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Synthesis of *meta*-C₆H₄[C(1-pyrazolyl)₂(2-pyridyl)]₂, a fixed geometry bitopic heteroscorpionate and the crystal structure of its unusual square planar silver(I) complex

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Abstract

The reaction between bis(1-pyrazolyl)sulfone (prepared in situ by the reaction between NaH, Hpz, and SOCl₂ in THF) and $C_6H_4[C(O)(2-py)]_2$ in THF catalyzed by CoCl₂ yields *m*-C₆H₄[C(pz)₂(2-py)]₂ (1, pz = pyrazolyl, py = pyridyl) in moderate yield, along with 1-[C(pz)₂(2-py)]-4-[C(O)(2-py)]C₆H₄. The potentially bitopic ligand 1 reacts with AgPF₆ to yield [Ag(1)₂](PF)₆ (3), regardless of the stoichiometry of reagents used in the preparation. X-ray structural analysis of this silver complex shows that two ligands bond to a silver in a κ^2 -fashion via the pyrazolyls in one C(pz)₂(py) group in each ligand while the other is non-coordinated. The AgN₄C chelate rings adopt a boat conformation and the silver resides in an unusual square planar coordination environment. Non-covalent forces organize the two-dimensional structure of **3** such that it approaches a layered inorganic–organic hybrid material. Reaction of C₆H₅[C(pz)₂(2-py)] and AgPF₆ yields {Ag(κ^2 -C₆H₅[C(pz)₂(2-py)]₂)(PF₆) (4). The structure is disordered but the ligands are bidentate, the nitrogen donor atoms are in a square planar coordination environment about the silver and the overall structure is similar to **3**.

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Keywords: Bitopic heteroscorpionate ligand; Square planar silver complex

1. Introduction

Current interest in coordination networks is driven in part by the desire to combine the variety in structural, physical, and spectroelectrochemical properties of both the inorganic and organic constituents with the practicality and function of zeolite-type materials [1,2]. Recent work published by Wenbin Lin's group is testament to the potential for the realization of such a goal [3,4]. Advances in the design of polytopic ligands, which serve as organic spacers between two or more metal centers, have been instrumental to this area of research. Over recent years, our group has been interested in exploring the preparation and coordination chemistry of a variety of polytopic poly(pyrazolyl)methane ligands. We have prepared bitopic tetra-(pyrazolyl) compounds that contain two bis(pyrazolyl)methane units linked by either a flexible methylene or a semi-rigid ferrocenyl group, and have explored their coordination chemistry with silver [5,6]. Additionally, we have reported on the preparation of coordination polymers that incorporate semi-rigid organic spacers based on polytopic tris(pyrazolyl)methanes of the type $C_6H_{6-n}[CH_2OCH_2C(pz)_3]_n$ (n = 2, 4 [7-9]; pz = pyrazolyl ring). The use of poly(pyrazolyl)methane ligands linked by rigid organic spacers would be of interest toward the preparation of either large metallacycles of predefined geometry or the development of coordination networks with a predictable arrangement of metal centers within the material. To this end, we have prepared $\alpha, \alpha, \alpha', \alpha'$ -tetrakis(1-pyrazolyl)- α , α' -bis(2-pyridyl)-1,3-xylene, m-C₆H₄[C(pz)₂ (2-py)]₂ (1, py = pyridyl ring), a potentially bitopic heteroscorpionate, that can be envisioned as a 120° rigid organic spacer. In this paper we will detail the preparation of 1 and outline our initial observations regarding its coordination chemistry with silver hexafluorophosphate. For

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comparison, the related chemistry involving the monotopic analogue, $C_6H_5[C(pz)_2(2-py)]$ (2), will also be described.

2. Experimental

2.1. General

Solvents for synthetic procedures, and spectroscopic studies were dried by conventional methods and distilled under N₂ atmosphere immediately prior to use. The compound m-C₆H₄[C(O)(2-py)]₂ was prepared as described previously [10]. All other reagents were used as received from Aldrich Chemical Co. Silica gel (0.040-0.063 mm, 230-400 mesh) used for chromatographic separations was purchased from Fischer Scientific. Silver hexafluorophosphate was stored and handled under a purified nitrogen atmosphere in a drybox. Robertson Microlit Laboratories performed all elemental analyses. Melting point determinations were made on samples contained in sealed glass capillaries by using an Electrothermal 9100 apparatus and are uncorrected. Mass spectrometric measurements recorded in ESI(+) mode were obtained on a Micromass Q-Tof spectrometer whereas those performed by using direct probe analyses were made on a VG 70S instrument. NMR spectra were recorded by using either a Varian Mercury 400 or a Varian Inova 500 instrument, as noted within the text. Chemical shifts were referenced to solvent resonances at either $\delta_{\rm H}$ 7.27, $\delta_{\rm C}$ 77.2 for CDCl₃, or $\delta_{\rm H}$ 2.05, $\delta_{\rm C}$ 29.8 for acetone-d₆.

2.2. Ligand preparation

The preparation of $C_6H_5C(pz)_2(2-py)$ has been described previously [11], however, in this contribution an alternate purification step and additional characterization data are provided. The title bitopic derivative was prepared by using an analogous procedure. Therefore, only the quantity of reagents, solvent, reaction time, and the details of chromatographic separation are described below for each.

