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Synthesis and structural characterization of the adducts of silver(I) perchlorate and nitrate with triphenylphosphine and bis(pyrazolyl)methane ligands of 1:1:1 stoichiometry

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Abstract

Six new adducts of the form $\mathrm{AgX:PPh_3:H_2C(pz^x)_2}$ (1:1:1) ($\mathrm{H_2C(pz^x)_2 = H_2C(pz)_2}$ = bis(pyrazolyl)methane or $\mathrm{H_2C(pz^{Me2})_2}$ = bis(3,5-dimethylpyrazolyl)methane; X = $\mathrm{ClO_4}$, $\mathrm{NO_3}$, $\mathrm{SO_3CF_3}$) have been synthesized and characterized by analytical, spectroscopic (IR, far-IR, ^{1}H and ^{31}P NMR) and two of them also by single crystal X-ray diffraction studies for comparison with counterpart adducts with 2,2′-bipyridyl (‘bpy’) derivatives reported in a previous paper, the bpy-derived ligands forming five-membered chelate rings, while the present $\mathrm{H_2C(pz^x)_2}$ should, potentially, form six-membered rings. Such is the case, the two adducts exhibiting quasi-planar $\mathrm{N_2AgP}$ coordination environments, perturbed by the approach of the oxyanion, unidentate in the case of the perchlorate but, in the case of the nitrate, an interesting disordered aggregate of differing unidentate modes.

Keywords: Silver(I) complexes; Phosphines; N-donor ligands; Pyrazolylmethanes; X-ray; NMR

1. Introduction

In previous papers [1,2], we have described the synthesis and structural and spectroscopic characterization of a diverse array of adducts of 1:1:1 stoichiometry formed between AgX (X = perchlorate or nitrate (also carboxylate [3], not relevant here)), tertiary phosphine, and *N*,*N*′-bidentate bases derivative of 2,2′-bipyridyl (‘bpy’), the latter capable of forming five-membered chelate rings; a number of adducts of ‘dpa’ (= bis(2-pyridyl)amine), potentially and actually capable of forming six-membered rings were also described. A number of group 11 metal complexes containing bis(pyrazol-1-yl)methanes (bidentate N-donor ligands firstly reported by Trofimenko [4]) has been recently described: closed-shell $\mathrm{[AgL_2]^+}$ [5–8] and $\mathrm{[CuL_2]^+}$ [9,10] (L = RR′C(pz)$_2$, R,R′ = H, Me, Ph, CH$_2$Ph, py, Fc) species, $\mathrm{[Cu_2(\mu\text{-}X)_2L_2]}$ [11,12] (X = halogen or pseudo-halogen), $\mathrm{[CuL(NCMe)_2]^+}$ and $\mathrm{[CuL(NCMe)]^+}$ [13], L being bidentate chelate. A dinuclear $\mathrm{[Ag_2(\mu\text{-}L)_2](OTf)_2}$ (OTf = trifluoromethanesulfonate) in which the ligand bridges both silver centres, has been also described [14]. Our group has reported the formation of adducts between copper salts and bidentate ligands $\mathrm{[H_2C(pz^x)_2]}$ also in the presence of ancillary ligands such as mono- or bidentate P-donors [15,16], and, in the above context, we were interested to explore the nature of any counterpart silver adducts to the above, using for the purpose $\mathrm{H_2C(pz)_2}$ = bis(pyrazolyl)methane and $\mathrm{H_2C(pz^{Me2})_2}$ = bis(3,5-dimethyl)pyrazolylmethane, potentially capable of forming

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six-membered chelate rings as demonstrated elsewhere [8]. We record the results of this work hereunder.

