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Structural characterization of 1:1 adducts of silver(I) (pseudo-) halides (AgX, X = NCO, Cl, Br, I) with $Ph_2E(CH_2)EPh_2$ (E = P, As) ('dp(p/a)m') and 4:3 adducts of copper(I) halide (CuX, X = Cl, Br, I), containing trinuclear cations, of the form $[X_2Ag_3(dppm)_3]X$ and $[X_2Cu_3(dppm)_3](CuX_2)$ and the novel neutral $[(OCN)_3Ag_3(dpam)_3]$

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Abstract

The extension of systematic structural definition of arrays of the form $MX:EPh_3$ (1:*n*) (M = univalent coinage metal, X = (pseudo-)halide, E = P, As, Sb, *n* = integer (1–4)) into complexes of chelate congeners with ligands of the form 'dpex' ($Ph_2E(CH_2)_xEPh_2$):MX:dpex (1:*n*) is commenced. Syntheses, spectroscopic features and single crystal X-ray structural characterizations are reported for 1:1 adducts of bis(diphenylphosphine)methane ('dppm') with silver(I) (pseudo-)halides, AgX (X = Cl, Br, I, NCO), and for their arsenic ('dpam') Cl, NCO counterparts AgX:dpam (1:1), also for an array of 4:3 adducts of copper(I) halides (CuX, X = Cl, Br, I) with dppm. All species recorded here (the novel molecular $[(OCN)_3Ag_3(dpam)_3]$ excepted) contain trinuclear cations, as $[X_2A_3g(dpem)_3]X(\cdot nS)$ and $[X_2Cu_3(dppm)_3](CuX_2)(\cdot nS)$, enabling systematic comparison between a wide diversity of species.

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

1. Introduction

A recent series of papers has augmented and summarized the contemporary status of the structural definition of families of simple complexes of the form $MX:EPh_3$ (1:*n*), M = univalent copper or silver, X = simple halide or pseudohalide (Cl, Br, I, SCN) or oxyanion (ClO_4, NO_3, or simple carboxylate), E = P, As, Sb, *n* = 1 [1,2], 2 [3], 3 [4], 4 [5]. Similar adducts MX:L (1:*n*) *n* = 1, 2 (predominantly 1) have been extensively but sporadically defined for the derivative bidentate ligands dpex ($Ph_2E(CH_2)_xEPh_2$), *x* integral (predominantly 1), E = P (predominantly), As, (Sb (not at all)), studies carried out predominantly for copper(I) with extensive studies also for gold(I), complexes of silver(I) being relatively neglected. The latter is the starting point for the present

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body of work which focusses substantially on that metal, with adjunct studies on copper(I) counterparts or relatives; gold complexes, often rather different in nature, are referred to only where they give added point to copper/silver comparisons or trends. We define the accessible ligands dppx as 'dppm' ($x = 1$), 'dppe' ($x = 2$), 'dppp' ($x = 3$), 'dppb' ($x = 4$), 'dppn' ($x = 5$), 'dpph' ($x = 6$), 'dppf' ($Ph_2P(Fc)PPh_2$) ('Fc' = $(C_5H_4)Fe(C_5H_4)$). Structurally defined adducts of the form MX:L (1:2) are remarkably few in number and defined for a limited variety of ligands, all with E = P. An ionic binuclear form is defined for $[(P,P'\text{-dppe})Ag(P\text{-dppe-}P')_2Ag(P,P'\text{-dppe})](NO_3)_2$ [6], the others being mononuclear, of the ionic form $[M(P,P'\text{-dppx})_2]^+X^-$ with four-coordinate metal for dppe: $[Cu(dppe)_2](ClO_4)$ [7], tfa ($\equiv F_3CCO_2$) [8], PF_6 [9], $[Ag(dppe)_2](NO_3)$ [10], dppp: $[Cu(dppp)_2](ClO_4)$ [11,12], (BF_4) [7], $[Ag(dppp)_2](SCN)$ [13], dppf: ($[Cu(dppf)(dppfO)](BF_4)$ [14]), $[Ag(dppf)_2](ClO_4)$ [15], (BF_4) [16] and three-coordinate $[Ag(P,P'\text{-dppp})(P\text{-dppp})](X)$ in $[Ag(dppp)_2]$ Cl, Br, I, CN [13]. The only other arrays with *m*:*n* MX:L stoichiometry with $n/m > 1$ are the 2:3 adducts, binuclear $[Ag(P\text{-dppm-}P')_3Ag](NO_3)_2$ [17] $[((P,P'\text{-dppf})M)_2\ (P\text{-dppf-}P)]X_2$ for M/X = Cu/ClO_4 [18], Ag/PF_6 [19] and the related $[((P,P'\text{-dppx})M)_2X_2\ (P\text{-dppx-}P)]$ for dppf/HCO_2/Ag [20] and for dppe/Cu, X = Cl [21,22], I [7,23], N_3 [24], with $[\{(P,P'\text{-dppe})(MeCN)Cu\}_2(P\text{-dppe-}P')](ClO_4)$ [25] an interesting variant. Seemingly, no adducts with dpex (E = As, Sb) as ligands have been defined with such stoichiometries.