2.3. Preparation of $m-C_6H_4[C(pz)_2(2-py)]_2$, $\alpha, \alpha, \alpha', \alpha'$ tetrakis(1-pyrazolyl)- α, α' -bis(2-pyridyl)-1,3-xylene, (1)

A mixture of 2.9 mmol SO(pz)₂ [from 0.14 g (5.9 mmol) NaH, 0.40 g (5.9 mmol) Hpz and 0.21 ml (2.9 mmol) SOCl₂], 0.43 g (1.5 mmol) C₆H₄[C(O)(2-py)]₂, and 60 mg (30 mol% of C₆H₄[C(O)(2-py)]₂) CoCl₂ in 80 ml THF were heated at reflux for four days. After work-up, chromatographic separation of the product mixture on SiO₂ by using Et₂O as the eluent afforded 0.16 g (0.55 mmol) C₆H₄[C(O)(2-py)]₂ from the first pale yellow band ($R_f = 0.7$ on TLC plate) and 0.14 g (0.34 mmol) of

 $1-[C(pz)_2(2-py)]-4-[C(O)(2-py)]C_6H_4$, 1a, as a colorless solid from the second pale yellow band ($R_{\rm f} = 0.3$ TLC plate). Mp 113–115 °C. IR (cm⁻¹): v_{co} 1669 (br, vs). ¹H NMR (400 MHz, CDCl₃) 8.68 (d, J = 4 Hz, 1H, H₆py*CO*), 8.62 (d, J = 4 Hz, 1H, H₆-py), 8.16 (m, 1H, aryl), 8.00 (d, J = 8 Hz, 1H, H₃-pyCO), 7.98 (s, 1H, aryl), 7.85 (ddd, J = 8, 8, 2 Hz, 1H, H₄-pyCO), 7.73 $(ddd, J = 8, 8, 2 Hz, 1H, H_4-py, 7.68 (d, J = 1 Hz, 2H,$ H₃-pz), 7.56 (d, J = 2 Hz, 2H, H₅-pz), 7.49 (m, 2H, aryl), 7.45 (ddd, J = 8, 4, 1 Hz, 1H, H₅-pyCO), 7.32 $(ddd, J = 8, 4, 1 Hz, 1H, H_5-py), 7.24 (d, J = 8 Hz, 1H,$ H₃-py), 6.33 (d, J = 2 Hz, 2H, H₄-pz). ¹³C NMR (101.62 MHz, CDCl₃) 193.0 (C=O), 158.3 (C₂-py), 154.9 (C₂-py*CO*), 148.9 (C₆-py*CO*), 148.6 (C₆-py), 140.9 (C₅-pz), 139.7 (C₃-aryl), 137.2 (C₄-pyCO), 137.1 (C₄py), 136.0 (C₁-aryl), 133.8 (C₄-aryl), 132.6 (C₃-pz), 131.9 (C_{2.6}-aryl), 128.1 (C₅-aryl), 126.4 (C₃-py*CO*), 124.9 (C₃py), 124.6 (C₅-py*CO*), 123.9 (C₅-py), 106.1 (C₄-pz), 87.1 (C_{α}) . Direct probe MS *m*/*z* (Rel. Int. %) [assgn]: 406(32) $[M]^+$, 338(100) $[M-Hpz]^+$, 328(21) $[M-py]^+$, 233(29) $[C(C_6H_4)(pz)py]^+$, 182(12) $[PhC(O)py]^+$, 78(37) $[py]^+$. After complete elution of 1a, the column was sequentially flushed with acetone, acetonitrile, acetonitrile/ methanol (1:4) which after combining these fractions and evaporating the solvents gave 0.27 g (0.51 mmol, 34% based on $C_6H_4[C(O)(2-py)]_2$ of 1 as a pale yellow solid. Mp 223–225 °C dec. ¹H NMR (400 MHz, CDCl₃) 8.61 (d, J = 4 Hz, 2H, H₆-py), 7.69 (ddd, J = 8, 8, 2 Hz, 2H, H₄-py), 7.61 (d, J = 1 Hz, 4H, H₃-pz), 7.53 (d, J = 2 Hz, 4H, H₅-pz). 7.31 (t, J = 8 Hz, 1H, H₅-aryl), 7.29 (ddd, $J = 8, 4, 2, Hz, 2H, H_5$ -py), 7.18–7.13 (m, 4H, aryl and H₃-py), 6.28 (d, J = 2 Hz, 2H, H₄-pz). ¹H NMR (400 MHz, acetone- d_6) 8.57 (d, J = 5 Hz, 2H, H₆py), 7.82 (ddd, J = 7, 7, 2 Hz, 2H, H₄-py), 7.57 (d, J = 1Hz, 4H, H₃-pz), 7.50 (d, J = 2 Hz, 4H, H₅-pz). 7.40 $(ddd, J = 7, 5, 2 Hz, 2H, H_5-py), 7.33 (t, J = 8 Hz, 1H,$ H₅-aryl), 7.25 (s, 1H, aryl), 7.13 (d, J = 8 Hz, 2H, aryl), 7.09 (dd, J = 7, 2 Hz, 2H, H₃-py), 6.32 (dd, J = 2, 1 Hz, 4H, H₄-pz). ¹³C NMR (101.62 MHz, CDCl₃) 158.3 (C₂py), 148.6 (C₆-py), 140.7 (C₅-pz), 138.8 (C_{ipso}-Ph), 136.9 (C₄-py), 133.7 (aryl), 132.6 (C₃-pz), 129.2 (C_{4/6}-aryl), 128.2 (C₂-aryl), 124.8 (C₃-py), 123.8 (C₅-py), 105.9 (C₄pz), 87.2 (C_{α}). HRMS-Direct probe (*m*/*z*): Anal. Calc. for $C_{30}H_{24}N_{10}^+$ 524.2185. Found: 524.217. Direct probe MS m/z (Rel. Int. %) [assgn]: 524(2) [M]⁺, 456(100) [M- $Hpz]^+$, 389(36) [M-2pz]⁺, 378(31) [M-pz-py]⁺, 322(19)[M-3pz]⁺, 310(18) [M-2pz-py]⁺, 78(12) [py]⁺.

