16}N_6O_{12}SZn$: C, 19.84 (19.64); H, 3.33 (3.26); N, 17.36 (17.57). IR (KBr) ν/cm^{-1}: 3524(vs), 3104(w), 1626(m), 1384(vs), 1167(w), 1121(w), 1060(s), 1015(s), 865(w), 825(m), 749(w), 648(w), 611(w), 542(w).

Synthesis of $\{[Zn(pyz_2SO)(H_2O)_2](ClO_4)_2\}_\infty$ (6). Dipyrazinyl sulfoxide (21 mg, 0.1 mmol) was dissolved in 3 mL of actonitrile and then added to a 2 mL solution of $Zn(ClO_4)_2\cdot 6H_2O$ (38 mg, 0.1 mmol) in water with stirring. After filtration, the clear solution was left to slowly evaporate in air. Colorless crystals of **6** were obtained. Yield: 30.68 mg (61%). Anal. Calcd (Found)

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Table 1. Crystallographic Data of pyz$_2$SO and **1**−**7**

	pyz$_2$SO	**1**	**2**	**3**	**4**	**5**	**6**	**7**
empirical formula	$C_8H_6N_4OS$	$C_{10}H_9N_6O_4SAg$	$C_8H_6F_6N_4OPSAg$	$C_8H_6N_4O_7SCl_{1.5}Ag_{1.5}$	$C_{10}H_6F_3N_4O_3SAg$	$C_8H_{16}N_6O_{12}SZn$	$C_8H_{10}N_4O_{11}SCl_2Zn$	$C_{16}H_{16}N_8O_{12}S_2Cl_2Cd$
fw	206.23	417.16	459.07	517.21	427.12	485.70	506.53	759.77
cryst syst	triclinic	monoclinic	monoclinic	orthorhombic	monoclinic	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	Cm	$Pnma$	$C2/c$	$P\bar{1}$	$P2_1/n$	$P2_1/c$
a (Å)	5.869(1)	7.632(1)	11.077(2)	7.956(3)	12.609(1)	7.965(3)	7.677(4)	8.227(2)
b (Å)	7.445(1)	23.598(3)	10.226(2)	25.251(1)	9.923(1)	8.272(3)	14.166(8)	31.605(9)
c (Å)	11.101(2)	7.672(1)	6.020(9)	14.359(6)	21.372(2)	14.048(5)	15.577(8)	10.388(3)
α (deg)	76.989(3)	90	90	90	90	85.827(1)	90	90
β (deg)	85.121(4)	96.633(2)	112.153(3)	90	95.378(2)	75.428(1)	91.186(1)	106.453(5)
γ (deg)	72.163(3)	90	90	90	90	81.342(1)	90	90
V (Å^3)	449.78(1)	1372.5(3)	631.57(1)	2884.8(2)	2662.4(5)	885.01(6)	1693.64(2)	2590.4(1)
Z	2	4	2	8	8	2	4	4
D_{calc} (g/cm^3)	1.523	2.019	2.414	2.382	2.131	1.823	1.987	1.943
μ(Mo Kα) (mm^{-1})	0.328	1.650	1.969	2.521	1.725	1.582	1.956	1.288
R_1 [$I > 2\sigma(I)$][a]	0.0400	0.0372	0.0214	0.0410	0.0405	0.0268	0.0521	0.0477
wR_2 (all data)[b]	0.1077	0.0901	0.0513	0.1074	0.1078	0.0797	0.1552	0.1461
goodness-of-fit	1.023	1.121	1.071	1.061	1.043	1.092	1.051	0.997

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

for $C_8H_{10}Cl_2N_4O_{11}SZn$: C, 19.05 (19.33); H, 2.00 (2.21); N, 11.12 (11.33). IR (KBr) ν/cm^{-1}: 3462(m), 1656(w), 1410(m), 1105(vs), 1010(m), 866(w), 762(w), 633(s), 568(w), 464(w).

Synthesis of $\{[Cd(pyz_2SO)_2(H_2O)](ClO_4)_2\cdot H_2O\}_\infty$ (7). This compound is obtained by a similar procedure to that for **6**. Dipyrazinyl sulfoxide (21 mg, 0.1 mmol), $Cd(ClO_4)_2\cdot 6H_2O$ (39 mg, 0.1 mmol). Yield: 22.4 mg (58%). Anal. Calcd (Found) for $C_{16}H_{16}Cl_2N_8O_{12}S_2Cd$: C, 25.27 (25.64); H, 2.12 (2.20); N, 14.74 (14.57). IR (KBr) ν/cm^{-1}: 3545(m), 1621(m), 1455(w), 1397(m), 1291(w), 1113(vs), 1013(m), 940(w), 849(w), 750(w), 627(s), 546(w).

X-ray Crystallographic Studies. Single-crystal X-ray diffraction data of complex **5** was collected on a Kappa APEX II CCD diffractometer operating at 50 kV and 30 mA using Mo Kα radiation (λ = 0.71073 Å) at 293 K. All the others were collected on a Bruker Smart 1000 CCD diffractometer. Data reduction was performed using the SMART and SAINT software.[11] An empirical absorption correction was applied using the SADABS program.[12] All structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL program package.[13] The ordered atoms in each structure were refined with anisotropic displacement parameters, while the hydrogen atoms were placed in idealized positions and allowed to ride on the relevant carbon atoms. All positions of the hydrogen atoms of the water molecules in **5** and **6** were obtained from Fourier-difference maps. In complex **7**, the O2W is disordered at two positions with ratio of 0.8:0.2; thus the hydrogen atoms were not added and not included in the final refinement. Both O3 and O4 exhibit 2-fold positional disorder with the ratio of 0.6:0.4, respectively. O7 is disordered at two positions with the ratio of 0.7:0.3. The crystallographic data are listed in Table 1. CCDC 720518 (**5**), 720519 (**6**), 720520 (**3**), 720521 (**1**), 720522 (**2**), 720523 (**4**), 720524 (**7**), and 720525 (pyz$_2$SO) contain the supplementary crystal data for pyz$_2$SO and **1** to **7**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

The pyz$_2$SO Ligand. Single-crystal X-ray crystallographic analysis of dipyrazinyl sulfoxide (pyz$_2$SO) revealed that the C(sp^2)−S−C(sp^2) angle is 95.09(1)°, suggesting that pyz$_2$SO can be utilized as an effective corner linker for supramolecular assembly. The S=O bond length of 1.487(2) Å is comparable to the average value of 1.49 Å found in free alkyl sulfoxides.[2a] The IR spectrum shows a S=O stretching frequency at 1066 cm^{-1} and a shoulder band at 1021 cm^{-1}, resembling the IR spectrum of free DMSO (1055 cm^{-1}).[2a] The S−C(sp^2) bond distances (1.810(2) and 1.816(2) Å) lie within the statistical analysis range of 1.75−1.84 Å summarized by Calligaris.[2b] Notably, in the crystal structure of pyz$_2$SO, a pair of parallel S=O moieties (head-to-tail fashion) of two pyz$_2$SO molecules exhibit a dipolar sulfinyl···sulfinyl interaction with a S···O distance of 2.962(2) Å (Figure 1), which is shorter than the sum of van der Waals radii (3.30 Å).[14] Such an intermolecular sulfinyl···sulfinyl interaction is seldom reported in the literature.[15] A recent investigation of three types of sulfoxides with alkyl−alkyl, alkyl−aryl, and aryl−aryl arms by Fuller et al. revealed S···O distances ranging from 3.57 to 4.37 Å in the sulfinyl···sulfinyl contacts,[15a] which are much longer than those observed in the present case. This can be rationalized by the fact that the electron-deficient pyrazinyl rings of pyz$_2$SO significantly increase the net

