This is the author-created version of the following work:

Guo, Zhifang, Wang, Nicole, Blair, Victoria L., Izgorodina, Ekaterina I., Deacon, Glen B., and Junk, Peter C. (2022) *Facile synthesis and structures of silver formamidinates and pyrazolates.* **Australian Journal of Chemistry, 75 (8 & 9) pp. 558-565.**

Access to this file is available from:

https://researchonline.jcu.edu.au/74731/

Please refer to the original source for the final version of this work:

https://doi.org/10.1071/CH21282

Facile synthesis and structures of silver formamidinates and pyrazolates

Zhifang Guo, [a, b] Nicole Wang,[a] Victoria L. Blair,[a] Ekaterina I. Izgorodina,[a] Glen B. Deacon, [a] Peter C. Junk[b]*

[a]School of Chemistry, Monash University, Clayton 3800, Vic, Australia.

[b]College of Science & Engineering, James Cook University, Townsville 4811, Qld, Australia.

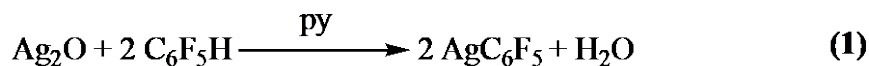*Corresponding author: peter.junk@jcu.edu.au

Abstract

Dinuclear silver formamidinates (FormH), [Ag$_2$(DFForm)$_2$(py)$_2$] (**1**) (DFForm = N,N′-bis(2,6-difluorophenyl)formamidinate), [Ag$_2$(mHForm)$_2$(py)$_3$] (**2**) and [Ag$_2$(mHForm)$_2$(CH$_3$CN)$_2$] (**2a**) (mHForm = N,N′-bis(2,3,4,6-tetrafluorophenyl)formamidinate), [Ag$_2$(pHForm)$_2$(py)$_3$] (**3**) (pHForm = N,N′-bis(2,3,5,6-tetrafluorophenyl)formamidinate), [Ag$_2$(PFForm)$_2$(py)$_3$] (**4**) (PFForm = N,N′-bis(2,3,4,5,6-pentafluorophenyl)formamidinate) and [Ag$_2$(DippForm)$_2$]·1.25CH$_2$Cl$_2$ (**5**) (DippForm = N,N′-bis(2,6-diisopropylphenyl)formamidinate), and polynuclear, mainly trinuclear, silver pyrazolates, [Ag$_3$(Ph$_2$pz)$_3$]$_2$ (**6**) (Ph$_2$pz = 3, 5-diphenylpyrazolate), [Ag(tBu$_2$pz)]$_4$ (**7**) (tBu$_2$pz = 3, 5-ditertbutylpyrazolate), [Ag$_3$(PhMepz)$_3$] (**8**) (PhMe = 3-methyl-5-phenylpyrazolate), [Ag$_3$(Phtpz)$_3$] (**9**) (Phtpz = 3-phenyl-5-(2-thienyl)pyrazolate), [Ag$_3$(ttfpz)$_3$] (**10**) (silver 3-(2-thienyl)-5-trifluoromethylpyrazolate) and [Ag$_2$(Me$_2$pz)(PPh$_3$)$_4$Cl] (**11**) (Me$_2$pz = 3,5-dimethylpyrazolate) were successfully synthesized in good yield by treating silver(I) oxide with the corresponding formamidines (FormH) or pyrazoles (pzH) either in pyridine or acetonitrile. These rapid, easily handleable and economical reactions are easily monitored by consumption of black silver oxide. All compounds are potential precursors in redox transmetallation reactions in the synthesis of lanthanoid and alkaline earth pyrazolate/formamidinate complexes.

Keywords

Silver complexes; formamidinates; pyrazolates; Crystal structures; One-pot reaction.

Introduction

Silver(I) metal-organic complexes, AgL (L = pyrazoles; amides; N-heterocyclic carbenes; polyfluoroaryls, etc.), are excellent transfer oxidising agents for the L groups to organic and metal compounds in redox transmetallation (RT) and redox transmetallation/protolysis (RTP) reactions, especially for rare earth and alkaline earth metal complexes.[1-3] Recently, we described a one-step synthetic route to AgC_6F_5 from silver oxide and pentafluorobenzene in pyridine with the exclusion of light, which provides a convenient method utilising air-stable commercial reagents [eq. (1)].[2] The reaction is easily monitored and the reagents are easy to handle. Diarylmercurials have been widely used in the RTP reactions,[4] but it is of interest to develop less toxic reagents as an alternative approach because of the toxicity of mercury.[5] AgC_6F_5 showed excellent oxidising abilities in the RTP reactions [eq.(2)].[2,6] Silver N-heterocyclic carbene complexes have also been utilised in RT reactions to synthesize Ln(II)/alkaline earth metal(II) complexes [eq.(3)], showing the suitability of the redox potentials of Ag complexes for use in RT reactions.[3] Syntheses of rare earth formamidinates and pyrazolates by RTP reactions are well developed.[4] Silver formamidinates and silver pyrazolates have potential to be useful in redox chemistry with electropositive metals, and various preparations of these silver reagents have been reported.

$$Ag_2O + 2\ C_6F_5H \xrightarrow{\ py\ } 2\ AgC_6F_5 + H_2O \qquad (1)$$

$$Ln + n\ AgC_6F_5 + n\ LH \longrightarrow Ln(L)_n + n\ Ag + n\ C_6F_5H \qquad (2)$$

$$Ln + n\ AgL \longrightarrow Ln(L)_n + n\ Ag \qquad (3)$$

Thus, the first silver formamidinate (silver N,N′-diphenylformamidine) was reported in 1956 by the reaction of silver acetate and N,N′-diphenylformamidine in pyridine yielding a dinuclear complex.[7] The first crystal structure of silver(I) N,N′-di-*p*-tolylformamidinate was reported in 1988 after using the same method.[8] Later, silver formamidinates were prepared by treating silver nitrate and ammonium hydroxide with various formamidine ligands.[9] Salt metathesis reactions, which are a general route to metal amides, utilising $AgNO_3$ and the alkali formamidinate led to intractable mixtures and formation of a black precipitate (Ag_2O). In 2014, silver formamidinates were obtained by the reaction of silver acetate and triethylamine with 2,6-dimethylphenylformamidine or 2,6-diisopropylphenylformamidine,[10] but long reaction times and heating were required.