2.4. Preparation of $C_6H_5[C(pz)_2(2-py)]$, α, α -bis(1pyrazolyl)- α -(2-pyridyl)toluene (2)

A mixture of 21 mmol SO(pz)₂ [from 1.0 g (42 mmol) NaH, 2.9 g (42 mmol) Hpz, and 1.5 ml (21 mmol) SOCl₂], 3.7 g (20 mmol) 2-benzoylpyridine, and 75 mg (3 mol% of 2-benzoylpyridine) CoCl₂ in 20 ml THF were heated at reflux for 15 h. After work-up,

chromatographic separation of the product mixture on SiO₂ with 50% Et₂O/hexanes afforded 2.2 g (37% based on 2-benzoylpyridine) of 2 as a colorless solid from the second colorless band ($R_{\rm f} = 0.4$ on TLC plate). Mp 138– 139 °C (lit. 123–125 °C [11]). ¹H NMR (400 MHz, $CDCl_3$) 8.70 (d, J = 4 Hz, 1H, H₆-py), 7.73 (ddd, J = 8, 8, 2 Hz, 1H, H₄-py), 7.70 (d, J = 1 Hz, 2H, H₃-pz), 7.57 (dd, J = 2, 1 Hz, 2H, H₅-pz). 7.41–7.35 (m, 3H, o- and *p*-H of Ph), 7.31 (ddd, J = 8, 4, 1 Hz, 1H, H₅-py), 7.24 $(d, J = 8 Hz, 1H, H_3-py), 7.20 (dd, J = 8, 2 Hz, 2H, m-$ H of Ph), 6.33 (d, J = 2 Hz, 2H, H₄-pz). ¹³C NMR (101.62 MHz, CDCl₃) 158.7 (C₂-py), 148.8 (C₆-py), 140.7 (C₅-pz), 139.6 (C_{ipso}-Ph), 137.0 (C₄-py), 132.6 (C₃pz), 129.4 (o- and p- of Ph), 128.2 (m-C of Ph), 124.3 (C₃-py), 123.7 (C₅-py), 105.8 (C₄-pz), 87.3 (C_α). Direct probe MS m/z (Rel. Int. %) [assgn]: 301(62) [M]+, 233(100) [M-Hpz]⁺, 223(86) [M-py]⁺, 167(99) [M-2Hpz]⁺, 77(28) [Ph]⁺.

2.5. Silver hexafluorophosphate complexes

2.5.1. Preparation of $\{Ag(\kappa^2 - m - C_6H_4[C(pz)_2(2-py)]_2)_2\}$ (*PF*₆), (**3**)

A mixture of 0.087 g (0.17 mmol) 1 and 0.042 g (0.17 mmol) AgPF₆ was dissolved in 15 ml of a 2:1 mixture of CH₃CN/acetone. After a reflux period of 6 h, trace gray solid was observed and solvent was removed by vacuum distillation. The resulting brown solid was washed sequentially with 5 ml each of Et_2O and hexanes. The insoluble residue was then extracted with 10 ml CH₃CN. The filtered extract was layered with 50 ml Et₂O and after allowing the solvents to diffuse overnight, the colorless crystals of $\{Ag(C_6H_4[C(pz)_2(2-py)]_2)_2\}(PF_6)$ (3) were isolated by filtration and were air-dried (84 mg, 78%). Mp, 205-210 °C dec. Anal. Calc. for C₆₀H₅₂N₂₀AgF₆O₂P, **3**·2 H₂O: C, 53.86 (53.98); H, 3.92 (3.53); N, 20.94 (20.81). ¹H NMR (400 MHz, acetone d_6) 8.60 (d, J = 4.5 Hz, 2H, H₆-py), 7.89 (ddd, J = 8, 8, 2 Hz, 2H, H₄-py). 7.64 (d, J = 1 Hz, 4H, H₃-pz), 7.52 (d, J = 2 Hz, 4H, H₅-pz), 7.47–7.40 (m, 3H, aryl), 7.15 (dd, J = 8, 2 Hz, 2H, H₅-py), 7.09 (d, J = 8 Hz, 2H, H₃-py), 6.95 (s, 1H, aryl), 6.38 (dd, J = 2, 1 Hz, 4H, H₄-pz).

