



## Research paper

# Structural characterization of some adducts of the form $[M_2(\mu\text{-dppm})_2(\text{MeCN})_x]X_2$ [ $M = \text{Cu, Ag}$ ; $X = \text{ClO}_4, \text{BF}_4, \text{PF}_6$ ; $\text{dppm} = (\text{Ph}_2\text{P})_2\text{CH}_2$ ; $x = 0\text{--}4$ ]



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## ARTICLE INFO

## Article history:

Received 28 June 2016

Received in revised form 6 September 2016

Accepted 9 September 2016

Available online 13 September 2016

## Keywords:

Copper(I)

Silver(I)

Crystal structure

dppm ligand

Binuclear complex

## ABSTRACT

Structural characterizations are reported for a number of adducts of the form  $[M_2(\mu\text{-dppm})_2(\text{MeCN})_x]X_2$  ( $M = \text{univalent Cu, Ag}$ ;  $X = \text{ClO}_4, \text{BF}_4, \text{PF}_6$ ;  $\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$ ;  $x = 0\text{--}4$ ) for (a)  $M = \text{Cu}$ ,  $X = \text{BF}_4$ ,  $x = 4$  (**1**), **3** (**2**); (b)  $M = \text{Ag}$ ,  $x = 2$ ,  $X = \text{BF}_4$  (**3**),  $X_2 = \text{PF}_6, \text{PO}_2\text{F}_2$  (**4**). Within derivatives **1** and **2**, we find four- and three-coordinate copper atoms within the one species, with two and one acetonitrile molecules being coordinated, respectively; in **3** and **4**, significant bridging interactions between the  $\text{BF}_4$  and  $\text{PO}_2\text{F}_2$  anions, and the silver atoms of the dimer respectively, are found. Electrospray-ionisation mass spectral studies of **2** and **4** in MeCN solution show that MeCN is only weakly bonded to the  $M_2(\text{dppm})_2$  core, the ions of major intensity being  $[\text{Cu}_2(\text{dppm})_2(\text{BF}_4)]^+$  and overlapping  $[\text{Cu}_2(\text{dppm})_2]^{2+}/[\text{Cu}(\text{dppm})]^+$  for **2**, and  $[\text{Ag}(\text{dppm})_2(\text{PO}_2\text{F}_2)]^+$  and  $[\text{Ag}_2(\text{dppm})_2]^{2+}$  for **4**.

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## 1. Introduction

The syntheses of a number of adducts of the form  $[M_2(\mu\text{-dppm})_2(\text{MeCN})_x]X_2$  ( $M = \text{univalent Cu or Ag}$ ,  $X = \text{quasi-spherical, non-coordinating anion } (\text{ClO}_4^-, \text{BF}_4^-, \text{PF}_6^-)$ ,  $\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$ ,  $x = 0\text{--}4$ ) are recorded. Several of these [ $M = \text{Cu}$ ,  $X = \text{BF}_4$ ,  $x = 4$  (**1**), **3** (**2**);  $M = \text{Ag}$ ,  $x = \text{BF}_4$ ,  $x = 2$  (**3**);  $X_2 = \text{PF}_6/\text{PO}_2\text{F}_2$  (**4**)] have been structurally characterized by single-crystal X-ray studies, taking the binuclear form  $[(\text{MeCN})_m\{M(\text{dppm})\}_2(\text{NCMe})_n]X_2$  [ $m, n = 0, 1$  or  $2$  ( $m + n = x$ )] for the defined examples. Such complexes are generally regarded as well-defined and stable, appropriate for use as intermediates or starting materials in more extended synthetic excursions. In the course of one such, recorded in an accompanying paper [1], referring to previous studies [2,3] defining the  $\text{Cu}/X/x = 2, 4$ , arrays at the level of analysis, a preparation following that recorded for the  $x = 2$  adduct was undertaken, with an incidental parallel determination of its crystal structure, in the expectation of obtaining that adduct, which might, somewhat unusually, exhibit three-coordinate copper(I) in such a species. In the event, while the structure determination demonstrated the presence of the  $x = 4$  form, a subsequent repetition of the synthesis

with acetonitrile content diminished by dilution in dichloromethane resulted in the novel  $x = 3$  adduct (**2**). Related determinations were carried out on a number of silver(I) adducts, with the intent of defining all accessible species across the anions  $\text{ClO}_4^-$ ,  $\text{BF}_4^-$ ,  $\text{PF}_6^-$  for  $M = \text{Cu, Ag, Au}$ ; there are, of course, numerous examples from series derivative of other less innocent anions and/or solvents, which may or may not interact with the metal atom themselves. We report this work hereunder.

## 2. Results and discussion

## 2.1. Syntheses

The complexes were synthesised according to literature accounts from  $\text{CuI}$  or  $\text{AgNO}_3$  and an equivalent amount of dppm in the presence of the appropriate anion ( $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ) [2,3], and recrystallised from pure solvents (MeCN) or solvent mixtures (MeCN/ $\text{CH}_2\text{Cl}_2$  or  $\text{Et}_2\text{O}$ ) as detailed in the Experimental section. In the case where one of the anions is modelled more credibly as  $\text{PO}_2\text{F}_2$ , we surmise that partial hydrolysis of the  $\text{PF}_6^-$  anion has occurred.