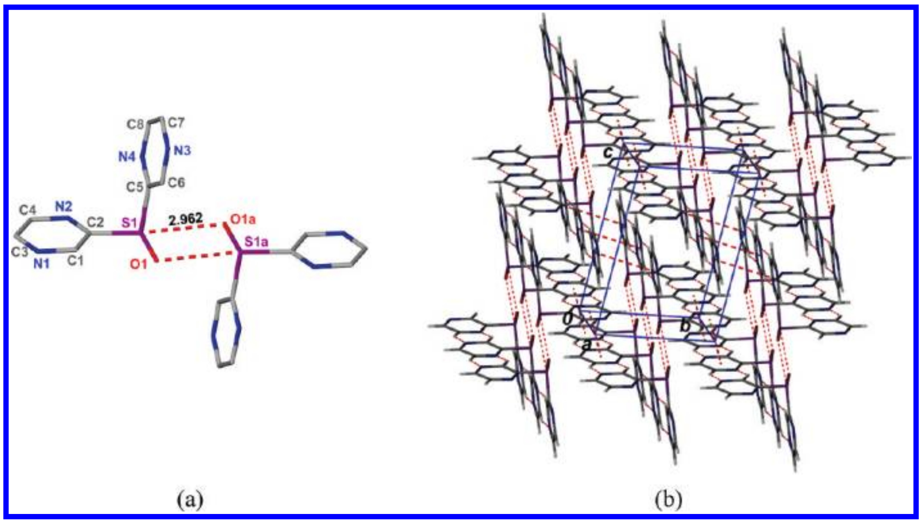

Figure 1. (a) Intermolecular sulfinyl···sulfinyl interactions in the crystal structure of dipyrazinyl sulfoxide (pyz_2SO). Symmetry code: a $-x + 1, -y + 1, -z + 2$. (b) Stacking diagram of the pyz_2SO molecules. The thick red, dashed lines represent $\pi \cdots \pi$ interactions.

positive charge localized on the sulfur atom. Further structural analysis revealed that the pyz_2SO molecules are arranged along the *a* axis in a head-to-tail fashion, and adjacent molecules interconnect via two pairs of complementary C−H···N hydrogen bonds (C1a−H1Aa···N2: 2.694(3) Å, 146(3)°; C3−H3A···N1a: 2.707(3) Å, 146(3)°; C8−H8A···N3a: 2.721(4) Å, 145(3)°; C6a−H6Aa···N4: 2.731(2) Å, 143(1)°. a: $x + 1, y, z$), leading to an infinite chain (Figure 1b). Sulfinyl···sulfinyl and $\pi \cdots \pi$ stacking (centroid···centroid 3.982, 4.037 Å) interactions occur between the formed chain structures parallel to the *a* axis, engendering a three-dimensional framework.

Anion-Tuning Effect in Complexes 1 to 4. Recent studies indicated that various anions are capable of playing an important role in the construction of supramolecular architectures.[16] The anion-controlled self-assembly by use of the interesting anion−π interaction has been reported in several literature sources.[10] Although silver complexes $\{[Ag(pyz_2SO)](NO_3)\cdot CH_3CN\}_\infty$ (**1**), $\{[Ag(pyz_2SO)](PF_6)\}_\infty$ (**2**), $[Ag_3(pyz_2SO)_2(ClO_4)_3]_\infty$ (**3**), and $[Ag(pyz_2SO)(CF_3CO_2)]_\infty$ (**4**) were obtained by similar synthetic procedures, different resulting coordination architectures, such as a (4,4) network in **1** and **2**, a necklace-like assembly in **3**, and a ladder-type structure in **4**, were achieved by employing different counteranions. The two pyrazinyl rings of the clamp-like pyz_2SO ligand favorably embrace the respective anion via an anion−π interaction, whereas variation of the geometry and bulk of the coexisting anion affects the molecular dimension of pyz_2SO, thus leading to diverse supramolecular assemblies.

$\{[\mathbf{Ag(pyz_2SO)](NO_3)\cdot CH_3CN}\}_\infty$ (**1**). In the crystal structure of complex **1**, the pyz_2SO ligand adopts a μ_3-bridging mode **A** with two 1-positional N atoms and the S=O group (S=O at 1.491(2) Å) arranged in an *anti*-mode (Scheme 1). Each Ag(I) is surrounded by three pyz_2SO ligands in a square-planar coordination geometry and further coordinated by one acetonitrile molecule and one nitrate anion at axial positions (CH_3CN: N6a···Ag1 2.783(5) Å, a: $-x + 1, -y + 1, -z$; NO_3^-: O2···Ag1 2.603(4) Å).[17] The pyz_2SO ligands bond to the metal center at the equatorial positions through two 1-positional N atoms and two 4-positional N atoms, generating a (4,4) network with the four-coordinated Ag(I) as nodes and pyrazinyl rings as linkers (Figure 2a). It is noteworthy that all the sulfinyl (S=O) groups of pyz_2SO are oriented on the same side of the (4,4) network, where acetonitrile molecules are located, whereas the nitrate anions are arranged on the other side. Therefore, the layer structure has two different surfaces (Figure 3a).

In this way, the layers are stacked in a A−B···B−A mode (face-to-face) to generate a three-dimensional framework with interlayer separations of 5.52 and 6.68 Å, respectively (Figure 3a), wherein adjacent layers are interconnected and alternatively stabilized by sulfinyl···sulfinyl and anion−π interactions. Each pair of parallel S=O groups interact in a head-to-tail fashion with an S···O contact of 3.014(3) Å. The interaction mode is the same as that in the crystalline form of pyz_2SO. As shown in Figure 4a, one oxygen atom, O4, of nitrate is embraced by the pyrazinyl rings of pyz_2SO at the metallocycle corner of the (4,4) network with $O\cdots pyz_{centroid}$ distances of 3.13 and 3.39 Å, which are comparable to the

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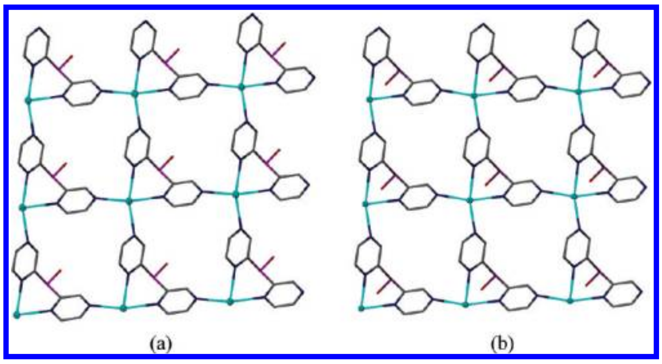

Figure 2. The (4,4) coordination network in (a) {[Ag(pyz$_2$SO)](NO$_3$)·CH$_3$CN}$_\infty$ (**1**) and (b) {[Ag(pyz$_2$SO)](PF$_6$)}$_\infty$ (**2**).