2.5.2. Preparation of $\{Ag(\kappa^2-C_6H_5[C(pz)_2(2-py)])_2\}$ (PF₆) (4)

A solution of 0.333 g (1.10 mmol) $C_6H_5[C(pz)_2(2-py)]$ in 10 ml THF was added by cannula to a solution of 0.139 g (0.550 mmol) AgPF₆ in 10 ml THF under a nitrogen atmosphere. A colorless solid precipitated within a few minutes of mixing and the resulting suspension was stirred 4 h. The product mixture was then separated by cannula filtration. The insoluble colorless solid was washed with two 5 ml portions of Et₂O and dried under vacuum to leave 0.435 g (92% yield) of {Ag(C₆H₅[C(pz)₂(2-py)])₂}(PF₆) as a colorless solid. Crystals suitable for X-ray structural studies were grown by layering an acetone solution with Et₂O and allowing the solvents to diffuse. Mp, 175–178 °C crystals become opaque and shatter; 187-188 °C dec. to green-gray solid. ¹H NMR (400 MHz, acetone-d₆) 8.59 (d, J = 4 Hz, 1H, H₆-py), 7.98 (ddd, J = 8, 8, 2 Hz, 1H H₄-py), 7.62 (d, J = 1 Hz, 2H, H₃-pz), 7.59–7.49 (br m, 6H, H₅-pz and aryl), 7.04 (d, J = 8 Hz, H₃-py), 6.85–6.83 (br m, H₅-py and aryl), 6.46 (dd, J = 2, 1 Hz, H₄-pz). ¹³C NMR (101.62 MHz, acetone-d₆) 157.5 (C₂-py), 150.4 (C₆-py), 142.8 (C₃-pz), 139.5, 138.9, 135.0, 131.0 (C₅pz), 129.8, 129.7, 126.1, 125.8, 106.8 (C₄-pz), 88.0 (C_α). HRMS-ESI(+) (m/z): Anal. Calc. for [M-PF₆]⁺, C₃₆H₃₀N₁₀Ag⁺: 709.1702. Found: 709.1706. ESI(+) MS m/z (Rel. Int. %) [assgn]: 709 (100) [AgL₂]⁺, 449 (29) [AgL(CH₃CN)]⁺, 408 (2) [AgL]⁺, 302 (65) [HL]⁺, 234 (60) $[HL-pz]^+$.

2.6. Crystallography

2.6.1. X-ray structure determinations of $\{Ag(\kappa^2-m-C_6H_4[C(pz)_2(2-py)]_2)_2\}(PF_6), (3) \text{ and } \{Ag(\kappa^2-C_6H_5 [C(pz)_2(2-py)]_2\}(PF_6) \cdot acetone (4 \cdot acetone)$

A colorless prism of 3 and a colorless prismatic crystal of 4-acetone were each mounted onto the end of a thin glass fiber using inert oil. X-ray intensity data were measured in the dark at 190(2) K in the nitrogen cold stream of a Bruker SMART APEX CCD-based diffractometer system (Mo K α radiation, $\lambda = 0.71073$ A [12]. A total of 1800 raw data frames of width 0.3° in ω were collected at three different ϕ angles, with an exposure time of 15 and 20 s per frame for 3 and 4 acetone, respectively. The data collections covered the entire sphere of reciprocal space. The first 50 frames of each were re-collected at the end of the data set to monitor crystal decay. The raw data frames were integrated into reflection intensity files using SAINT+ [12], which also applied corrections for Lorentz and polarization effects. The final unit cell parameters are based on the leastsquares refinement of 6425 reflections with $I > 5(\sigma)I$ from the data set for 3 and 3377 reflections with $I > 5(\sigma)I$ from the data set for 4-acetone. Analysis of the data showed negligible crystal decay during the data collections and no absorption corrections were applied (see Table 1).

2.6.2. Structure refinement of 3

The compound crystallized in the triclinic system; the space group $P\overline{1}$ was confirmed by successful solution and refinement of the structure. The structure was solved by direct methods followed by difference Fourier synthesis, and refined by full-matrix least-squares against F^2 , using the SHELXTL software package [13]. The Ag and P atoms both lie on centers of symmetry; all other atoms are on general positions. The asymmetric unit is made up of the Ag ion, one C₆H₄[C(pz)₂ (2-py)]₂ ligand, and half a PF₆⁻ anion. The PF₆⁻ anion is

| Table 1 | | |
|-----------------------------------|--|--|
| Experimental and crystal data for | $\{Ag(\kappa^2 - m - C_6H_4[C(pz)_2(2-py)]_2)_2\}(PF_6), (3), and$ | $\{Ag(\kappa^2-C_6H_5[C(pz)_2(2-py)])_2\}(PF_6)$ (4) |