## 2.2. Solution studies

Electrospray-ionisation mass spectra (ESI-MS) were recorded in positive and negative ion modes using solutions of **2** and **4** in (a)

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MeCN and (b) MeOH. Prominent peaks were identified by high-resolution mass measurements, and by matching of isotope patterns. In general, the results indicate that the MeCN found in the solid-state structures is not strongly attached to the metal centre, as there were no significant binuclear ions containing MeCN, even under the mildest conditions. Exchange of anions for formate ( $\text{HCO}_2^-$ ), used as a calibration standard, gave rise to ions such as  $[\text{Cu}_2(\text{dppm})_2(\text{HCO}_2)]^+$ .

The mass spectra are cleaner in MeCN. For **2**, spectra gave mainly  $[\text{Cu}_2(\text{dppm})_2\text{BF}_4]^+$  with varying weaker signals from  $[\text{Cu}_2(\text{dppm})_2\text{X}]^+$  ( $\text{X} = \text{CO}_2\text{H}$ , Cl, F) from adducts formed with adventitious anions in the mass spectrometer. Deprotonation of (presumably) the  $\text{CH}_2$  group of dppm led to  $[\text{Cu}_2(\text{dppm})_2-\text{H}]^+$ . An isotopic envelope centred at  $m/z$  448 could be assigned to two overlapping species  $[\text{Cu}_2(\text{dppm})_2]^{2+}$  and  $[\text{Cu}(\text{dppm})]^+$ , while under mild conditions a  $[\text{Cu}(\text{dppm})(\text{MeCN})]^+$  signal was observed.

For the silver compound **4** the two major ions were  $[\text{Ag}_2(\text{dppm})_2(\text{PO}_2\text{F}_2)]^+$  and  $[\text{Ag}_2(\text{dppm})_2]^{2+}$ , with only very weak signals from  $[\text{Ag}_2(\text{dppm})_2\text{X}]^+$  ( $\text{X} = \text{PF}_6$ , Cl). In this case the doubly-charged envelope at  $m/z$  492 did not contain detectable  $[\text{Ag}(\text{dppm})]^+$ , suggesting that  $[\text{Ag}_2(\text{dppm})_2]^{2+}$  is more robust than the copper analogue under comparable mass spectrometer conditions.

In the negative ion spectra, the only peaks observed were  $[\text{BF}_4]^-$  and  $[\text{Na}(\text{BF}_4)_2]^-$  (from **2**) or  $[\text{PF}_6]^-$  and  $[\text{PO}_2\text{F}_2]^-$  (from **4**).

In MeOH, the spectra of **2** and **4** contained ions similar to those seen in MeCN as the main species but were less clean, with other peaks arising from exchange or fragmentation processes, not all of which could be assigned. Both complexes gave a signal assigned to higher aggregates such as  $[\text{M}_3(\text{dppm})_x\text{Cl}_2]^+$  ( $x = 2, 3$ ), though whether these arose from rearrangement processes in the mass spectrometer, or from traces of  $[\text{M}_3(\text{dppm})_3\text{Cl}_2]\text{Cl}$  as a possible impurity in the original sample is not clear.

### 2.3. Structure determinations

A number of arrays of the form  $[\text{M}_2(\text{dppm})_2(\text{MeCN})_x]\text{X}_2 \cdot \text{S}$  ( $\text{X} = \text{ClO}_4$ ,  $\text{BF}_4$ ,  $\text{PF}_6$ ) have now been structurally characterized, as summarized in Table 1, which also includes data for the present studies.

Previously recorded structures of this type for  $\text{M} = \text{Cu}$  solvated with MeCN [2–4] all have  $x = 4$ , i.e., two MeCN ligands per four-coordinated ( $\text{CuP}_2\text{N}_2$ ) copper(I) atom; there are no examples with  $x < 4$ . With silver(I), the only MeCN-solvated example reported