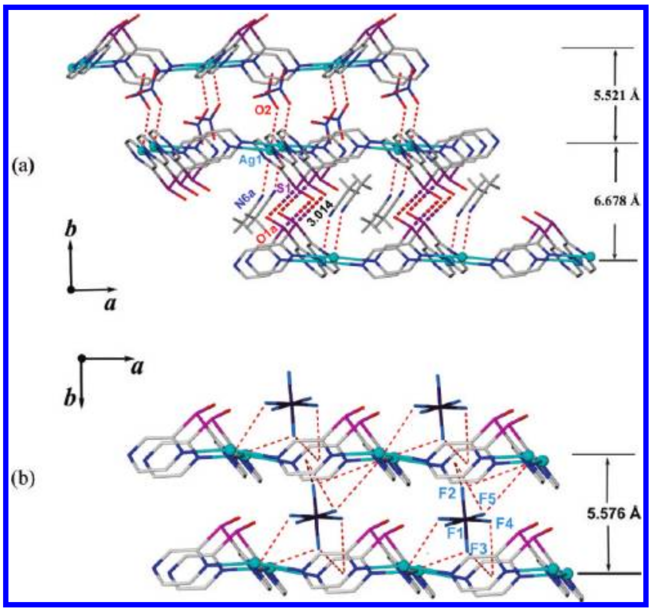

Figure 3. (a) Stacked structure of **1**. The thick dashed lines represent sulfinyl···sulfinyl interactions, while anion−π interactions are omitted for clarity. Symmetry code: a $-x + 1, -y + 1, -z$. (b) Anion−π interaction bridging stacked layers in **2**.

reported nitrate···pyrazine interactions in {Ni[bis(2-pyrazylmethyl)sulfide](NO$_3$)$_2$}$_\infty$,[18a] but slightly longer than the nitrate···π(triazine) interactions involving the 1,3,5-triazine ring in Zn(dipicatriz)(NO$_3$)$_2$ and [Cu$_3$(dipicatriz)(NO$_3$)(H$_2$O)$_6$](NO$_3$) (dipicatriz = 2,4,6-tris-(di-2-picolylamina)[1,3,5]-triazine)[18b] due to the less π-acidic nature of the pyrazine ring. The observed contacts are also in good agreement with the results of a CSD survey study [O(nitrate)···pyz$_{\mathrm{centroid}}$ mean 3.10 Å].[10f] The distances O···C/N(ring atoms) range from 3.263(5) to 3.806(6) Å, and the angle φ of the O···π axis to the pyrazinyl plane lies within the range 80.9−84.8°. The detailed anion−π interaction geometries are listed in Table 3.

{[**Ag(pyz$_2$SO)**](**PF$_6$**)}$_\infty$ (**2**). In the crystal structure of complex **2**, a (4,4) coordination network similar to that of **1** is obtained, as shown in Figure 2b. Another kind of μ_3-bridging pyz$_2$SO ligand with two 1-positional N atoms and the S=O group in the *syn*-mode exists in **2**. The sulfoxide oxygen chelates a silver atom via weak O···Ag bonding, which combines with the 1-pyrazinyl N atoms to generate a new μ_3-bridging ligation mode, **B** (Scheme 1). The S=O bond length of 1.502(4) Å is slightly longer than those in free pyz$_2$SO (1.487(2) Å) and complex **1** (1.491(2) Å), which can be attributed to the weak sulfoxide O···Ag interaction (O1a···Ag1 2.646(4) Å, a: $x + 1/2, y - 1/2, z$). The increase in S=O bond length is commonly found in the protonated and η^1-O coordinated alkyl sulfoxides due to the reducing bond order.[2a,b] The detailed molecular dimensions are listed in Table 2.

As compared with complex **1**, the formed layers in **2** are stacked in a A−B···A−B (face-to-back) mode with the bulky hexafluorophosphate residing between adjacent layers, as shown in Figure 3b, wherein the S=O groups are oriented on the same side of the (4,4) network. This face-to-back stacking mode excludes the occurrence of a sulfinyl···sulfinyl interaction in **2**. Each PF$_6^-$ anion is embraced by the wings of pyz$_2$SO and located at one metallocycle corner of the (4,4) network through anion-(F)−π(pyrazinyl) interactions, in which two fluorine atoms interact with the lower layer and three other F atoms approach the pyrazinyl rings of the opposite above layer (Figures 3b, 4b). The F···pyz$_{\mathrm{centroid}}$ distances vary from 3.23 to 3.53 Å, being comparable with the reported value of anion(F)−pyrazinyl interactions in a CSD study [F(PF$_6^-$)···pyz$_{\mathrm{centroid}}$ mean 3.10 Å].[10f] Distances F···C/N(ring atoms) range from 3.115(5) to 3.864(6) Å, and detailed anion−π contact geometries are listed in Table 3 for comparison.

The different conformations of the pyz$_2$SO ligand and stacking modes of the resulting (4,4) net layers in **1** and **2** may be ascribed to the steric effect of anions. In complex **2**, the bulky PF$_6^-$ with weak coordination ability leads to a further separation from the Ag(I) center, thus forming the face-to-back stacking rather than the face-to-face stacking mode in **1**. However, the interlayer distance of 5.576 Å in **2** is only slightly longer than that of 5.521 Å in **1**, which implies that the bulky PF$_6^-$ anions in **2** are effectively buried within the cavities via multiple anion−π interactions. For the pyz$_2$SO dimension, the angle of C(sp^2)−S−C(sp^2) in **2** is 95.01(2)°, being almost equal to that of 95.29(1)° in **1**. The molecular dimensions of pyz$_2$SO are listed in Table 2 for comparison, and Figure 4b illustrates the interactions between anion and metallocycle via anion−π interactions.

[**Ag$_3$(pyz$_2$SO)$_2$(ClO$_4$)$_3$**]$_\infty$ (**3**). Although the pyz$_2$SO coordination mode **A** found in **1** also exists in the crystal structure of **3** (Figure 5), a different bonding environment of the silver centers results in an infinite chain structure. The two independent Ag(I) ions in the asymmetric unit (Ag1 and Ag2) exhibit different coordination environments. Ag1 lies on a crystallographic 2-axis, being surrounded by a pair of chelating pyz$_2$SO ligands employing their 1-pyrazinyl N atoms and one weakly chelating perchlorate (Cl2-type) at an O8···Ag1 distance of 2.830(8) Å. Ag2 is surrounded by two 4-pyrazinyl N atoms belonging to separate pyz$_2$SO ligands and four oxygen atoms from three perchlorates: one perchlorate (Cl1-type) binds to it at a Ag2−O4 bond length of 2.554(5) Å, while the other two (Cl2-type) exhibit much weaker connections involving oxygen atoms O2d, O4d, and O5b at 2.729(6), 2.712(5), and 2.843(5) Å,

