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New oligo-/poly-meric forms for MX:dpex (1:1) complexes ($M = Cu^I$, Ag^I; X = (pseudo-)halide; dpex = $Ph_2E(CH_2)_xEPh_2$, E = (P), As; $x = 1, 2$)

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Abstract

Single-crystal X-ray structural characterizations of MX:dpam (1:1) ('dpam' = $Ph_2AsCH_2AsPh_2$) are reported for MX = AgCl, Br; CuI, CN/Cl (all isomorphous) and AgI, AgSCN, CuSCN arrays, all being of the novel form $[(\mu\text{-X})\{M(\mu\text{-X})(\mathit{As}\text{-dpam-}\mathit{As}')_2M'\}]_\infty$, essentially the familiar $M(E\text{-dpem-}E')_2M'$ binuclear array with both 'bridging' and (linking) 'terminal' (pseudo-)halides involved in the polymer. A different arrangement of bridging and linking entities is found with AgX:dpae $(1:1)_{2(\infty|\infty)}$, X = Br, NCO, 'dpae' = $Ph_2As(CH_2)_2AsPh_2$, now comprising $[M(\mu\text{-X})_2(\mathit{As}\text{-dpae-}\mathit{As})M]$ kernels linked by *As*-dpae-*As*′, while in the thiocyanate analogue $Ag\binom{SCN}{NCS}Ag$ units are linked by the dpae ligands into a two-dimensional web. Synthetic procedures for all adducts have been reported. All compounds have been characterized both in solution (^1H, ^{13}C, ^{31}P NMR, ESI MS) and in the solid state (IR).

Keywords: Silver; ^{31}P NMR; ESI MS; X-ray crystal structure; Diphosphine

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1. Introduction

In the preceding pair of papers [1,2], we have described the structural definition of adducts of the form MX:dpem (1:1) (MX = simple coinage metal(I) (Cu, Ag) salt, dpem ≡ $Ph_2E(CH_2)EPh_2$ (E = P, As)) in which the complex species were discrete. These arrays were largely exclusive of X = (pseudo-)halide/dpam adducts (AgCl, NCO excepted); many of the latter systems, which we have found to present in polymeric form, are described hereunder.

For dpee ≡ $Ph_2E(CH_2)_2EPh_2$ ligands, there are, by comparison, remarkably few derivatives of this type which have been structurally characterized beyond MX:dppe (1:2), these of the form $[M(dppe)_2]^+X^-$ as described in [1], and restricted seemingly to only a handful of complexes of the form MX:dppe (2:3) (see [3]), or, for dpae, MX:dpae (2:1) [4]; the current limitations we believe to be a consequence of a significant tendency on the part of dpee to link metal atoms in a *trans*-oid more intractable/often insoluble disposition in polymeric arrays, a limited selection of AgX:dpae (1:1) adducts as defined below being offered which assist this conjecture. We describe here the spectroscopic and structural characterization of an extended series of adducts of 1:1 stoichiometry MX:dpex to assist our understanding of the Ag(I) species containing (diphosphine or) diarsine ligands, present both in solid and solution.

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2. Experimental

2.1. Materials and methods

All chemicals were purchased from Aldrich and Lancaster and used without further purification. Elemental analyses (C,H,N,S) 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. ^{1}H-, ^{13}C and ^{31}P-NMR spectra were recorded on a VXR-300 Varian spectrometer (300 MHz for ^{1}H, 75.0 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 shift in ppm versus 85% H_3PO_4. The electrical conductances of the acetone, dichloromethane, DMSO and acetonitrile solutions were measured with a Crison CDTM 522 conductimeter at room temperature. Positive and negative electrospray mass spectra were obtained with a Series 1100 MSI detector HP spectrometer, using an acetonitrile mobile phase. Solutions (3 mg/ml) for electrospray ionization mass spectrometry (ESI-MS) were prepared using reagent grade acetone or acetonitrile. For the ESI-MS data, masses and intensities were compared to those calculated by using the IsoPro Isotopic Abundance Simulator Version 2.1 [5]; peaks containing silver(I) and copper ions are identified as the centers of isotopic clusters.

2.2. Syntheses

2.2.1. Syntheses of the silver and copper complexes

The colorless complexes described were obtained by crystallization, by slow evaporation, cooling, or interdiffusion, of solutions of millimolar stoichiometry of the metal(I) salt and dpam, dppm or dpae ligand in a few ml of the specified solvent. Some silver(I) and copper complexes were amenable to synthesis as pure bulk samples, analyses and spectral data for which are given below.

2.2.1.1. AgCl : dpam(1:1) · $1\frac{1}{2}$py (**1**). dpam (0.397 g, 1.0 mmol) was added at room temperature to a pyridine (py) solution (10 ml) of AgCl (0.143 g, 1.0 mmol). The solution was stirred overnight, then diethyl ether was added (5 ml). A colorless precipitate formed which was stirred for 3 h, then filtered off and washed with diethyl ether to give complex **1** as a colorless crystalline solid in 80% yield. M.p. 246 °C dec. ^{1}H NMR ($CDCl_3$, 293 K): δ 2.83 (s, 2H, CH_{2dpam}), 7.2–7.5 (m, 20H, C_6H_5), 7.7 (pt, 3H CH_{py}), 8.7 (m, 4.5H, CH_{py}). ^{13}C NMR ($CDCl_3$, 293 K): δ 24.30 (s, CH_{2dpam}), 128.95, 128.25, 132.94, 136.2 (C_{arom}), 124br, 138.2, 149.9 (C_{py}). IR (nujol, cm^{-1}): 3065w, 3045w (CH_{arom}), 1592w, 1576w, 1560w (C≡C); 582m, 552w, 476m, 458m, 410w, 401w, 329m, 310m, 268w, 150br. ESI MS (+): 1195 [100] $[Ag_2Cl(dpam)_2]^+$. *Anal.* Calc. for $C_{65}H_{59}Ag_2As_4Cl_2N_3$: C, 53.16; H; 4.05; N, 2.86. Found: C, 53.32; H, 4.02; N, 2.85%. Λ_m (CH_2Cl_2, 10^{-4} M): 0.5 Ω^{-1} mol^2 cm^{-1}.