Trinuclear silver pyrazolates were reported by using water sensitive sodium pyrazolates and silver nitrate,[11-12] sodium pyrazolates with $AgBF_4$,[13] and pyrazoles with $Ag(O_2CPh)$.[14] Further trinuclear silver pyrazolates were synthesized from silver(I) oxide and the corresponding pyrazoles by refluxing overnight in various solvents.[15] Tetrameric silver(I) 3,5-ditertbutyl-pyrazolate was prepared by treating 3,5-di-*tert*-butylpyrazole with silver nitrate and triethylamine[16] or from sodium 3,5-di-*tert*-butylpyrazolate with silver nitrate.[17]

In this paper, we report a general route to both dinuclear silver formamidinates and trinuclear/tetranuclear silver pyrazolates by the reaction of silver(I) oxide with the corresponding formamidines (FormH) or pyrazoles (pzH) in pyridine or acetonitrile, often with very short reaction times. The reaction was easily monitored and proceeds rapidly to completion. The method has been established in high yields by utilizing five different formamidines and six 3,5-disubstituted pyrazoles to study the pKa range and the steric demands of the formamidines and pyrazoles.

Results and discussion

Synthesis of silver pyrazolates and formamidinates

The silver formamidinates, $[Ag_2(DFForm)_2(py)_2]$ **(1)**, $[Ag_2(mHForm)_2(py)_3]$ **(2)**, $[Ag_2(mHForm)_2(CH_3CN)_2]$ **(2a)**, $[Ag_2(pHForm)_2(py)_3]$ **(3)**, $[Ag_2(PFForm)_2(py)_3]$ **(4)**, and $[Ag_2(DippForm)_2]\cdot1.25CH_2Cl_2$ **(5)** and silver pyrazolates, $[Ag_3(Ph_2pz)_3]_2$ **(6)**, $[Ag(tBu_2pz)]_4\cdot CH_2Cl_2$ **(7)**, $[Ag_3(PhMepz)_3]\cdot0.5CH_2Cl_2$ **(8)**, $[Ag_3(Phtpz)_3]$ **(9)**, $[Ag_3(ttfpz)_3]$ **(10)**, $[Ag_2(Me_2pz)(PPh_3)_4Cl]$ **(11)** were prepared by treating Ag_2O with the desired weak acids [the appropriate formamidines (FormH) and pyrazoles (RR′pzH)] (**Scheme 1**) in pyridine or acetonitrile with the exclusion of light. The reaction could be easily monitored through the disappearance of Ag_2O (an insoluble black powder). The reactions to synthesis silver formamidinates (**1-5**) were generally complete in 1-2 min at room temperature, except for the bulky DippFormH, which was stirred overnight in either solvent. Formamidines are expected to have low acidities as they should be comparable with those of amidines (pKa 17-30).[18] In the absence of experimental data, pKa values of DFFormH and DippFormH have been calculated using DFT (for more detail see the Supporting Information) with following results:

	DMSO	THF
DFFormH	26.5	31.1
DippFormH	28.4	33.4

As might be expected, the less bulky DFFormH with electron withdrawing fluorine substituents is more acidic. At first sight, the reaction seems surprising with the weaker acid HForm displacing the stronger acid water. We have previously synthesized silver polyfluorophenyl derivatives by reacting silver oxide with polyfluorobenzenes having pKa values of 23-29.[2] Analogous syntheses of silver pyrazolates (6-11) took longer, 20 minutes to overnight, depending on the acidity of the pyrazoles, which have pKa values in the range 12.9-19.8.[19] This also suggests that acidities themselves are not determining the reaction outcome. However it is known that use of polar solvents can enhance basicities, [20] and this may be a main driver of the reactions if the basicity of silver oxide is increased. In addition the polynuclear silver structures with argentophilic interactions (below) assist. Pyrazole/Ag$_2$O reactions have previously been used to prepare silver pyrazolates, generally in toluene or benzene with longer reaction times than for the current reactions.[15a-d] Of the present silver pyrazolates, only Ag(tBu$_2$pz) has been made from Ag$_2$O, with use of refluxing diethyl ether as solvent. [15e]