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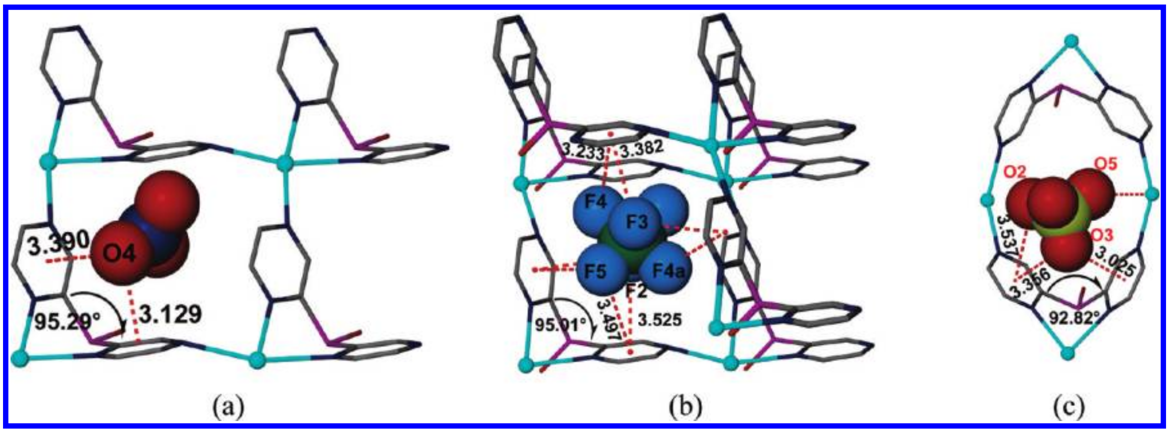
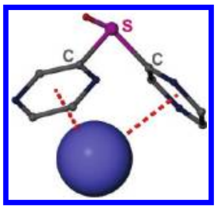


Figure 4. Illustrations of different anions residing within the metallocycles of **1** (a), **2** (b), and **3** (c) and structural details of the anion−π interaction in each case. Symmetry code in (b): a x, $-y$, z.

Table 2. Ligation Modes, Anion−π Interactions, and Molecular Dimensions of pyz$_2$SO and Its Metal Complexes



compound	ligation mode	S=O with respect to 1-prazinyl N atoms	S=O bond length (Å)	C−S−C angle (deg)	anion−π interaction	anion embraced by Pyz$_2$SO
pyz$_2$SO		*anti*	1.487(2)	95.09(1)		
1	**A**	*anti*	1.491(2)	95.29(1)	yes	yes
2	**B**	*cis*	1.502(4)	95.01(2)	yes	yes
3	**A**	*anti*	1.480(3)	92.82(2)	yes	yes
4	**C**	*anti*	1.486(3)	94.71(2)	yes	no
5	**D**	*cis*	1.484(1)	96.57(8)	no	
6	**E**	*cis*	1.512(2)	94.95(2)	yes	yes
7	**F** and **G**	*cis*	1.496(3)	94.1(2)	yes	yes
		cis	1.501(3)	92.5(2)	yes	yes

respectively (Figure 5a). Successive Ag1 nodes and pairs of Ag2 atoms are linked by a pair of μ_3-bridging pyz$_2$SO ligands to form a necklace-like infinite chain.

Further scrutiny reveals that the ClO_4^- anion plays a key role in forming the necklace-like infinite chain in **3**. The perchlorate anion has a weaker coordination ability with respect to nitrate[19] (in **1**) and less bulk compared with pentafluorophosphate (in **2**). As shown in Figure 5b, the Cl1-type perchlorate is bound to the Ag2 center of a vicinal chain and interacts with two pyrazinly rings of one pyz$_2$SO ligand via O(perchlorate)···π interactions (O2b···pyz$_{centroid}$ 3.537 Å, O3b···pyz$_{centroid}$ 3.356/3.025 Å; symmetry code: b $-x$, $-y+1$, $-z+1$), while the third oxygen atom (O5b) of the Cl1-type perchlorate weakly binds to silver atom Ag2 within a metallocycle. Such multiple driving forces with the perchlorates lead to the smaller pyz$_2$SO C(sp^2)−S−C(sp^2) angle of 92.82(2)° in **3**, in contrast to the angle of 95.09(1)° in free pyz$_2$SO, 95.29(1)° in **1** and 95.01(2)° in **2** (Figure 4c). Consequently, a necklace-like chain structure comprising small metallocycles is formed in **3**, rather than the larger square one in the (4,4) network of **1**, in which just one O atom of the nitrate ion is involved in an anion−π interaction (Figure 4). In Table 2, the molecular dimensions of neat pyz$_2$SO are compared with the corresponding values in its silver(I) complexes **1**−**3** that contain different anions. In the case of the weakly bound perchlorate (Cl2-type), it acts as a linker to consolidate adjacent necklace-like chains stacking along the *a* axis through contacts between two π-acidic pyrazinyl rings and O6 (O···pyz$_{centroid}$ 3.310 Å) (Figure 5b). In this complex, the mean value of O···pyz$_{centroid}$ is 3.307 Å, being slightly longer than the surveyed result of 3.16 Å [O(ClO_4^-)···pyz$_{centroid}$ mean].[10f] The distances of O···C/N(ring atoms) lie within the range 3.025−3.537 Å, and detailed anion−π interaction geometries are illustrated in Table 3 for comparison.

Through these anion−π and O···Ag interactions, the necklace-like chains in **3** mutually interconnect in a shoulder-by-shoulder fashion to form a layer parallel to the *ab* plane. Adjacent layers are stacked along the *c* axis through the linkage of S=O···π(pyrazinyl) (O···pyz$_{centroid}$ 3.207 Å, S=O···pyz$_{centroid}$ 125.0°, Figure 6a) and weak O···Ag (above-mentioned O2d···Ag2 2.729(6) Å; O4d···Ag2 2.712(5) Å, Figure 5a) interactions to generate a three-dimensional framework (Figure 6b). The measured distance of O···pyz$_{centroid}$ is shorter than the sum of van der Waals radii (3.25 Å) of the

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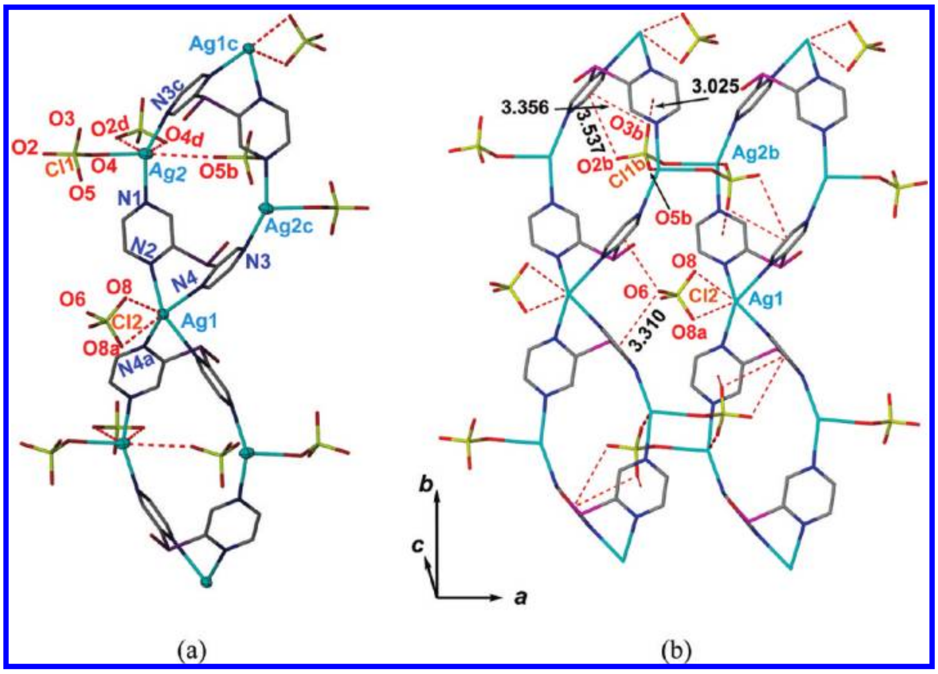
Table 3. Geometries of the Anion−π Interactions with the Pyrazinyl Ring in This Study