| | 3 | 4-acetone |
|---|-------------------------------|-------------------------------|
| Formula | $C_{60}H_{48}AgF_6N_{20}P$ | $C_{39}H_{36}AgF_6N_{10}OP$ |
| Mw | 1302.02 | 913.62 |
| Crystal system | triclinic | triclinic |
| Space group | $P\bar{1}$ | $P\overline{1}$ |
| a (Å) | 8.620(1) | 8.316(1) |
| b (Å) | 12.427(2) | 10.256(2) |
| <i>c</i> (Å) | 13.683(2) | 12.191(2) |
| α (°) | 105.464(2) | 73.002(3) |
| β (°) | 91.531(2) | 75.898(3) |
| γ (°) | 98.713(2) | 79.908(3) |
| V (Å ³) | 1392.8(3) | 958.2(3) |
| Ζ | 1 | 1 |
| $\rho_{\rm calc} \ (\rm g/cm^3)$ | 1.552 | 1.583 |
| $\mu \text{ (mm}^{-1})$ | 0.473 | 0.645 |
| θ range (°) | 1.56-26.41 | 1.78–26.48 |
| Index range | $-10 \leq h \leq 10$ | $-10 \leq h \leq 10$ |
| | $-15 \leq k \leq 15$ | $-12 \leq h \leq 12$ |
| | $-17 \leq l \leq 17$ | $-15 \leq h \leq 15$ |
| Total (independent) reflections | 12879 (5695) | 8836 (3941) |
| Final <i>R</i> indices $[I > 2\sigma(I)]$ | $R_1 = 0.0434, wR_2 = 0.0960$ | $R_1 = 0.0439, wR_2 = 0.0872$ |
| R indices (all data) | $R_1 = 0.0584, wR_2 = 0.1012$ | $R_1 = 0.0718, wR_2 = 0.0964$ |
| Largest different peak/hole (e/Å3) | 0.617/-0.311 | 0.556/-0.258 |

disordered over two orientations in an 80/20 ratio. All non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were placed in calculated positions and refined as riding atoms.

2.6.3. Structure refinement of 4-acetone

This compound crystallized in the triclinic system where the space group $P\bar{1}$ was confirmed by successful solution and refinement of the structure. The structure was solved by a combination of direct methods and difference Fourier synthesis, and refined by full-matrix least-squares against F^2 , using the SHELXTL software package [13]. The Ag and P atoms lie on a centers of symmetry; all other atoms are on general positions. The asymmetric unit is made up of the Ag ion, one $C_6H_5[C(pz)_2(2\mbox{-}py)]$ ligand, half a PF_6^- anion, and half an acetone molecule of crystallization. All components of the crystal (cation, anion, solvent) are affected by disorder. The ligand bound to Ag is disordered over all three possible κ^2 , κ^0 conformations allowed by the combination of two pyrazolyl rings (pz) and one pyridyl ring (py). Only the donor rings are affected; the central methine carbon and the pendant phenyl ring behave normally. Referring to the ring numbering scheme in Figure 5a, the average composition of ring "1n" is 0.75 pz/0.25 py; that of ring "2n" is 0.75 pz/0.25 py, and that of ring "3n" is 0.50/0.50 pz/py. These values were arrived at by initially refining the pz/py composition of each ring with a free variable constrained to sum to unity (SHELX FVAR card), and then fixing the ring occupation factors at reasonable values, such that the overall composition of the ligand would be $PhC(pz)_2py$. The PF_6^- anion is rotationally disordered about one F–P–F axis in a 0.59/0.41 ratio. Finally, the acetone molecule of crystallization is disordered about an inversion center. To achieve a stable refinement, a total of 13 restraints (SHELX EADP and SADI) were employed. Eventually, all non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were placed in calculated positions and refined using a riding model. Solution and refinement in the space group *P*1 resulted in the same ligand pz/py ring and PF₆ disorder, as well as unstable ring geometries and large correlations between inversion-related atoms. Therefore, the disorder model in *P*1 was retained.

3. Results and discussion

3.1. Syntheses of ligands

The bitopic and monotopic aryl scorpionates 1 and 2, respectively, were prepared by the CoCl₂ catalyzed rearrangement reaction between bis(1-pyrazolyl)sulfone (prepared in situ by the reaction between NaH, Hpz, and SOCl₂ in THF) and the appropriate aryl(pyridyl)ketone in THF (Scheme 1). While the reaction to produce the monotopic derivative 2 as described in the literature proceeded smoothly (over the period of about one day), longer reaction times were necessary in order to obtain appreciable quantities of the corresponding bitopic derivative 1. Even after four days at reflux, the starting material was only 60% consumed and the reaction produces a 1:2 mol ratio of the mono-derivatized compound 1a and the desired bitopic compound 1. The two products are easily separable by column





chromatography since **1** is strongly retained on silica whereas **1a** is not. It should be noted that yields of either **1** or **2** were not improved by using $CO(pz)_2$ as a replacement for $S(O)(pz)_2$. The low yields and long reaction times for the preparation of **1** and **2** can be contrasted with the preparation of $HC(pz)_2(py)$ by using similar conditions (45%, 4 h) [14]. These observations are consistent with those originally made by Thé and Peterson who indicated that the relative reactivity order for $CoCl_2$ catalyzed rearrangement of aryl carbonyls was: $PhC(O)H > PhC(O)CH_3 \gg Ph_2C(O)$ [15].

Regardless of the stoichiometry of reagents (mol ratios of 2, 1, and 0.5 were investigated), the reactions between silver hexafluorophosphate and either 1 or 2 always produced $[Ag(1)_2](PF)_6$ (3), and $[Ag(2)_2][PF_6]$ (4), respectively, as indicated from elemental analyses, mass spectral data, and X-ray diffraction studies (vide infra). The insensitivity of the product's metal:ligand mol ratio on the stoichiometry of reactants is fairly common in silver chemistry and has been reported previously for reactions between silver salts and a series of tris(pyrazolyl)methane ligands [16]. Compounds 3 and 4 are hygroscopic but otherwise air stable colorless solids that can be stored for weeks without appreciable decomposition under ambient light. Each is soluble in acetonitrile, moderately soluble in acetone, slightly soluble in methylene chloride, but insoluble in most other common (less polar) solvents. The NMR spectra of each compound in acetone- d_6 show one set of resonances that differ from those of the pure ligand by a downfield shift. This result for 3, where the stoichiometry and solid state structure (vide infra) indicate the presence of both free and coordinated $C(pz)_2(py)$ groups, can be explained by fast exchange between coordinated and non-coordinated ends of the ligand on the NMR time scale, in accord with the known lability of silver compounds.