Upon completion, the reaction mixtures were concentrated and the products crystallised. Good to high yields (80-95%) of crystalline products were obtained after concentrating the reaction mixtures or recrystallization from dichloromethane (CH$_2$Cl$_2$). In the attempt to prepare [Ag(Me$_2$pz)] from the reaction of Ag$_2$O and Me$_2$pzH, we had difficulties in obtaining good quality crystalline material due to insolubility, perhaps suggesting the compound is a coordination polymer. A few colourless crystals were obtained after adding a small amount of PPh$_3$ to facilitate the crystallization process from CH$_2$Cl$_2$. Rather than the silver pyrazolate being obtained, [Ag$_2$(Me$_2$pz)(PPh$_3$)$_4$Cl] (11) was isolated in low yield, which only allowed characterisation by X-ray crystallography, IR and melting point. Complexes [Ag$_2$(DippForm)$_2$]·1.25CH$_2$Cl$_2$, [Ag$_3$(Ph$_2$pz)$_3$]$_2$, [Ag(tBu$_2$pz)]$_4$·CH$_2$Cl$_2$ and [Ag$_3$(PhMepz)$_3$]·MeOH have previously been prepared by salt metathesis reactions.[10,11,14,16]
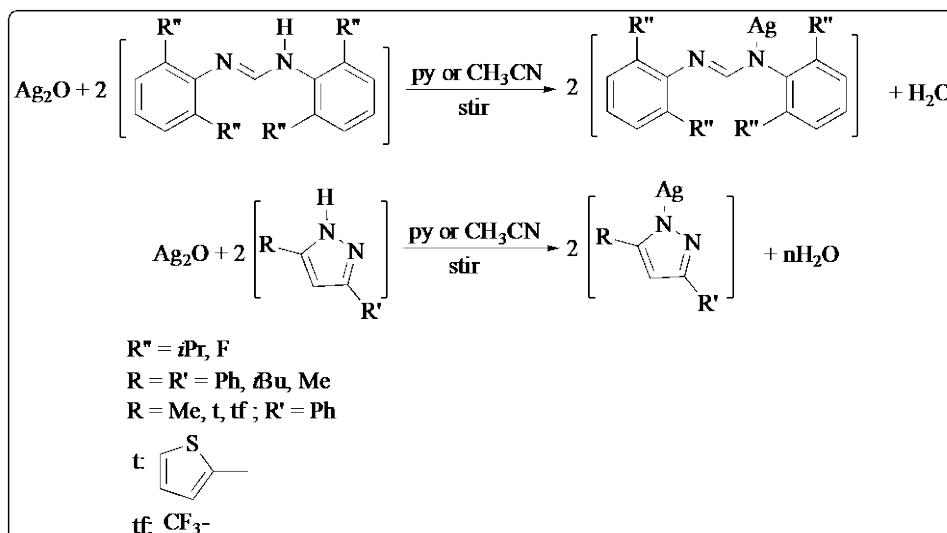
Scheme 1 The synthetic route to silver metal-organic compounds

Complexes **1-10** gave microanalyses for the bulk products as expected for the composition indicated by X-ray crystallography. The ^{1}H NMR spectra of silver formamidinates (**1-5**) showed a resonance of NC*H*N at *ca.* 8.14-7.97 ppm, and silver pyrazolates (**6-9**) showed an H4-resonance at *ca.* 6.70-5.95 ppm. Pyridine resonances were observed in the ^{1}H NMR spectra of **1-4** and a CH$_3$CN resonance was observed in **2a**. As some ^{1}H NMR spectra were recorded for single crystals directly removed from saturated solutions, some spectra showed an excess of interstitial solvent molecule. Thus, complexes [Ag$_2$(DippForm)$_2$]·1.25CH$_2$Cl$_2$ (**5**), [Ag(*t*Bu$_2$pz)]$_4$·CH$_2$Cl$_2$ (**7**) and [Ag$_3$(PhMepz)$_3$]·0.5CH$_2$Cl$_2$ (**8**) showed a resonance of CH$_2$Cl$_2$ at *ca.* 5.22-5.31 ppm, and a CH$_2$Cl$_2$ resonance was also observed for complex [Ag$_2$(*p*HForm)$_2$(py)$_3$] (**3**), which was recrystallized from CH$_2$Cl$_2$. For complexes **1** and **3**, there was excess py integration in the ^{1}H NMR spectra. By contrast, **2a** lost one CH$_3$CN ligand and **4** lost one py before the spectrum was recorded.

Molecular structures

Single crystals of [Ag$_2$(DippForm)$_2$]·1.25CH$_2$Cl$_2$ (**5**), [Ag$_3$(Ph$_2$pz)$_3$]$_2$ (**6**) and [Ag(*t*Bu$_2$pz)]$_4$·CH$_2$Cl$_2$ (**7**) had unit cell parameters in agreement with their respective reported X-ray data.[10,11,16] [Ag$_3$(PhMepz)$_3$]·0.5CH$_2$Cl$_2$ (**8**) had similar unit cell parameters to those of its methanol solvate, [Ag$_3$(PhMepz)$_3$]·MeOH.[14] Structures of **1-4** and **9-11** are shown in **Figure 1-5**, which also list important bond distances and angles.

Silver formamidinates

Dinuclear structures of silver formamidinates **1-5** have an inversion centre through the midpoint of the Ag-Ag vector. Selected bond lengths and angles are shown in **Table 1**.

[Ag$_2$(DFForm)$_2$(py)$_2$] **(1)** crystallizes in the triclinic space group *P*-1. The silver ions in complex **1** are four coordinate (**Figure 1**) with two N(N1, N2#) from the chelating DFForm ligands, one N(N3) from the py ligand, and one argentophilic Ag-Ag# interaction. The Ag−N1 and Ag−N2# bond distances of 2.170(2) and 2.166(2) Å are longer than those in Ag$_2$(XylForm)$_2$ (XylForm = N,N′-bis(2,6-dimethylphenyl)formamidinate) [2.098(1) and 2.108(1)Å],[10] owing to the fluorine substituents causing weaker basicity of the DFForm ligand The Ag-N3 (py) bond length of 2.521(2) Å is longer than Ag–N (N1 and N2# from DFForm ligand), which is consistent with the difference in ligand charge. The Ag−Ag bond length of 2.8947(9) Å is longer than that in Ag$_2$(XylForm)$_2$ [2.7527(3) Å] and Ag$_2$(DippForm)$_2$ [2.7544(6) Å], but shorter than the sum of two van der Waals radii: 1.72 Å of Ag.[21] All the bond distances are near to those of the thf solvate [Ag$_2$(DFForm)$_2$]·3thf.[22]
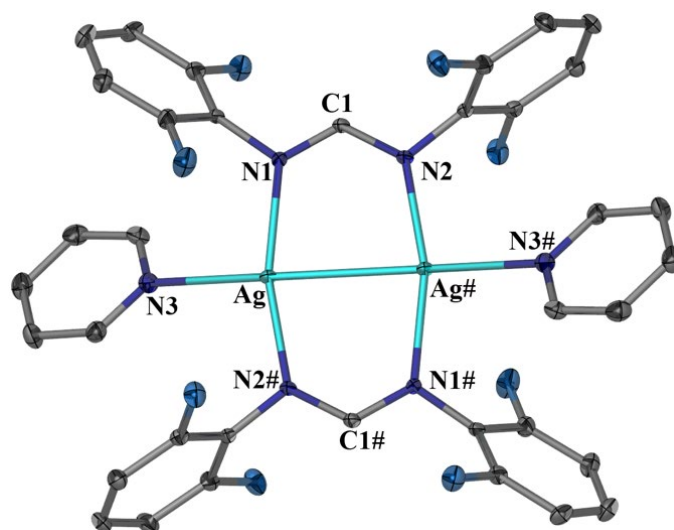