Among the remaining structurally defined adducts 1:1 stoichiometry is predominant, the most numerous category here being the trinuclear $[(\mu_3\text{-}X)_2M_3(dppm)_3]X^{(\prime)}$ array, found only for dppx = dppm, with X (as unidentate donor) not only comprising the anion types listed above but also terminal alkyne and more complex systems. The 'simple' X arrays thus defined for M = Cu are $[(\mu_3\text{-}X)_2M_3(dppm)_3]X^{(\prime)}$ for X = Cl [26], Br [27–29], Br/ClO_4, I [30,31], $C{\equiv}CPh$ [32] with $X_2X' = C{\equiv}C^tBu,Cl/(PF_6)$ [33] and $C{\equiv}CPh,Cl/BF_4$ [32] interesting organometallic variants, representative of the possibility of heterogeneity within the cluster, by the incorporation of a pair of different anions, or anion plus solvent, or different metals, with the possible consequence of different charge. Beyond these possibilities, $[XCu_3(dppm)_3](Y)_2$, X, Y = $OH/(BF_4)$ [34], $C{\equiv}C^tBu/(PF_6)$ [35], and $[Cu_3(\mu_3\text{-}I)_2(\mu_2\text{-}I)(dppm)_2]$ [36] are interesting structural variants. For M = Ag, systems X = $Cl/(ClO_4)$ [37], I [31], Br [38,39], $C{\equiv}CPh/(Cl)$ [40] have been defined for $[X_2Ag_3\text{-}(dppm)_3](X^{(\prime)})$, with $[(C{\equiv}C(p\text{-}NO_2C_6H_4))Ag_3(dppm)_3\ ](BF_4)_2$ [41] a novel variant.

In the present work, initially we focus our attention on the relatively deficient array of trinuclear silver(I)/dppm species, synthesizing and structurally defining a more complete and extended series for $[X_2Ag_3(dppm)_3]X$, for X = Cl, Br and I (new phases), *N*CO and also for $[X_2Ag_3(dpam)_3]X$, X = Cl, *N*CO (the latter the neutral $[(OCN)_3Ag_3(dpam)_3]$ ('dpam' = $Ph_2As(CH_2)AsPh_2$)); for copper(I) it is shown that a series of CuX:dppm (4:3) stoichiometry, hitherto structurally undefined [42], is, in fact, an array of the form $[Cu_3X_2(dppm)_3]X'$ also, for $X' = (CuX_2)$. We present these results below.

2. Experimental

2.1. Materials and methods

All syntheses and handling were carried out under an atmosphere of dry oxygen-free dinitrogen, using standard Schlenk techniques. 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 VXR-300 Varian spectrometer (300 MHz for ^1H, 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 H_3PO_4 85%. 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 [43]; 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 complexes

The silver(I) complexes, $[Ag_3X_2(dppm)_3]X$ (X = Cl, Br, I, NCO) were also readily obtained as colourless crystals (sometimes solvated) in bulk by the standing and cooling of warm solutions, stoichiometric on the millimolar scale, of AgX with dppm in piperidine (Cl, Br, I) or ethanol (NCO), the chloride and cyanate being di-and mono-solvates, and the bromide a new phase.

*2.2.1.1. Synthesis of $[Ag_3Cl_2(dppm)_3]Cl\cdot 2pip$ (**1**).* dppm (0.384 g, 1.0 mmol) was added at room temperature to a piperidine (pip) solution (10 ml) of AgCl (0.143 g, 1.0 mmol). After the addition, the solution was stirred