complex	atom(X)	X···C(N) range/Å	X···centroid distance/Å	X···plane distance/Å	φ/deg[a]
1	O4	3.263(5)−3.482(5)	3.129	3.116	84.8
		3.412(6)−3.806(6)	3.390	3.347	80.9
2	F2	3.258(3)−4.009(4)	3.525	3.256	67.3
	F3	3.178(6)−4.060(4)	3.382	3.138	68.1
	F4	3.115(4)−3.864(4)	3.233	3.078	72.3
	F5	3.423(5)−4.044(4)	3.497	3.356	73.6
3	O6	3.238(6)−3.860(5)	3.310	3.195	74.8
	O3	3.336(6)−3.893(8)	3.356	3.268	77.8
		3.233(5)−3.374(5)	3.025	3.020	86.6
	O2	3.173(6)−4.330(7)	3.537	3.126	62.3
4	F1	3.262(6)−4.223(6)	3.527	3.253	67.3
	F2	3.465(5)−4.042(6)	3.499	3.398	76.1
6	O7	3.212(7)−4.297(8)	3.530	3.212	65.5
	O8	2.808(5)−3.933(6)	3.147	2.809	63.2
	O2	3.333(6)−4.035(6)	3.437	3.286	72.9
7	O10	3.215(9)−3.676(9)	3.165	3.110	79.3
		3.441(7)−3.816(9)	3.352	3.316	81.6
	O6	3.294(12)−4.116(9)	3.487	3.252	69.8

[a] Angle of the X···π axis to the plane of the pyrazinyl cycle.



(a) (b)

Figure 5. (a) Coordination environments of two independent Ag(I) ions in $[Ag_3(pyz_2SO)_2(ClO_4)_3]_\infty$ (**3**). Symmetry codes: a $x, -y+3/2, z$; b $-x-1, -y+1, -z+1$; c $-x, -y+1, -z+1$; d $x+1/2, y, -z+3/2$. (b) Linkage of perchlorate ions between necklace-like chains in **3**. Symmetry codes: a $x, -y+3/2, z$; b $-x, -y+1, -z+1$.

interacting atoms (taking the half-thickness of a phenyl ring as 1.85 Å[20] and the van der Waals radius of O as 1.40 Å).[14] The S═O···π(pyrazinyl) interaction represents one type of lone-pair aromatic affinity[21] that is not well documented, whose contact fashion is analogous to that of the C═O···π(pyridyl) interaction reported by us recently.[21h] A recent thorough CSD survey by Reedijk et al.[21j] indicates that such X═O···π (X = any element of the period) commonly occurs in the crystal structures of small molecules, although its role in the construction of supramolecular frameworks has been seldom explored.

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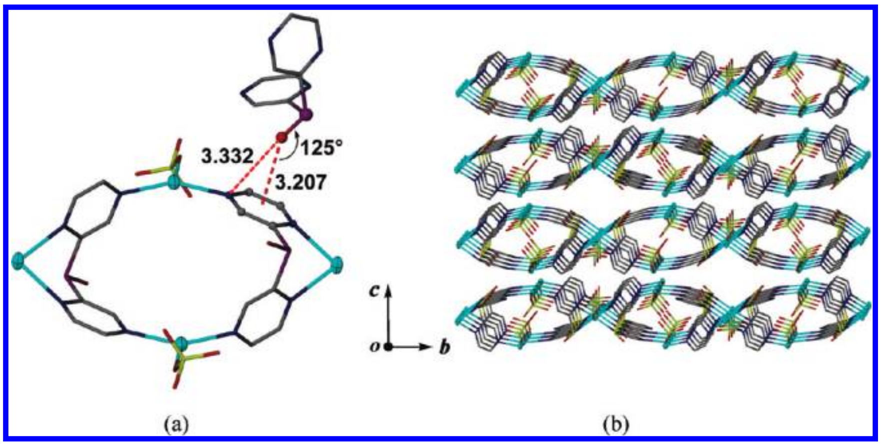

Figure 6. (a) Geometrical details of the S=O···π interaction in complex **3**. (b) Stacking of layers in **3** parallel to the *ab* plane. All the noncovalent interactions are omitted for clarity.

[Ag(pyz$_2$SO)(CF$_3$CO$_2$)]$_\infty$ (4). In the crystal structure of **4**, the Ag(I) atom adopts a distorted tetrahedral N_2O_2-coordinaton geometry with two pyz$_2$SO ligands and two trifluoroacetate anions around it (Figure 7a). The pyz$_2$SO ligand behaves as a μ_2-bridging ligand to coordinate to two Ag(I) atoms via one 1-pyrazinyl and one 4-pyrazinyl N atom of independent rings, exhibiting ligation mode **C** (Scheme 1). An infinite ladder-like chain structure is assembled along the [110] and [110] directions with a pair of μ_2-η^1:η^1 trifluoroacetate anions bridging adjacent Ag(I) atoms.

Apparently, the stronger bonding ability of trifluoroacetate relative to NO_3^-, PF_6^-, and ClO_4^- [19] plays a crucial role in the assembly of **4**, engendering a dense ladder-type structure rather than the metallocyclic motifs as in **1** to **3**. In addition, the anion−π(pyrazinyl ring) and sulfinyl···sulfinyl interactions also contribute to the stabilization of the three-dimensional framework in **4**. As shown in Figure 7b, two fluorine atoms (F1 and F2) of triflouoacetate bond to the same pyrazinyl ring from an adjacent chain with F···pyz$_{centroid}$ distances of 3.50 and 3.53 Å (Table 3), respectively, which are slightly longer than the mean R−F···pyz$_{centroid}$ distance of 3.16 Å from a CSD statistical study.[21j] Compared with the anion−π interaction in **1**−**3** with anions each embraced by both pyrazinyl rings of the same pyz$_2$SO, the trifluoroacetate anion lies outside of the wing-like pyz$_2$SO ligand and interacts with only one pyrazinyl ring. A sulfinyl···sulfinyl interaction occurs between a pair of parallel S=O groups of adjacent chains with an S···O distance of 3.143(3) Å, which is longer than those in neat pyz$_2$SO (2.962(2) Å) and **1** (3.014(3) Å), being shorter than the sum of van der Waals radii (3.30 Å).[14]

Complexes of Zn(II) and Cd(II). Metal ions with octahedral coordination geometry are widely used as nodes to construct metal−organic frameworks (MOFs). Herein, we also synthesized several Zn(II) and Cd(II) complexes of dipyrazinyl sulfoxide (pyz$_2$SO), namely, {[Zn(pyz$_2$SO)(H$_2$O)$_4$](NO$_3$)$_2$·H$_2$O}$_\infty$ (**5**), {[Zn(pyz$_2$SO)(H$_2$O)$_2$](ClO$_4$)$_2$}$_\infty$ (**6**), and {[Cd(pyz$_2$SO)$_2$(H$_2$O)](ClO$_4$)$_2$·H$_2$O}$_\infty$ (**7**), wherein the pyz$_2$SO acts as a chelating and bridging ligand (Scheme 1) to flexibly link the octahedral metal ions to form zigzag (**5** and **7**) and linear (**6**) chain structures. Differing from the pyz$_2$SO ligation modes (**A**−**C**) in compounds **1** to **4**, ligation modes **D** and **E** of pyz$_2$SO are observed in complexes **5** and **6**, respectively, while modes **F** and **G** coexist in **7**.