Figure 1. Molecular structure of **1** with non-hydrogen atoms represented by 50% probability thermal ellipsoids

Table 1. Selected bond lengths (Å) and angles (°) for silver formamidinates **1-4**

	1	2	2a	3	4
Bond lengths					
Ag-N1	2.1699(18)	2.239(2)	2.145(2)	2.241(4)	2.246(2)
Ag-N2	2.1663(19)	2.307(2)	2.148(2)	2.254(5)	2.263(3)
Ag-N3	2.521(2)	2.396(2)	2.475(9)	2.417(5)	2.412(3)
Ag-N4	-	2.452(3)	-	2.585(6)	2.557(3)

Ag-Ag	2.8947(9)	2.8185(12)	2.8150(8)	2.8868(10)	2.8979(7)
Bond angles					
N1- Ag -Ag#	81.92(6)	85.46(6)	85.33(7)	83.96(11)	85.03(6)
N1- Ag -N2#	159.93(7)	143.12(12)	166.51(9)	146.36(17)	145.05(9)
N3- Ag -Ag#	154.99(5)	163.49(9)	153.9(2)	149.35(13)	152.11(7)
N1- Ag –N3	95.96(7)	93.93(7)	99.0(2)	105.38(16)	104.24(9)
N3- Ag -N2#	103.69(7)	107.73(8)	94.0(2)	102.71(17)	103.66(10)
Ag-N4-Ag#	-	61.36(8)	-	67.89(17)	69.03(9)

[Ag$_2$(mHForm)$_2$(py)$_3$] **(2)** **(Figure 2 left)** and [Ag$_2$(mHForm)$_2$(CH$_3$CN)$_2$] **(2a)** **(Figure 2 right)** were prepared from different solvents. Compound **2** crystallized in the monoclinic space group *C*2/*c*, and **2a** in the monoclinic space group *P*2$_1$/*c*. The molecular structure of **2** is five-coordinate with two N atoms (N1, N2#) from the chelating *m*HForm ligands, two N(N3, N4) from the py ligands, and one Ag-Ag# interaction, while **2a** is four-coordinate with two N atoms (N1, N2#) from the chelating *m*HForm ligands, one N (N3) from the CH$_3$CN ligand, and one Ag-Ag# bond. The average Ag−N(N1, N2# from *m*HForm) bond distance in **2** 2.273(3) Å is longer than that in **2a** [2.147(3) Å], as expected for the coordination number difference. The average Ag–N (**2**) (N3, N4 from py) bond length of 2.424(2) Å is shorter than Ag–N (**2a**) (N3 from CH$_3$CN) 2.475(9) Å, but they are both longer than Ag–N (N1, N2#). The Ag−Ag bond interaction of 2.819(1) Å in **2** is nearly identical to that in **2a** [2.8150(8) Å].
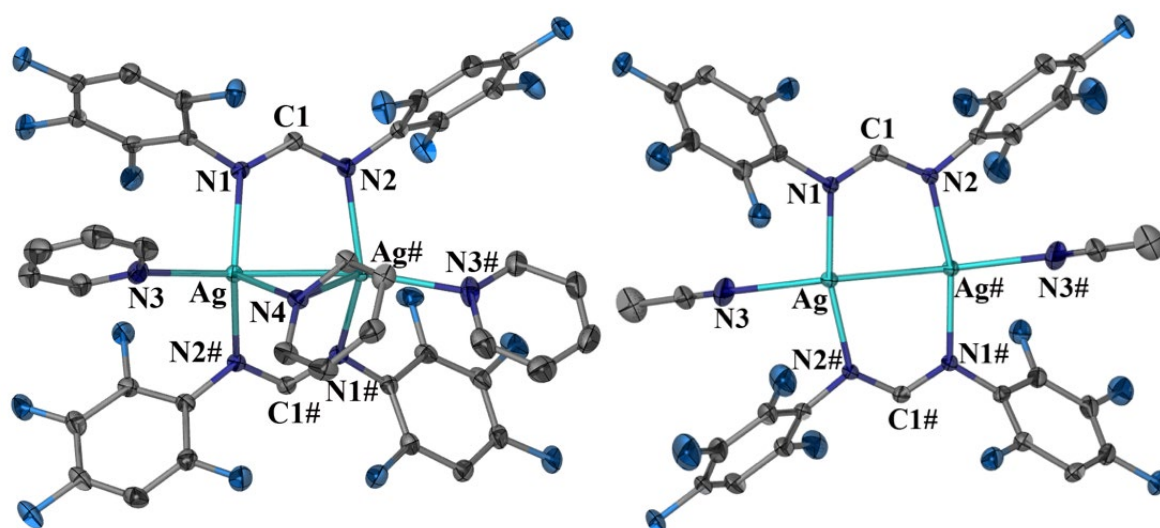