The results of single crystal X-ray diffraction study of **3** reveal the monotopic nature of the potentially bitopic ligand **1**. An ORTEP diagram is given in Fig. 1 and important bond distances and angles are provided in Table 2. In the solid state, two ligands are bonded to one silver in a κ^2 -fashion via two pyrazolyl groups; the



Fig. 1. Two views of the structure of the cation in Ag(κ^2 -m-C₆H₄[C(pz)₂(2-py)]₂)₂(PF₆) (3). Top: ORTEP diagram with 50% thermal ellipsoids. Bottom: ball and stick view emphasizing planar geometry of nitrogens about silver. Hydrogen atoms have been omitted for clarity in each.

Table 2 Selected bond distances and angles in $\{Ag(\kappa^2-m-C_6H_4[C(pz)_2(2-py)]_2)_2\}(PF_6), 3$

| Bond distances (Å) | | | | | | |
|--------------------|------------|-------------------|------------|------------------|------------|--|
| Ag-N(11) | 2.398(2) | N(11)–N(12) | 1.365(3) | N(12)–C(1) | 1.482(3) | |
| Ag-N(21) | 2.279(2) | N(11)–N(12) | 1.365(3) | N(11)–N(12) | 1.365(3) | |
| Pond angles (°) | | | | | | |
| bond angles () | | | | | | |
| N(11)-Ag-N(21) | 76.95(8) | N(11)–Ag–N(21a) | 103.05(8) | N(11)–Ag–N(11a) | 180.00 (0) | |
| N(21a)–Ag–N(11a) | 76.95(8) | N(21)–Ag–N(11a) | 103.05(8) | N(21)–Ag–N(21a) | 180.00 (0) | |
| Ag-N(11)-C(13) | 132.46(18) | Ag-N(11)-N(12) | 121.56(18) | N(11)-N(12)-C(1) | 119.59(18) | |
| C(11)-N(12)-C(1) | 127.60(20) | N(12)-C(1)-N(22) | 110.62(18) | C(31)-C(1)-C(2) | 112.89(18) | |
| C(1)-N(22)-N(21) | 119.25(20) | C(21)-N(22)-N(21) | 111.60(20) | Ag-N(21)-N(22) | 124.55(2) | |
| Ag-N(21)-C(23) | 129.20(2) | | | | | |

Symmetry transformation: -x + 1, -y + 1, -z + 2.

pyridyl part of the bonded $C(pz)_2(py)$ group is not coordinated to the silver(I). On each ligand, one of the two $C(pz)_2(py)$ groups is not bonded to a silver(I).

One striking feature of the structure is the planar coordination geometry of the nitrogen donor atoms about silver. There are two short and two longer Ag–N bonds (the silver atom resides on an inversion center) of 2.279 and 2.398 A involving Ag-N(21) and Ag-N(11), respectfully. These distances are comparable to those found in related systems [5,6,23]. Since the sum of the four N-Ag-N angles is 360°, the coordination geometry about silver can best be described as distorted square planar where the distortion occurs as an elongation along one axis of the plane (rectangular planar coordination). An inspection of Fig. 1 would appear to suggest, using the scorpionate vernacular, that the planar arrangement is forced by the aryl group serving as a 'non-venomous' stinger. While it would be surprising to have C- rather than N-coordination, aryl coordination has been observed in other systems [26,27]. In the case of 3, the closest contact between silver and the pyridyl ring is associated with the ipso carbon, C(31), (bottom of Fig. 1) where the corresponding Ag-C(31) bond distance of 3.193 Å is outside the 2.4–2.9 Å range found for η^1 silver(I)-arene π complexes [17–19]. As far as we are aware, there are only five other examples of tetracoordinate silver complexes that exhibit square planar coordination geometry as opposed to the more typical tetrahedral or distorted tetrahedral geometries [20,21]. The AgN_4C ring adopts a boat conformation (Fig. 2(a)). If silver is assigned to the bow and C(1) to the stern, the puckering parameters originally defined by Cremer and Pople [22] are Q = 0.910, $\theta = 83.1^{\circ}$, and $\phi = 1.78$. The latter two values may be compared to those for an ideal boat conformation ($\theta = 90^{\circ}$ and $\phi = 0$) and for an ideal half-boat ($\theta = 54.7^{\circ}$ and $\phi = 0$); the puckering amplitude O in these cases would depend on the bond lengths between the ring atoms. It should be noted that the related compound $\{Ag[(pz)_2CMe_2]_2\}(ClO_4)$ [23] contains two different AgN₄C six-member rings and each adopts a slightly distorted half-boat conformation (Fig. 2(b)). The puckering parameters $Q = 0.662, 0.634; \theta = 73.2^{\circ},$



Fig. 2. Comparison of the AgN_4C chelate rings and coordination geometry about silver between (a) square planar compound **3** (with boat conformation) and (b) distorted tetrahedral $Ag[(pz)_2CMe_2]_2(ClO_4)$ (with a half-boat conformation).