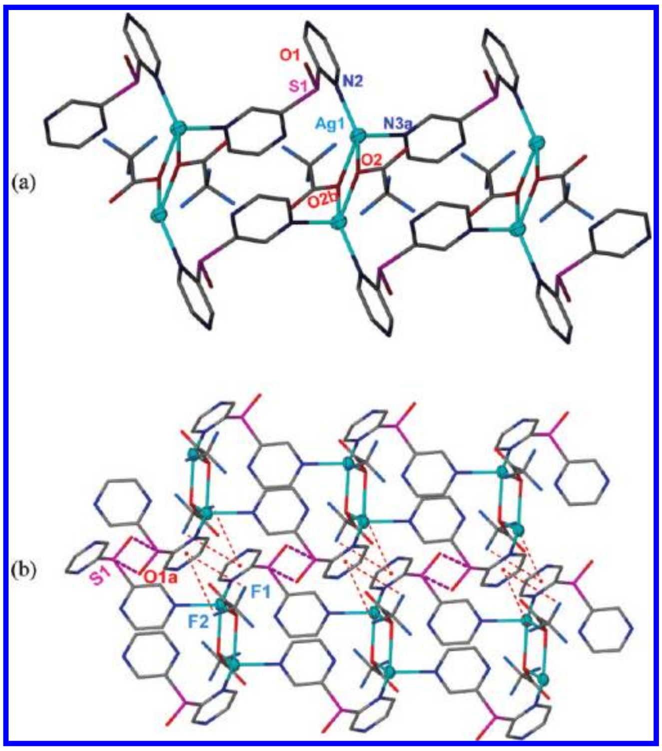

Figure 7. (a) Ladder-like chain in [Ag(pyz$_2$SO)(CF$_3$CO$_2$)]$_\infty$ (**4**). Symmetry codes: a $x + 1/2$, $y - 1/2$, z; b $-x$, $-y$, $-z + 1$. (b) Anion−π (thin dashed lines) and sulfinyl···sulfinyl (thick dashed lines) interactions between parallel ladder-like chains in **4**. Symmetry code: a $-x$, $-y + 1$, $-z + 1$.

{[Zn(pyz$_2$SO)(H$_2$O)$_4$](NO$_3$)$_2$·H$_2$O}$_\infty$ (5). In complex **5**, pyz$_2$SO ligands link adjacent Zn(II) atoms via the μ_2-bridging mode (mode **D**, Figure 8a, C(sp^2)−S−C(sp^2) angle = 96.57(8)°) to generate an infinite zigzag chain along the [101] direction. The centrosymmetric octahedral Zn(II) atom is surrounded by a pair of 4-pyrazinyl N atoms of two pyz$_2$SO ligands [Zn−N 2.169(2) and 2.196(2) Å] and four aqua ligands [Zn−O 2.072(1) and 2.095(1) Å]). Two aqua ligands O1W and O4W further serve as hydrogen-bonding donors to connect with one nitrate group (N6-type) and two pyrazinyl N atoms (N2 and N4), thus assembling the zigzag chains into a layer

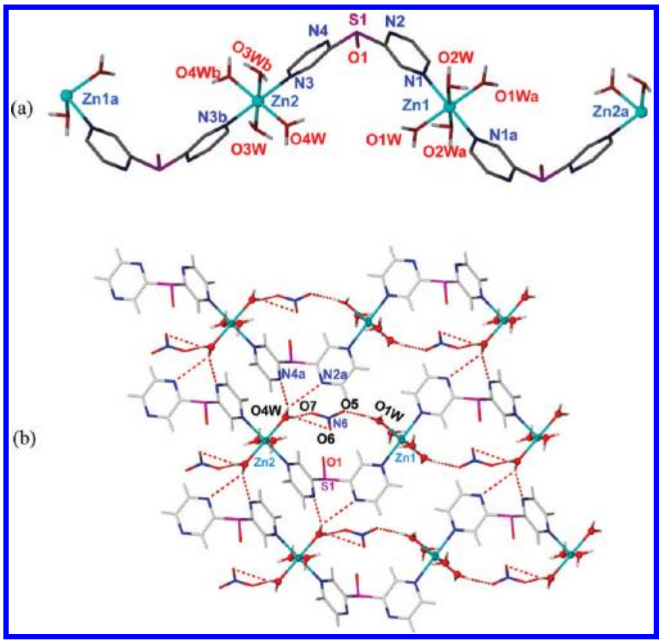

Figure 8. (a) Coordination environment of Zn(II) in $\{[Zn(pyz_2SO)(H_2O)_4](NO_3)_2\cdot H_2O\}_\infty$ (**5**). Symmetry codes: a $-x+2, -y+1, -z+1$; b $-x+1, -y+2, -z+1$. (b) Hydrogen-bonded layer in **5**. Symmetry code: a $x, y+1, z$.

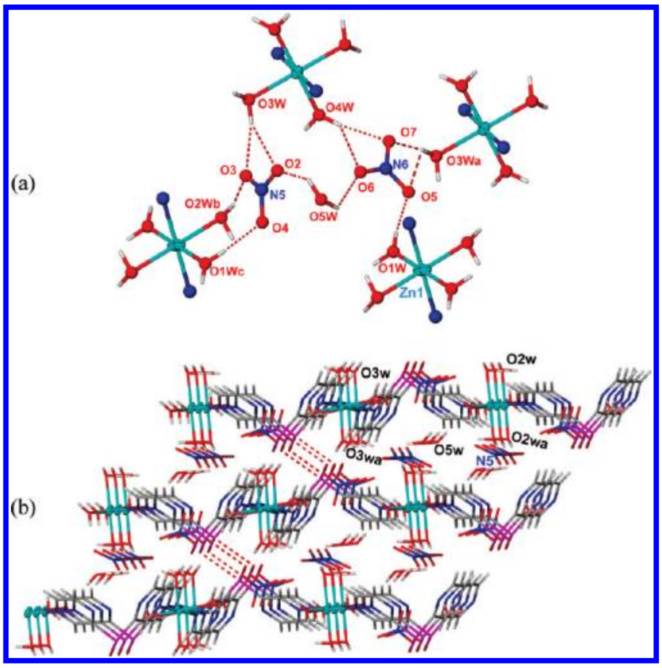

Figure 9. (a) Hydrogen bonding between nitrate anions and water molecules in **5**. Symmetry codes: a $x+1, y, z$; b $x-1, y+1, z$; c $-x+1, -y+2, -z+1$. (b) Three-dimensional framework in **5** viewed along the *b* axis. The dashed lines represent sulfinyl···sulfinyl interactions. All other noncovalent interactions are omitted for clarity.

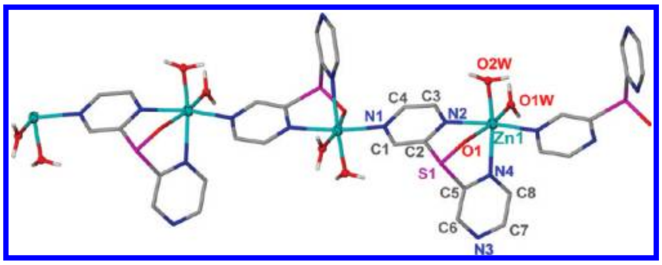

Figure 10. Infinite linear chain structure in $\{[Zn(pyz_2SO)(H_2O)_2](ClO_4)_2\}_\infty$ (**6**). Selected bond lengths (Å): Zn1−O1W 2.033(3), Zn1−O2W 2.060(3), Zn1−N1 2.122(3), Zn1−O1 2.130(2), Zn1−N2 2.220(3), Zn1−N4 2.295(3), S1−O1 1.512(2), S1−C5 1.810(3), S1−C2 1.818(3). Bond angles (deg): O1−S1−C5 101.22(1), O1−S1−C2 101.76(1), C5−S1−C2 94.95(2).