Figure 2. Molecular structure of **2** and **2a** with non-hydrogen atoms represented by 50% probability thermal ellipsoids

[Ag$_2$(*p*HForm)$_2$(py)$_3$] **(3)** (**Figure 3 left**) and [Ag$_2$(PFForm)$_2$(py)$_3$] **(4)** (**Figure 3 right**) crystallize in the orthorhombic space group *P*2$_1$2$_1$2. Although compounds **2**, **3** and **4** have different F-substitution patterns on the formamidine ligands, their structures are similar. The silver atoms of structures **2**, **3** and **4** are five-coordinate with two N atoms (N1, N2#) from the chelating formamidine ligands, two atoms (N3, N4) from the py ligands, and one Ag-Ag# interaction. The bond lengths and angles are similar despite the different-substitution patterns.
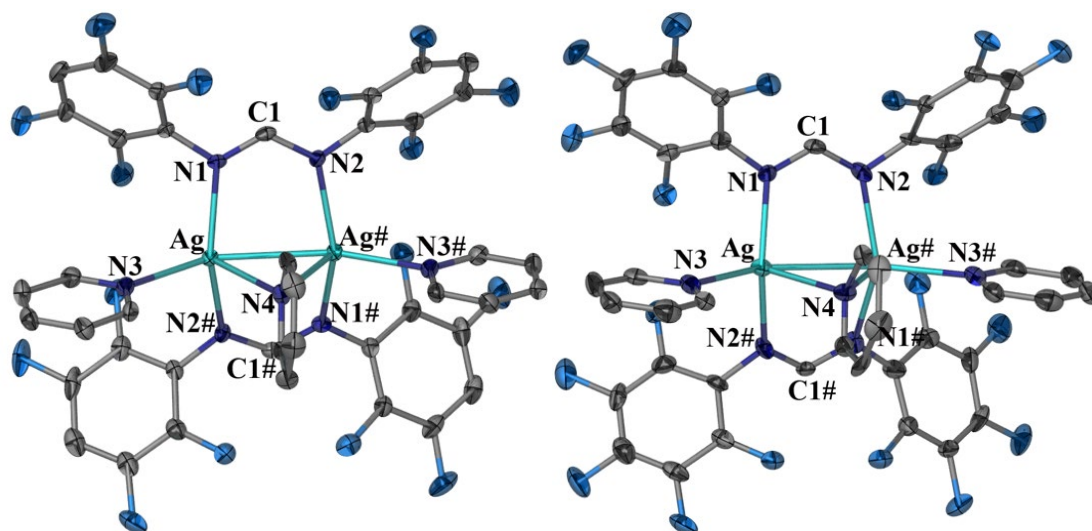

Figure 3. Molecular structure of **3** and **4** with non-hydrogen atoms represented by 50% probability thermal ellipsoids

Silver pyrazolates

[Ag$_3$(Phtpz)$_3$] **(9)** (**Figure 4 left**) crystallizes in the triclinic space group *P*-1, and [Ag$_3$(ttfpz)$_3$] **(10)** (**Figure 4 right**) crystallizes in the monoclinic space group *C*2/*c*. Both are trinuclear structures with an essentially planar nine-membered Ag$_3$N$_6$ metallacycle. The Ag-N bond lengths are 2.074(12)-2.127(9) Å. All Ag-atoms are two-coordinate with approximately linear geometry, as indicated by N−Ag−N angles in the 171.4(4)-178.4(3)° range. The shortest Ag…Ag intramolecular interactions in the metallacycle are 3.379 Å in **9** and 3.451 Å in **10**. These Ag$\cdots$Ag distances are close to the sum of the van der Waals radii of two silver atoms (3.44 Å),[21] but longer than the Ag-Ag distance in the open-shell metallic silver (2.889 Å),[23] but the proximity is probably just a consequence of the structural arrangement.
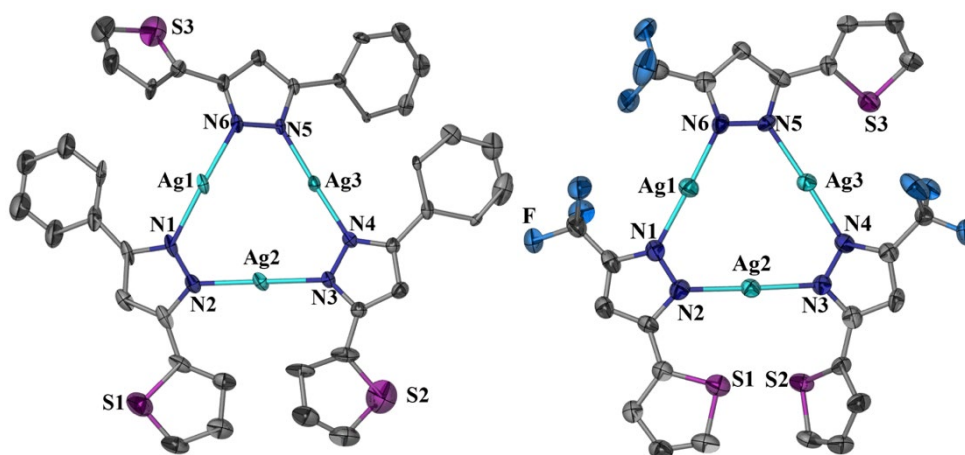
Figure 4. Molecular structure of **9** and **10** shown with 50% probability thermal ellipsoids; hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): **9** **[Ag$_3$(Phtpz)$_3$]** Ag1-Nl 2.133(12), Ag1-N6 2.106(11), Ag2-N2 2.074(12), Ag2-N3 2.108(10), Ag3-N4 2.077(10), Ag3-N5 2.077(10); N6-Ag1-N1 171.4(4), N3-Ag2-N2 177.6(4), N4-Ag3-N5 177.8(4); **10 [Ag$_3$(ttfpz)$_3$]** Ag1-Nl 2.095(9), Ag1-N6 2.092(9), Ag2-N2 2.127(9), Ag2-N3 2.093(8), Ag3-N4 2.094(8), Ag3-N5 2.105(8), N6-Ag1-N1 178.6(4), N3-Ag2-N2 177.7(3), N4-Ag3-N5 178.4(3).