2. Experimental

All syntheses and handling were carried out in the air. All chemicals were purchased from Aldrich and Lancaster and used without further purification. Elemental analyses (C, H, N) were performed in-house with a Fisons Instruments 1108 CHNS-O Elemental Analyser. IR spectra were recorded from 4000 to 100 cm^{-1} with a Perkin–Elmer System 2000 FT-IR instrument. ^1H, ^{13}C and ^{31}P NMR spectra were recorded on a Mercury Plus Varian 400 NMR spectrometer (400 MHz for ^1H, 100 MHz for ^{13}C, and 162.1 MHz for ^{31}P) or on a Varian VXR-300 (300 MHz for ^1H, 75 MHz for ^{13}C, and 121.4 MHz for ^{31}P). H and C chemical shifts are reported in ppm versus $SiMe_4$, P chemical shifts in ppm versus H_3PO_4 85%.

2.1. Syntheses

Safety note. Perchlorate salts of metal complexes with organic ligands are potentially explosive! Only small amounts of materials should be prepared, and these should be handled with great caution.

2.1.1. $AgClO_4$:PPh_3:$H_2C(pz)_2$ (1:1:1) (**1**)

To a MeCN solution containing 0.207 g (1.0 mmol) of $AgClO_4$ and 0.262 g (1.0 mmol) of triphenylphosphine, 0.148 g (1.0 mmol) of $H_2C(pz)_2$ was added. The reaction was stirred under reflux for 14 h in a round-bottomed flask protected from the light. The solution was then evaporated and the residue washed with diethyl ether. A precipitate formed that has been identified as compound **1** (80% yield); m.p. 148–150 °C. *Anal.* Calc. for $C_{25}H_{23}N_4AgClO_4P$: C, 48.61; H, 3.75; N, 9.07. Found: C, 49.01; H, 3.64; N, 9.01%. IR (nujol, cm^{-1}): 3113w (CH) 1962w br, 1888w br, 1822w br, 1770w br (ClO_4), 1584w, 1514s (C⋯C, C⋯N), 1082 sbr 620 br, (ClO_4), 522s, 492s, 439m, 401m. ^1H NMR ($CDCl_3$): δ, 6.30 (br, 2H, $H4_{pz}$), 6.57 (br, 2H, CH_2), 7.27–7.43 (m, 17H, $CH_{Ph} + H5_{pz}$), 8.20 (br, 2H, $H3_{pz}$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 15.5 (d, br, ^1J ($^{31}P, Ag) = 710$ Hz).

2.1.2. $AgNO_3$:PPh_3:$H_2C(pz)_2$ (1:1:1) (**2**)

Compound **2** was prepared following a procedure similar to that reported for **1** by using $AgNO_3$ (0.169 g, 1.0 mmol), PPh_3 (0.262 g, 1.0 mmol) and $H_2C(pz)_2$ (0.148 g, 0.1 mmol); m.p. 138–140 °C. *Anal.* Calc. for $C_{25}H_{23}N_5AgO_3P$: C, 51.74; H, 3.99; N, 12.07. Found: C, 51.92; H, 4.03; N, 11.65%. IR (nujol, cm^{-1}): 3102w (CH), 1891w, 1826w, 1766, 1741br (NO_3), 1584w, 1572w, 1517s (C⋯C, C⋯N), 1360brm 1309s br, 1284m (NO_3) 612w, 520m, 493m, 442w, 409w. ^1H NMR ($CDCl_3$): δ, 6.25 (t, 2H, $H4_{pz}$), 6.49 (s, 2H, CH_2), 7.44 (m, 15H, CH_{Ph}), 7.48 (s, 2H, $H5_{pz}$), 7.98 (d, 2H, $H3_{pz}$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 15.0 (s, br); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 223 K): 15.4 (d, br, $^1J(^{31}P, Ag) = 680$ Hz).

2.1.3. $AgSO_3CF_3$:PPh_3:$H_2C(pz)_2$ (1:1:1) (**3**)