(Figure 8b). As shown in Figure 9a, a hydrogen-bonded adhesive unit composed of two nitrate groups (N5 and N6) and one water molecule (O5W) connects with the octahedral $ZnN_2(OW)_4$ units of adjacent layers, thus generating a three-dimensional network (H-bonding parameters are listed in Table S1 of the Supporting Information). Presumably the existence of these multiple hydrogen bonds hinders the formation of an anion−π interaction in complex **5**. On the other hand, a sulfinyl···sulfinyl interaction (O···S distance of 2.940(2) Å) between a pair of head-to-tail S=O groups, which is similar to that in the crystal structure of free pyz_2SO and complexes **1** and **4**, occurs between adjacent layers to consolidate the overall three-dimensional framework, as shown in Figure 9b.

$\{[\mathbf{Zn(pyz_2SO)_2(H_2O)}](\mathbf{ClO_4})_2\}_\infty$ **(6).** In the crystal structure of **6**, the zinc(II) atom is surrounded by two aqua ligands (O1W and O2W) and two pyz_2SO molecules to achieve octahedral N_3O_3-coordination geometry. Two 1-pyrazinyl N atoms and the S=O group chelate on one zinc(II) atom (Zn−O 2.130(2) Å, Zn−N 2.220(3) and 2.295(3) Å) in the *syn*-mode and one 4-pyrazinyl N atom bonds to the second zinc(II) atom, forming a new ligation mode, **E** (Scheme 1). The S=O bond length is markedly lengthened to 1.512(2) Å as compared with those in complexes **1**−**5** because of its ligation to the zinc(II) center. In comparison with the weak O(sulfoxide)···Ag interaction in **2**, stronger Zn−O(sulfoxide) bonding in **6** leads to much smaller N−C−S=O torsion angles of 26.8(3)°/29.6(3)°, in contrast to that of 34.1(3)° in **2**.

Such μ_2-bridging pyz_2SO (mode **E**) links the octahedral Zn(II) ions via one 1-pyrazinyl and one 4-pyrazinyl nitrogen atom at the axial positions to form an infinite linear chain (Figure 10). The perchlorate anions function as linking units to assemble the chains into a higher-dimensional framework (Figure 11a). Three kinds of interactions are involved for the linking perchlorate, namely, OW−H···O(perchlorate) and C−H···O-(perchlorate) hydrogen bonding and anion−π(pyrazinyl) interactions, as illustrated in Figure 11b (Table S2 in the Supporting Information contains the H-bonding parameters). For example, the Cl2-type ClO_4^- forms hydrogen bonds with aqua ligands (O1W−H···O9, O2W−H···O9) and anion−π interactions with the pair of wing-like rings of a pyz_2SO (O8···$pyz_{centroid}$ 3.147 Å, O7···$pyz_{centroid}$ 3.530 Å). Another perchlorate (Cl1-type) is hydrogen-bonded to O2W (O2W−H2WB···O4) and interacts with the same pyrazinyl ring (O···$pyz_{centroid}$ 3.437 Å), thereby engendering an anion···π···anion contact mode (Figure 11b). The $C(sp^2)-S-C(sp^2)$ angle of 94.95(2)° in **6** is a bit larger than that of 92.82(2)° in **3**, and the corresponding molecular dimension of pyz_2SO is detailed in Table 2. The multiple anion−π interactions of ClO_4^- conceivably account for the structural differences between **5** and **6**. Table 3 shows detailed anion−π contact geometries in this complex, the mean O$\cdots$pyz$_{centroid}$ of 3.371 Å being comparable with that of 3.307 Å in complex **3**.

{[Cd(pyz$_2$SO)$_2$(H$_2$O)](ClO$_4$)$_2$·H$_2$O}$_\infty$ (7). Complex **7** was obtained by a similar synthetic procedure to that for **6**. Two new ligation modes of the pyz$_2$SO ligand, namely, terminal mode **F** and μ_2-bridging mode **G** (Scheme 1), are found in complex **7**. The S=O group together with the 1-pyrazinyl N atom readily chelates a metal center as in **6**. The bonding difference of pyz$_2$SO in **6** and **7** is that just one 1-pyrazinyl N atom is involved in the $\kappa^2 N,O$-chelating mode of **F** and **G** in **7**; the other 1-pyrazinyl N2 atom exhibits only a weak N$\cdots$Cd bonding interaction at 2.722(4) Å (Figure 12), rather than two such nitrogen atoms in the $\kappa^3 N,N,O$-chelating mode (**E**) in **6** (Figure 10). This may be due to the larger ionic radius of Cd(II) in contrast to Zn(II), so that the former cation favorably binds with three pyz$_2$SO ligands. Because of Cd−O-(sulfinyl) bonding, the bond lengths of S=O (1.496(3) Å in mode **F**; 1.501(3) Å in mode **G**) are longer than that of 1.487(2) Å in neat pyz$_2$SO, but comparable to that of 1.512(2) Å in **6** (Table 2).

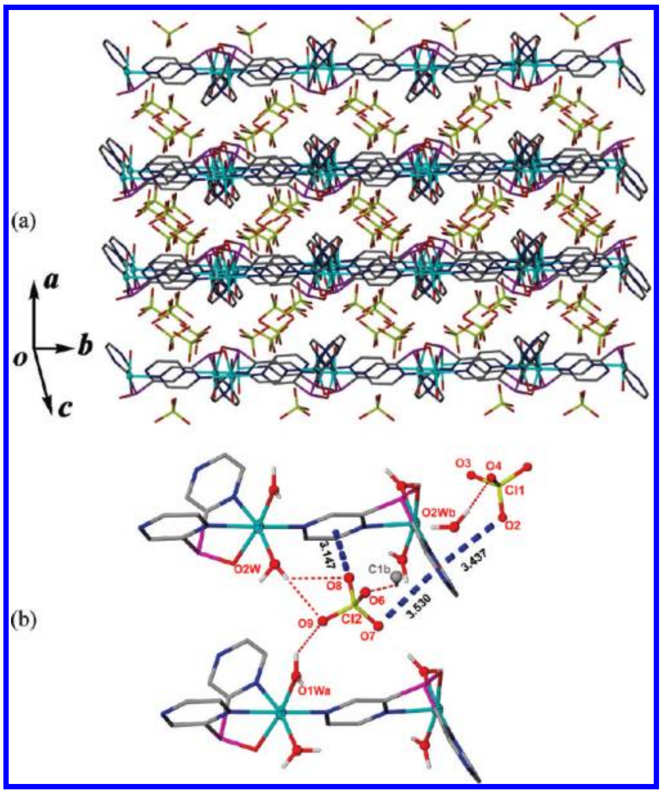

Figure 11. (a) Three-dimensional framework in **6**. All noncovalent interactions are omitted for clarity. (b) Hydrogen-bonding and anion−π interactions in **6**. Symmetry codes: a $-x+1, y, z$; b $-x+1, -y+1, -z+2$.