[Ag$_2$(Me$_2$pz)(PPh$_3$)$_4$Cl] (**11**) (**Figure 5**) crystallizes in the tetragonal space group $I4_1$. Two Ag atoms are bridged by chloride and 3, 5-dimethylpyrazolate ligands. To each Ag are also coordinated two P atoms from two triphenylphosphine molecules. The Ag-Cl distance is 2.645(1) Å and the Ag-P distance is 2.470(1)-2.479(1) Å, which are in good agreement with values found in the similar compound [Ag$_2$(PPh$_3$)$_4$Cl$_2$], containing four P and two Cl atoms.[24] The Ag…Ag distance 3.820 Å agrees well with the Ag…Ag distance found in [Ag$_2$(PPh$_3$)$_4$Cl$_2$], a value which is longer than the sum of the van der Waals radii (3.44Å),[21] suggesting that there is no Ag–Ag interaction.
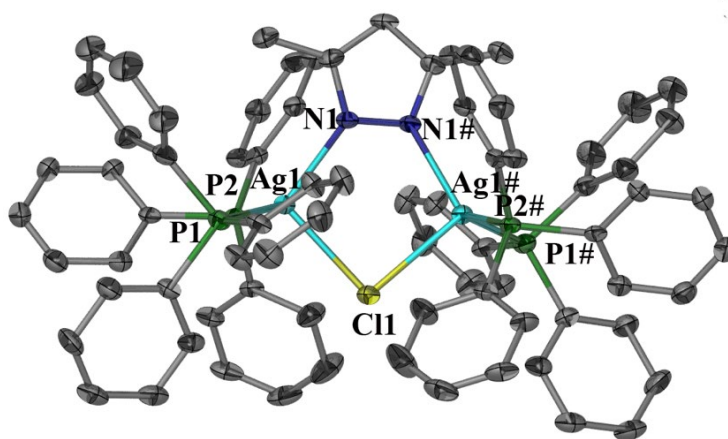
Figure 5. Molecular structure of **11** shown with 50% probability thermal ellipsoids; hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ag-Cl 2.6451(14), Ag-P1 2.4696, Ag-P2 2.4794(14), Ag-N1 2.269(4)

Conclusions

In summary, silver metal-organic compounds (silver formamidinates and silver pyrazolates) have been synthesized from Ag_2O and very weak acids (formamidines and pyrazoles) in pyridine or acetonitrile. This general route provides a convenient and economical method for the synthesis of silver complexes. The crystal structures provide interesting trinuclear and dinuclear silver metal-organic structures, especially those with argentophilic Ag-Ag interactions. The Ag pyrazolates and formamidinates, are potential redox transmetallation reagents in rare earth and alkaline earth chemistry.

Acknowledgements

Conflicts of interest

There are no conflicts of interest to declare.

Experimental

General

The compounds described here were prepared and handled using vacuum-nitrogen line technique and a dry box. IR spectra were recorded as Nujol mulls between NaCl plates using an FTIR instrument within the range 4000–500 cm^{-1}. ^{1}H NMR spectra were recorded on a Bruker DPX 300MHz spectrometer or a Bruker 400MHz instrument. Microanalyses were determined by the Elemental Analysis Service, London Metropolitan University. Melting points were determined in sealed glass capillaries under nitrogen and are uncalibrated. CH_3CN and CH_2Cl_2 were distilled over calcium hydride, degassed and stored over dried 3Å molecular sieves. Pyridine was distilled over potassium hydroxide, degassed and stored over dried 4Å molecular sieves. $CDCl_3$ was pre-dried by 4Å molecular sieves. Crystals were immersed in crystallography oil, and were measured on a Bruker X8 APEXII SCXRD or the MX1 beamlines at the Australian Synchrotron. Crystal data and refinement details are given in **Table S1**. CCDC number 2115782-2115790 for complexes **1**, **2**, **2a**, **3**, **4**, and **8-11**, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General procedure for 1-5

Silver oxide Ag_2O (0.5 mmol), FormH (1.0 mmol) and pyridine (10 mL) or acetonitrile (10 mL) were stirred under nitrogen at room temperature until all the black Ag_2O was consumed. The reaction mixtures were concentrated under vacuum. If the crystals did not obtain, the crystallization method is described with the individual compounds. All the processes were operated in dark, and the Schlenk flasks were protected with Al foil.

[Ag$_2$(DFForm)$_2$(py)$_2$] (1)

The reaction completed in 1 minute in py. Colourless crystals (0.336g, 90%, M.p.258-260°C) were obtained after concentrated under vacuum. IR (Nujol) 1617s, 1552vs, 1265s, 1218s, 1148m, 1096m, 1062s, 1004vs, 878w, 778s, 742m, 704m cm^{-1}. ^{1}H NMR (400 MHz, 25°C, CDCl$_3$, ppm): δ= 8.56 (m, 20H, *o*-H(py)), 8.14(s, 2H, NCHN), 7.61(m, 10H, *p*-H(py)), 7.19 (m, 20H, *m*-H(py)), 6.83 (m, 12H, -C$_6$F$_2$H$_3$) with more py from the solution. Elemental analysis calcd (%) for C$_{36}$H$_{24}$Ag$_2$F$_8$N$_6$ (MW, 908.35): C, 47.60; H, 2.66; N, 9.25. Found: C, 47.53; H, 2.58; N, 8.98 %.