Compound **3** was prepared following a procedure similar to that reported for **1** by using $AgSO_3CF_3$ (0.256 g, 1.0 mmol), PPh_3 (0.262 g, 0.1 mmol) and $H_2C(pz)_2$ (0.148 g, 0.1 mmol); m.p. 168–171 °C. *Anal.* Calc. for $C_{26}H_{23}AgF_3N_4O_3PS$: C, 46.79; H 3.47; N, 8.39. Found: C, 47.21; H, 3.67; N, 8.12%. IR (nujol, cm^{-1}): 3137 (CH), 1573w, 1557w, 1537w, 1515m, 1504w ν(C⋯C, C⋯N), 1281s, 1245m, 1224m, 1211m, 1165m, 1140m 1093m (O_3SCF_3), 640s, 571m, 520s, 496s, 437m, 401m, 365m . ^1H NMR ($CDCl_3$): δ, 6.31 (t, 2H, $H4_{pz}$), 6.70 (s, 2H, CH_2), 7.38 (d, 2H, $H5_{pz}$), 7.45 (m, 15H, CH_{Ph}), 8.35 (d, 2H, $H3_{pz}$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 16.1 (d, br, $^1J(^{31}P, Ag) = 727$ Hz).

2.1.4. $AgClO_4$:PPh_3:$H_2C(pz^{Me2})_2$ (1:1:1). MeCN (**4**)

To an MeCN solution containing 0.207 g (1.0 mmol) of $AgClO_4$ and 0.262 g (1.0 mmol) of triphenylphosphine, 0.408 g (2.0 mmol) of $H_2C(pz^{Me2})_2$ was added. The reaction was stirred under reflux for 24 h in a round-bottomed flask protected from the light. A colorless precipitate formed which was filtered off, washed with MeCN and identified as compound **4**. Upon slow evaporation at room temperature of the mother liquor, small crystals were formed that were identified as compound **4**; m.p. 158–160 °C. *Anal.* Calc. for $C_{31}H_{34}AgClN_5O_4P$: C, 52.08; H, 4.79; N, 9.80. Found: C, 52.40; H, 4.72; N, 9.71%. IR (nujol, cm^{-1}): 3132w (CH), 2250w (C–N), 1990w br, 1901w br, 1820w br, 1780w br (ClO_4), 1556s ν(C⋯C, C⋯N), 1074 sbr, 1031br $\nu(ClO_4)$, 625s br, 500s, 470w, 429w. ^1H NMR ($CDCl_3$): δ, 1.98 (s, 6H, 5-CH_{3pz}), 2.00 (s, 3H, CH_3CN), 2.48 (s, 6H, 3-CH_3pz), 5.89 (s, 2H, $H4_{pz}$), 6.31 (s, 2H, CH_2), 7.47 (m, 15H, CH_{Ph}). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 294 K): 15.9 s br. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 223 K): 15.8 (d br, $^1J(^{31}P, Ag) = 680$ Hz).

2.1.5. $AgNO_3$:PPh_3:$H_2C(pz^{Me2})_2$ (1:1:1) (**5**)

Compound **5** was prepared following a procedure similar to that reported for **4** by using $AgNO_3$ (0.169 g, 1.0 mmol), PPh_3 (0.262 g, 1.0 mmol) and $H_2C(pz^{Me2})_2$ (0.408 g, 2.0 mmol); m.p. 197–198 °C. *Anal.* Calc. for $C_{29}H_{31}AgN_5O_3P$: C, 54.73; H, 4.91; N, 11.00. Found: C, 54.92; H, 4.78; N, 11.2%. IR (nujol, cm^{-1}): 3156w (CH) 1887w, 1830w, 1745w, 1678w, 1587w (NO_3) 1557s, 1521s, (C⋯C, C⋯N), 1340br, 1300br, 1260br (NO_3), 521s, 503m, 489s, 470w, 441w, 426w, 345w, 324w, 279w, 253w. ^1H NMR ($CDCl_3$): δ, 1.95 (s, 6H, 5-CH_{3pz}), 2.43 (s, 6H, 3-CH_{3pz}), 5.83 (s, 2H, $H4_{pz}$), 6.33 (s, 2H, CH_2), 7.47 (m, 15H, CH_{Ph}). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): 15.6 (d, br, $^1J(^{31}P, Ag) = 574$ Hz).

2.1.6. AgO_3SCF_3:PPh_3:$H_2C(pz^{Me2})_2$ (1:1:1) (**6**)

Compound **6** was prepared following a procedure similar to that reported for **4** by using AgO_3SCF_3 (0.385 g,