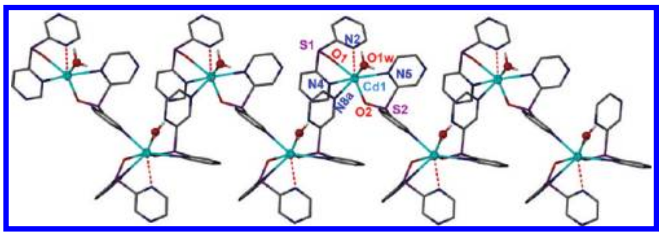

Figure 12. Infinite zigzag chain structure in {[Cd(pyz$_2$SO)$_2$(H$_2$O)]-(ClO$_4$)$_2$·H$_2$O}$_\infty$ (**7**). Symmetry code: a $x, -y+3/2, z-1/2$.

Each seven-coordinated Cd(II) ion in the CdN$_4$O$_2$-(OW) unit in **7** is linked by three pyz$_2$SO and one aqua ligand (Figure 12) to generate a zigzag chain along the *c* axis. A conglomerated three-dimensional framework (Figure 13a) is then formed through the linkage of these infinite chains by the perchlorate anions, which are accommodated within the interstices not only to provide charge balance but also to consolidate the overall lattice structure via anion−π interactions. As shown in Figure 13b, one perchlorate is embraced by two pyrazinyl rings (mode **F**), forming anion−π interactions via the contacts of oxygen atom O10 with the two pyrazinyl rings (Table 3). The other perchlorate group is also in contact with one pyrazinyl ring with a O6$\cdots$pyz$_{centroid}$ distance of 3.49 Å. In addition, the latter perchlorate is similarly embraced by two pyrazinyl rings of pyz$_2$SO (mode **G**) with the O(perchlorate)$\cdots$pyz$_{centroid}$ distance of 3.48/3.54 Å. The C(sp^2)−S−C(sp^2) angle exhibits diverse values on account of different bonding modes (94.1(2)° in mode **F**, 92.5(2)° in mode **G**). The O(perchlorate)$\cdots$pyz$_{centroid}$ distances in the range of 3.17−3.54 Å are comparable with those in the divalent zinc complex **6** (3.15−3.53 Å) and also agree well with the values of the O(perchlorate)$\cdots$pyz$_{centroid}$ interaction in reported copper complex Cu[(2-C$_4$H$_3$N$_2$)$_2$C(OH)$_2$]$_2$(ClO$_4$)$_2$[10h] and divalent Co(II) complexes {[Co(L)(MeCN)$_2$](ClO$_4$)$_2$}$_\infty$ [L = bis(2-pyrazylmethyl)sulfide].[18a]

IR Spectroscopic Study. Infrared spectroscopy is usually used as a common method to distinguish between

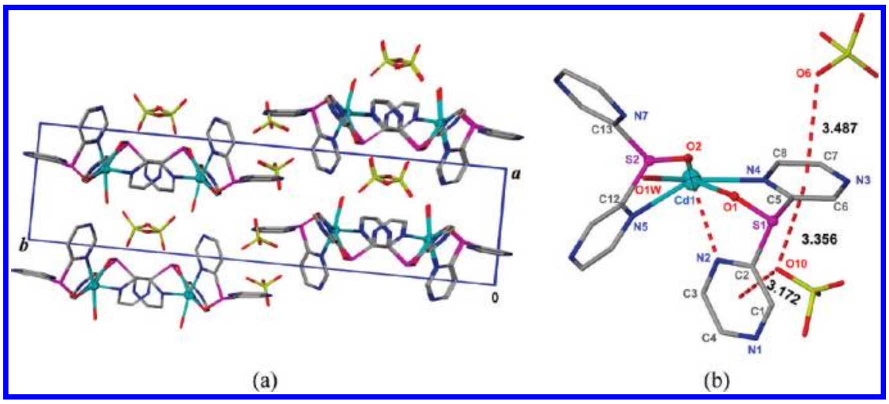

Figure 13. (a) Packing mode in **7** viewed along the *c* direction. (b) Anion$\cdots\pi\cdots$anion interaction in **7**. Selected bond lengths (Å): Cd1−O1W 2.272(4); Cd1−O2 2.283(4), Cd1−O1 2.345(3), Cd1−N4 2.461(4), Cd1−N5 2.489(4), N2$\cdots$Cd1 2.722(4) Å.

O- and S-bonding in alkyl sulfoxide metal complexes. With respect to free alkyl sulfoxide (1055 cm^{-1}), the ν(S=O) stretching frequency increases for a S-bonded ligand (1080−1154 cm^{-1}) but decreases for an O-bonded species (862−997 cm^{-1}), corresponding to the markedly shorter (S-bonded) and longer (O-bonded) S=O bond lengths.[2b−d] In complexes **1** to **7** and free dipyrazinyl sulfoxide (pyz_2SO), the measured values of ν(S=O) vary within a narrow rang (1060−1066 cm^{-1}). For the η^1-O-bonded S=O in complex **6** and **7**, the stretching band exhibits a slightly decreased shoulder peak at 1010 and 1013 cm^{-1}, respectively, as compared to the maximum absorption at 1021 cm^{-1} in the free pyz_2SO ligand. The ambiguous change of the stretching frequency with respect to the free pyz_2SO ligand may be ascribed to the steric effects of the κ^3*N*,*N*,*O*- and κ^2*N*,*O*-chelating mode in **6** and **7**, respectively.

Conclusions

We have synthesized the new multidentate dipyrazinyl sulfoxide (pyz_2SO) ligand and obtained a series of its group 11 and 12 metal complexes with various anions (**1**−**7**). In general, the 1-pyrazinyl N and O atoms of pyz_2SO chelate to a metal center while the peripheral 4-pyraziny N atom coordinates to another metal ion, leading to an extended coordination polymeric structure. Due to the π-acidic nature of the pyrazinyl ring and the local C_s geometry of the $C(sp^2)-S(O)-C(sp^2)$ group, the coexisting anion is preferentially embraced by the pair of pyrazinyl rings of the clamp-like pyz_2SO ligand via an anion−π interaction. Compared with NO_3^- and PF_6^-, ClO_4^- exhibits a propensity to engage in such contacts, which is reflected by an enhanced modification of the molecular dimensions and configuration of the pyz_2SO ligand (Table 2). Through this type of subtle anion tuning, multidentate pyz_2SO has the potential of functioning as a versatile mediator in the supramolecular assembly of various metal complexes. Flexible ligation modes (**A**−**G**) were revealed in these assemblies with the pyrazinyl nitrogen and/or the sulfoxide oxygen atoms coordinating to the metal ion(s), and the sulfoxide group (S=O) adopts an *anti*- or a *syn*-mode with respect to the two 1-pyrazinyl N atoms of pyz_2SO in accordance with steric demand and the onset of anion−π interactions. Furthermore, the sulfoxide group S=O is involved in dipolar sulfinyl···sulfinyl and S=O···π(pyrazinyl) interactions in the construction of the metal−organic supramolecular frameworks of **1** and **3**−**5**. To the best of our knowledge, the role of such noncovalent interactions in supramolecular assembly has seldom been discussed in the chemical literature, and the present study shows that the coordination chemistry of diheterocyclic sulfoxides is worthy of further investigation.

Acknowledgment. This work is dedicated to the memory of Prof. Robert Bau (1944-2008). Financial support by the Hong Kong Research Grants Council (GRF Ref. No. CUHK 402206) and the Wei Lun Foundation is gratefully acknowledged.

Supporting Information Available: Crystallographic data of pyz_2SO and **1**−**7**. This material is available free of charge via the Internet at http://pubs.acs.org.