72.5°; and $\phi = 6.6^{\circ}$, 5.5° were determined from the data obtained from the Crystallographic Information File extracted from the Cambridge Structural Database after a phase adjustment for consistency in atom labeling and normalization to allow meaningful comparison with 3 (Reference code; SIKYOA). The difference between the boat conformation of the AgN₄C ring in 3 and the halfboat conformation in $\{Ag[(pz)_2CMe_2]_2\}(ClO_4)$ is found in the fold angles involving the respective silver atoms (and to a lesser extent those involving the carbon atoms). The fold angle can be defined as being the deviation from planarity created by the displacement of one atom (at either the bow or stern) from the four (coplanar) atoms that would represent the deck of the boat. In the case of 3, the fold angles are the complement to those found in Fig. 2(a); that associated with silver is 32.3° whereas that associated with C(1) is 61.4°. The corresponding values in $\{Ag[(pz)_2CMe_2]_2\}(ClO_4)$ are 7.6° and 6.6° for those involving silver and 58.6° and 59.1° for those involving carbon.

Given that there does not to appear to be any significant silver(I)- π interactions in **3**, the unusual coordination environment about silver is likely due to both steric and electronic effects associated with the presence of multiple arene substituents bound to the central methane carbon. The relative orientations of the pyridyl and pyrazolyl groups in the ligands are supported by multiple intracationic CH··· π interactions as shown in Fig. 3. The distances and angles associated with the CH··· π interactions are given in Table 3 and are in



Fig. 3. View of the cation in 3 showing the intracationic CH- π interactions.

Table 3

Summary of non-covalent interactions involving $\{Ag(\kappa^2-m-C_6H_4-[C(pz)_2(2-py)]_2)_2\}(PF_6), 3$

| Donor (D)··· Acceptor (Å) | H···A (Å) | $C(H) \cdot \cdot \cdot A$ (°) | | | | |
|---|-----------|--------------------------------|--|--|--|--|
| (a) Intramolecular CH $\cdots \pi$ interactions | | | | | | |
| $C(11)H(11)\cdots Ct[N(11)]^{a}$ | 3.546 | 118.96 | | | | |
| $C(11)H(11)\cdots Ct[C(7)]$ | 3.032 | 121.35 | | | | |
| $C(21)H(21)\cdots Ct[C(7)]$ | 3.148 | 121.00 | | | | |
| $C(7)H(7)\cdots Ct[C(33)]$ | 2.961 | 130.53 | | | | |
| (b) Intermolecular interactions | | | | | | |
| $C(64)H(64)\cdots Ct[N(12)]$ | 3.13 | 123.7 | | | | |
| $C(63)H(63)\cdots Ct[N(12)]$ | 3.23 | 120.1 | | | | |
| $C(35)H(35)\cdots Ct[N(22)]$ | 3.14 | 145.8 | | | | |
| $C(23)H(23)\cdots F(3b)^b$ | 2.43 | 142.0 | | | | |
| $C(23)H(23)\cdots F(2a)^{b}$ | 2.46 | 147.8 | | | | |
| $C(32)H(32)\cdots F(1a)^b$ | 2.51 | 145.6 | | | | |
| $C(32)H(32)\cdots F(1b)^b$ | 2.57 | 143.4 | | | | |
| $C(33)H(33)\cdots F(2a)^b$ | 2.40 | 133.2 | | | | |
| $C(23)H(23)\cdots F(2b)^{b}$ | 2.58 | 155.5 | | | | |

^a Ct refers to centroid of the arene ring that contains the element denoted in brackets.

^bAn equivalent interaction is produced through inversion.

accord with accepted values [24]. Since the CH··· π interactions occur within each ligand rather than spanning both ligands in the cation, the total number of CH- π bonding interactions would not change if the AgN₄C chelate rings adopted a half-boat conformation similar to those observed in {Ag[(pz)₂CMe₂]₂}(ClO₄). Therefore, we attribute the unusual coordination environment about silver to the forces that arrange **3** into its three dimensional supramolecular structure.

The supramolecular structure of **3** approaches that of a inorganic–organic hybrid material where the silver centers and the hexafluourophosphate anions reside in layers in the crystallographinc *ab* planes. The inorganic layers are separated by organic ligands along the *c* axis where the interlayer separation is 13.7 Å as in Fig. 4. Pyridyl rings, located above and below the AgN₄ plane also separate the cation and anions in the 'inorganic layers'. There are two types of non-covalent interactions that assist in organizing **3** in the solid state; CH··· π interactions where both pyridyl rings of the ligand act as hydrogen donors and the silver bound pyrazolyl rings act as hydrogen acceptors and CH···F interactions involving the hexafluorophosphate anion and the acidic arene (pyrazolyl and pyridyl) hydrogens. Table 3