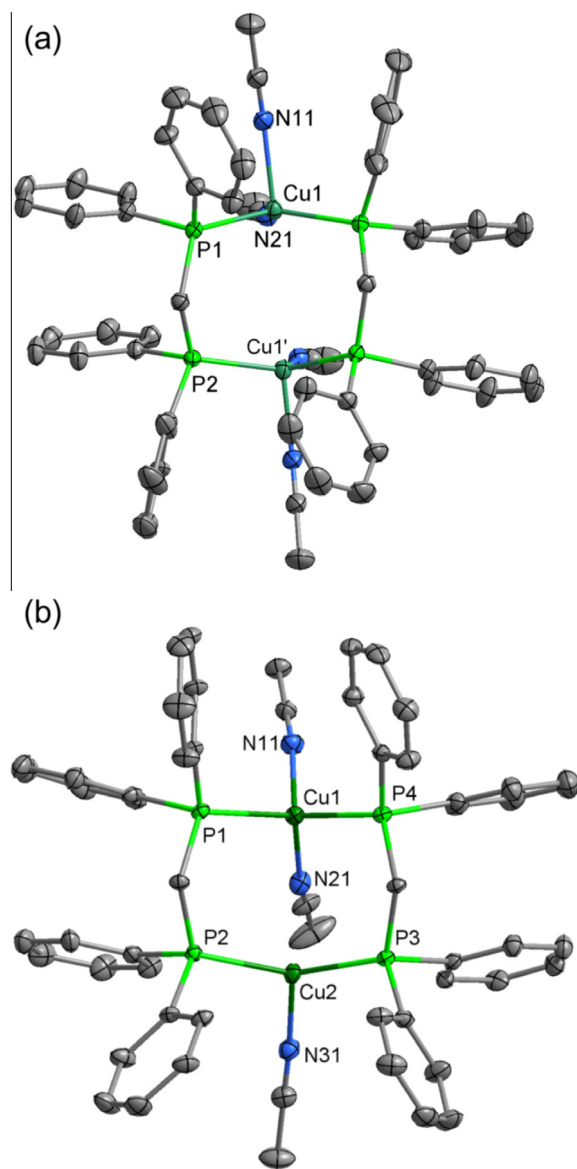


Fig. 1. Projection of the cation of  $[\text{Cu}_2(\text{dppm})_2(\text{MeCN})_4](\text{BF}_4)_2$  (**1**) (The primed atom is related by the 2-fold symmetry). (b) Projection of cation 1 of  $[\text{Cu}_2(\text{dppm})_2(\text{MeCN})_3](\text{BF}_4)_2 \cdot 0.5\text{CH}_2\text{Cl}_2$  (**2**).

Table 1

Crystallographic data for structurally characterized  $[\text{M}_2(\text{dppm})_2(\text{MeCN})_x]\text{X}_2 \cdot n\text{S}$  arrays. Data from the present study are also included.

M	X	Cpd	x	nS	Space group	Cat. symm.	a (Å)	b (Å)	c (Å)	$\beta$ (°)	V (Å <sup>3</sup> )	T (K)	CCDC refcode [Ref]
Cu	ClO <sub>4</sub>	<b>1</b>	4'	–	MonoC2/c	2	22.407(9)	13.052(6)	21.522(8)	108.69(3)	5962	RT	FEWVAE [2]
			4	–			22.1381(5)	12.7937(2)	21.2292(5)	108.510(2)	5702	100	This work
	BF <sub>4</sub>	<b>2</b>	4	–	P2 <sub>1</sub>	1 (x2)	22.411(13)	12.915(7)	21.510(12)	108.814(10)	5893	RT	QITGAD <sup>†</sup> [14]
			3	½CH <sub>2</sub> Cl <sub>2</sub>			11.6384(2)	21.1095(4)	23.2836(4)	91.651(2)	5718	100	This work
Ag	ClO <sub>4</sub>	–	–	–	Mono P2 <sub>1</sub> /n	$\bar{1}$	10.654(1)	17.364(2)	13.914(2)	104.601(1)	2491	300	RACXAV01 [5]
	BF <sub>4</sub>	3	–	Ortho Pca2 <sub>1</sub>	1	16.2494(3)	15.1087(3)	20.5511(4)	–	5046	100	This work	
	ClO <sub>4</sub>	–	–	Mono P2 <sub>1</sub> /n	$\bar{1}$	11.6819(14)	15.2304(16)	16.349(2)	107.548(10)	2774	173	NAQMOH [6]	
	ClO <sub>4</sub>	2	–	P2 <sub>1</sub> /c	$\bar{1}$	11.448(3)	15.179(4)	17.694(5)	117.47(4)	2728	295	RACXAV [5]	
	½(PF <sub>6</sub> ·PF <sub>2</sub> O <sub>2</sub> )	<b>4</b>	2	–	Ortho P2 <sub>1</sub> 2 <sub>1</sub> 2	2	14.9710(2)	20.8098(2)	8.72190(10)	–	2717	100	This work
Au	ClO <sub>4</sub>	–	–	–	Mono P2 <sub>1</sub> /n	$\bar{1}$	10.569(4)	17.648(6)	13.797(5)	105.287(5)	2482	293	NEQNIH [7]
	BF <sub>4</sub>	–	–	–	Mono P2 <sub>1</sub> /a	$\bar{1}$	15.047(5)	17.462(3)	10.532(2)	117.59(2)	2452	298	JAMKJ [8]
	PF <sub>6</sub>	–	–	–	Ortho Pnma	2	20.6825(10)	21.0325(9)	13.2577(6)	–	5767	293	MUVVEE [9]

<sup>†</sup> Notable is a structure with an overall  $x = 4$  stoichiometry, only three of these being coordinated, i.e.,  $[\text{Cu}_2(\mu\text{-dppm})_2(\mu_2\text{-NCMe})(\text{MeCN})_2](\text{ClO}_4)_2 \cdot \text{MeCN}$ : monoclinic, P2<sub>1</sub>/n.

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