2.2.1.2. AgBr : dpam(1:1) · $1\frac{1}{2}$py (**2**). Compound **2** has been obtained as a colorless crystalline solid using a similar procedure to that reported for **1**, in 70% yield. Recrystallization from MeCN yields **2**. M.p. 250 °C dec. ^{1}H NMR ($CDCl_3$, 293 K): δ 2.75 (s, 2H, CH_{2dpam}), 7.2–7.5 (m, 20H, C_6H_5), 7.7 (pt, 3H CH_{py}), 8.6 (m, 4.5H, CH_{py}). ^{13}C NMR ($CDCl_3$, 293 K): δ 24.53(s, CH_{2dpam}), 128.8, 128.9, 130.9, 136.2 (C_{arom}), 124br, 139.4, 149.9 (C_{py}). IR (nujol, cm^{-1}): 3065 (CH_{arom}), 1628w, 1592w, 1581w, 1573w (C≡C); 499sh, 480s, 470s, 459m, 449sh, 410w, 325m, 307m, 305w, 275w, 229vw, 203w, 156m, 119sbr, 113sbr, 92sbr. ESI MS (+): 1240 [100] $[Ag_2Br(dpam)_2]^+$. *Anal.* Calc. for $C_{65}H_{59}Ag_2As_4Br_2N_3$: C, 50.13; H; 3.82; N, 2.70. Found: C, 49.90; H, 4.01; N, 2.45%. Λ_m (CH_2Cl_2, 10^{-4} M): 1 Ω^{-1} mol^2 cm^{-1}.

2.2.1.3. AgI : dpam(1:1) · 7/4MeCN (**3**). dpam (0.397 g, 1.0 mmol) was added to a MeCN solution of AgI (0.234 g, 1.0 mmol). The solution was stirred overnight. A colorless precipitate formed which was stirred for 3 h, then filtered off and washed with diethyl ether to give a colorless crystalline solid in 75% yield. M.p. 182–185 °C dec. Recrystallization from MeCN yielded **3**. ^{1}H NMR ($CDCl_3$, 293 K): δ 2.75 (s, 2H, CH_{2dpam}), 7.2–7.5 (m, 20H, C_6H_5). ^{13}C NMR ($CDCl_3$, 293 K): δ 24.53(s, CH_{2dpam}), 128.8, 128.9, 130.9, 136.2 (C_{arom}). IR (nujol, cm^{-1}): 1573w (C≡C); 588m, 474m, 467m, 458m, 330m, 316m, 265w, 2094w, 196w, 150w, 122w, 90w. ESI MS (+): 1287 [100] $[Ag_2I(dpam)_2]^+$. *Anal.* Calc. for $C_{25}H_{22}AgAs_2I$ (unsolvated) C, 42.47; H; 3.14. Found: C, 42.13; H, 3.26%. Λ_m (CH_2Cl_2, 10^{-4} M): 1 Ω^{-1} mol^2 cm^{-1}.

2.2.1.4. AgSCN:dpam (1:1) (**4**). Compound **4** has been obtained as a colorless crystalline solid using a similar procedure to that reported for **1**, with pyridine as solvent (82% yield). M.p. >300 °C dec. ^{1}H NMR ($CDCl_3$, 293 K): δ 2.85 (s br, 2H, CH_{2dpam}), 7.2m, 7.4m (m, 20H, C_6H_5). ^{13}C NMR ($CDCl_3$, 293 K): δ 24.57 (s, CH_{2dpam}), 128.88, 129.12, 133.08, 138.31 (C_{arom}). IR (nujol, cm^{-1}): 3065w (CH_{arom}), 2137, 2084m (SCN), 1592w, 1579w (C≡C); 553w, 474m, 456m, 411w, 372m, 312m, 269w, 202w, 195w, 150w, 119w, 109w, 99w, 89w, 75w. ESI MS (+):1218 [100] $[Ag_2(SCN)(dpam)_2]^+$. *Anal.* Calc. for $C_{52}H_{44}Ag_2As_4N_2S_2$: C, 48.93; H; 3.47; N, 2.19; S, 5.02. Found: C, 48.71; H, 3.63; N, 2.05; S, 4.77. Λ_m (CH_2Cl_2, 10^{-3} M): 1 Ω^{-1} mol^2 cm^{-1}.

2.2.1.5. AgBr:dpae (1:1) · MeCN (**5**). dpae (0.409 g, 1.0 mmol) was added at room temperature to a 1:1 pyridine:MeCN solution 10 ml of AgBr (0.188 g, 1.0 mmol). The solution was stirred overnight. A colorless