Fig. 4. Supramolecular structure of **3** emphasizing the pseudo inorganic-organic layered structure. Large (green) polyhedra are disordered PF_6^- anions whereas the small (pink) polyhedra represent coordination sphere about silver. The red lines represent intercationic $CH \cdots \pi$ interactions. The $CH \cdots F$ interactions that associate cationic layers are highlighted and enclosed within the green polyhedra. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

provides bond distances and angles for the non-covalent interactions that support the pseudo-layered structure. There are 12 CH···F distances involving a disordered hexafluorophosphate anion and that are shorter than the limit of 2.6 Å suggested to be indicative of weak hydrogen bonding interactions (Table 3) [25]. The result of these interactions is to organize the cationic sheets along the *bc*-plane as in Fig. 4. In particular, within a given cation containing two meta-linked ligands, the hydrogens H(32) and H(33) situated meta- and para-, respectively, to the nitrogen atom of the pyridyl ring proximal to silver on one ligand and the hydrogen at the 3-position of the silver-bound pyrazolyl rings of the second ligand are each involved in short CH···F bonding interactions with the fluorines of both components of the disordered PF₆ anion. Each hydrogen interacts with a component of the orientationally disordered hexafluorophosphate anion such that the $CH \cdots F$ distances are never greater than 2.6 A. The $CH \cdots \pi$ interactions (Table 3) shown as red lines in Fig. 4 afford connectivity in a third dimension (the aaxis) such that the sheets depicted in Fig. 4 would stack directly on top of one another into and out of the plane of the paper, forming segregated anion and cation layers. The particular interactions that propagate along the *a*-axis occur between the pyridyl rings proximal to silver of one cation and the silver-bound pyrazolyl groups with the shorter Ag-N distance [Ag-N(21) 2.279(2)]. Those interactions involving the pyridyl rings on the 'silver-free' side of the meta-linked ligand of one cation and the silver-bound pyrazolyl group with the longer Ag-N distance [Ag-N(11) 2.398(2)] of support the overall structure (along the *c*-axis). The boat conformation of the AgN₄C rings is thought to maximize the total number of CH···F bonding and CH··· π interactions, thereby supporting the overall structure. A halfboat arrangement would place the acidic hydrogens of the pyridyl [H(32) and H(33)] and pyrazolyl groups [H(23)] at too great a distance for PF₆⁻ bridged CH···F interactions and would likely reduce the total number of CH··· π interactions. A future report will further address the role of groups bound to the central methine carbon on the intracationic and supramolecular structure of related silver derivatives.

In an effort to determine whether the structural motif found in **3** was unique to the meta-linked ligand or was a more common framework, an X-ray structural study of $\{Ag(\kappa^2-C_6H_5[C(pz)_2(2-py)])_2\}(PF_6)$ (**4**), the monotopic derivative of **3** was undertaken and the results are given in Fig. 5. One important feature of the structure is the nature of the disorder that afflicts the nitrogencontaining heterocycles of the ligand (Fig. 5(a)). As described in the experimental, the ligand bound to silver is disordered over all three possible κ^2 , κ^0 conformations allowed by the combination of two pyrazolyl and one pyridyl ring. Fig. 5(b) reveals one component of the disordered structure showing that the coordination geometry about silver is square planar, as in compound **3**. The overall structure again has the form of a pseudo-



Fig. 5. Results of single crystal X-ray analysis of $Ag(\kappa^2-C_6H_5[C(pz)_2(2-py)])_2(PF_6)$ (4) showing (a) ligand disorder and (b) one component of the disordered structure emphasizing the square planar geometry about silver and boat conformation of AgN_4C chelate rings.



Fig. 6. View of the pseudo-layered structure in the crystal of $Ag(\kappa^2-C_6H_5[C(pz)_2(2-py)])_2(PF_6)$ (4).

layered inorganic–organic hybrid material (Fig. 6) as in 3, however in the current case, the separation between layers is 10.3 Å. Unfortunately, detailed analysis of any other bond distances and angles in 4 is precluded since, with the exception of the silver atom, the phenyl ring and the central methine carbon of the cation, disorder affects all components of the structure (cation, anion, and solvent).

4. Conclusions

A potentially bitopic heteroscorpionate, $m-C_6H_4$ $[C(pz)_2(2-py)]_2$ (1), has been prepared by using the Peterson rearrangement reaction between two equivalents of SO(pz)₂ and one equivalent of $m-C_6H_4[C(O)(2-py)]_2$. The reactions between this ligand and silver hexafluorophosphate led only to a product with a 2:1 mol ratio of ligand to metal. X-ray structural analysis of this silver complex revealed that the ligand was bound to silver in a κ^2 -fashion via the pyrazolyl groups, the silver resided in an unusual square planar coordination environment, and the AgN₄C chelate ring adopted a boat conformation. While a half-boat arrangement is more typical of complexes with a $C(pz)_2Ag$ chelate ring, the unusual boat conformation was proposed to be due to energetics associated with the organization of the two-dimensional structure, specifically, the CH...F interactions between the hexafluorophosphate anion and hydrogen atoms of the ligand. These non-covalent forces, coupled with $CH \cdots \pi$ interactions, organize the two-dimensional structure of 3 such that it approaches a layered inorganic-organic hybrid material. The structure of the monotopic derivative $\{Ag(\kappa^2-C_6H_5[C(pz)_2(2-py)])_2\}$ (PF_6) (4) was highly disordered but also revealed the bidentate nature of the $C(pz)_2(2-py)$ scorpionate moiety towards silver and a square planar arrangement for coordination environment about the metal.

5. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam. ac.uk), CCDC 210455 for **3** and 210456 for **4**-acetone.

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