[Ag$_2$(*m*HForm)$_2$(py)$_3$] (2)

The reaction completed in 1 minute. Colourless crystals (0.392g, 88%, M.p.230-232°C) were obtained after concentrated under vacuum. IR (Nujol) 1610m, 1510vs, 1265s, 1259s, 1216m, 1169s, 1055s, 1004vs, 997m, 965m, 934s, 827s, 745m, 721m, 701s cm^{-1}. ^{1}H NMR (300 MHz, 25°C, CDCl$_3$, ppm): δ = 8.56 (m, 6H, o-H(py)), 8.07 (s, 2H, NCHN), 7.69 (m, 3H, p-H(py)), 7.29 (m, 6H, m-H(py)), 6.77 (m, 4H, -C$_6$F$_4$H). Anal. Calc. for C$_{41}$H$_{21}$Ag$_2$F$_{16}$N$_7$ (MW, 1131.39): C, 43.53; H, 1.87; N, 8.67. Found: C, 43.36; H, 1.89; N, 8.50 %.

[Ag$_2$(mHForm)$_2$(CH$_3$CN)$_2$] (2a)

The reaction completed in 2 minutes. Colourless crystals (0.408g, 91%, M.p.230-232°C) were obtained after concentrated under vacuum. IR (Nujol) 2293m, 2258m, 1686w, 1641m, 1580s 1516vs, 1261vs, 1173s, 1118m, 1051vs, 987m, 934s, 835s, 748m, 721s cm^{-1}. ^{1}H NMR (300 MHz, 25°C, CDCl$_3$, ppm): δ = 8.11(s, 2H, NCHN), 6.84 (m, 4H, -C$_6$F$_4$H), 2.03(m, 3H, -CH$_3$CN) lost one CH$_3$CN. Anal. Calc. for C$_{30}$H$_{12}$Ag$_2$F$_{16}$N$_6$ (MW, 976.20): C, 36.91; H, 1.24; N, 8.61. Found: C, 36.77; H, 1.17; N, 8.42%.

[Ag$_2$(pHForm)$_2$(py)$_3$] (3)

The reaction completed in 2 minutes. Colourless crystals (0.492g, 87%) were obtained after recrystallization from CH$_2$Cl$_2$. IR (Nujol) 1618m, 1570m, 1542m, 1507s, 1342m, 1261s, 1215m, 1198m, 1168s, 1101s, 1038s, 999m, 936m, 842w, 812m, 774m, 747s, 701m, 614s cm^{-1}. ^{1}H NMR (400 MHz, 25°C, CDCl$_3$, ppm): δ = 8.51 (m, 10H, o-H(py)), 8.14(s, 2H, NCHN), 7.60(m, 4H, p-H(py)), 7.22 (m, 5H, m-H(py)), 6.60 (m, 4H, -C$_6$F$_4$H), 5.23 (s, 1H, -CH$_2$Cl$_2$) with two more py and 0.5 CH$_2$Cl$_2$. Anal. Calc. for C$_{41}$H$_{21}$Ag$_2$F$_{16}$N$_7$ (MW, 1131.39): C, 43.53; H, 1.87; N, 8.67. Found: C, 43.39; H, 1.91; N, 8.47 %.

[Ag$_2$(PFForm)$_2$(py)$_3$] (4)

The reaction completed in 1 minute. Colourless crystals (0.461g, 95%) were obtained after concentrated under vacuum. IR (Nujol) 1615w, 1567s, 1504vs 1262s, 1215m, 1169s, 1149s, 1066s, 1034vs, 1017w, 981vs, 799m, 783m, 758s, 745s, 723m, 702s cm^{-1}. ^{1}H NMR (300 MHz, 25°C, CDCl$_3$, ppm): δ = 8.39 (m, 4H, o-H(py)), 7.97(s, 2H, NCHN), 7.59(m, 2H, p-H(py)), 7.19 (m, 4H, m-H(py)) lost one py. Anal. Calc. for C$_{41}$H$_{17}$Ag$_2$F$_{20}$N$_7$ (MW, 1203.35): C, 40.92; H, 1.42; N, 8.15. Found: C,41.02; H, 1.38; N, 8.21 %.

[Ag$_2$(DippForm)$_2$]·1.25CH$_2$Cl$_2$ (5)

The reaction completed after stirring overnight in both py and CH$_3$CN. Colourless crystals (0.409 g, 87%, M.p.240°C) were obtained after recrystallization from CH$_2$Cl$_2$. IR (Nujol)

1594s, 1555vs, 1336s, 1316s, 1259s, 1242s, 1198s, 1183s, 1103m, 1058m, 994w, 935m, 890w, 803s, 757s, 743s, 725s cm^{-1}. **5** crystallized in the monoclinic space group C2/c, a = 43.024(9) Å, b = 11.618(2) Å, c = 27.210(5) Å, β = 129.03(3)°, V = 10566(6) Å^3, which is similar to that reported in 2014,[10] monoclinic a = 42.914(3) Å, b =11.6524(9) Å, c = 27.242(2) Å, β = 129.0260(10) °, V = 10582.9(15) Å^3. ^{1}H NMR (400 MHz, 25°C, CDCl$_3$, ppm): δ= 7.20 (m, 2H, NCHN), 7.18 (m, 12H, Ph), 5.22 (s, 4H, CH$_2$Cl$_2$), 3.52 (m, 8H, CH), 1.19-1.10 (m, 48H, Me) with 0.75 more CH$_2$Cl$_2$. Both IR and ^{1}H NMR agreed with reported data,[10] except there was no peak of CH$_2$Cl$_2$ in ^{1}H NMR in reference. Anal. Calc. for C$_{51.25}$H$_{72.5}$Ag$_2$Cl$_{2.5}$N$_4$ (MW, 1049.02): C, 58.68; H, 6.97; N, 5.34. Found: C, 58.55; H, 7.01; N, 5.27 %.

General procedure for 6-11

Silver oxide Ag$_2$O (0.5 mmol) and pzH (1.0 mmol) and pyridine (10 mL) or acetonitrile (10 mL) were stirred under nitrogen at room temperature until all the black Ag$_2$O was gone. The reaction mixtures were dried under vacuum. Crystals were obtained after recrystallization from CH$_2$Cl$_2$ for **6-10**. All the processes were operated in dark, and the Schlenk flasks were protected with Al foil.

[Ag$_3$(Ph$_2$pz)$_3$]$_2$ (6)

The reaction completed in 20 minutes in both py and CH$_3$CN. Colourless crystals (0.286 g, 87%, M.p.262-264 °C) were obtained after recrystallization from dichloromethane (CH$_2$Cl$_2$). IR (Nujol) 1666m, 1261s, 1096s, 798s, 752s, 692s, 480m, 463s, 455m cm^{-1}. **6** crystallized in the monoclinic space group C2/c, a = 22.250(10) Å, b = 15.285(7) Å, c = 22.533(10) Å, β = 103.806(9)°, V = 7442(9) Å^3, which is similar to that reported in 2005,[11] monoclinic a = 22.199(4) Å, b = 15.232(3) Å, c = 22.496(5) Å, β = 103.73(3)°, V = 7389(3) Å^3. ^{1}H NMR (300 MHz, 25°C, CDCl$_3$, ppm): δ = 7.67-7.65(m, 4H, o-H(Ph)), 7.28-7.25(m, 2H, p-H(Ph)), 7.18-7.16(m, 4H, m-H(Ph)), 6.79(s, 1H, H4). Anal. Calc. for C$_{90}$H$_{66}$Ag$_6$N$_{12}$ (MW, 1962.77): C, 55.07; H, 3.39; N, 8.56. Found: C, 54.82; H, 3.20; N, 8.61 %.

[Ag(*t*Bu$_2$pz)]$_4$·CH$_2$Cl$_2$ (7)

The reaction completed in 5h in both py and CH$_3$CN. Colourless crystals (0.241 g, 84%, M.p.>300 °C) were obtained after recrystallization from CH$_2$Cl$_2$. IR (Nujol) 1543m, 1516m, 1413w, 1359s, 1329m, 1246s, 1124m, 1026w, 781s, 718s cm^{-1}. **7** crystallized in the monoclinic space group C2/c, a = 27.52(3) Å, b = 25.939(11) Å, c = 19.88(2) Å, β = 130.58(16)°, V = 10781(8) Å^3, which is similar to that reported in 2007,[16] monoclinic a = 27.808(3) Å, b = 26.087(3) Å, c = 20.091(3) Å, β =130.67(<1)°, V = 11054.283 Å^3. ^{1}H NMR (300 MHz, 25°C,

CDCl$_3$, ppm): δ = 5.95(s, 4H, H4), 5.30(s, -CH$_2$ (CH$_2$Cl$_2$)), 1.33(s, 72H, CMe$_3$). Anal. Calc. for C$_{45}$H$_{78}$Ag$_4$Cl$_2$N$_8$ (MW, 1233.53): C, 43.82; H, 6.37; N, 9.08. Found: C, 43.72; H, 6.46; N, 9.06 %.

[Ag$_3$(PhMepz)$_3$]·0.5CH$_2$Cl$_2$ (8)

The reaction completed after stirring overnight. Colourless crystals (0.219 g, 82 %, M.p.228-230°C) were obtained after recrystallization from CH$_2$Cl$_2$. IR (Nujol) 1602w, 1527w, 1495m, 1407w, 1339w, 1263m, 1145m, 1094m, 1066m, 1028w, 977m, 903w, 795w, 752s, 724w, 689m cm^{-1}. ^{1}H NMR (400 MHz, 25°C, CDCl$_3$, ppm): δ = 7.63-7.61(m, 6H, *o*-H(Ph)), 7.26-7.23(m, 9H, *p*-H(Ph) and *m*-H(Ph)), 6.23(s, 3H, H4), 5.31(s, 0.5H, -CH$_2$ (CH$_2$Cl$_2$)), 1.98 (s, 9H, -CH$_3$). Anal. Calc. for C$_{30.5}$H$_{28}$Ag$_3$ClN$_6$ (MW, 837.65): C, 43.73; H, 3.37; N, 10.03. Found: C, 43.51; H, 3.27; N, 9.89 %.

[Ag$_3$(Phtpz)$_3$] (9)

The reaction completed in 30 minutes in py and 2.5h in CH$_3$CN. Colourless crystals (0.267 g, 80%, M.p.260 °C) were obtained after recrystallization from CH$_2$Cl$_2$. **9** was recrystallized from many different solvents [CH$_2$Cl$_2$, CH$_2$Cl$_2$/CH$_3$CN and THF/Hexane]. All crystals gave the same unit cell, but all have either twinning or disorder problems. IR (Nujol) 1701s, 1650s, 1558m, 1261s, 1095s, 817s, 748m, 667s, 455s, 428s cm^{-1}. ^{1}H NMR (300 MHz, 25°C, CDCl$_3$, ppm): δ = 7.63-7.61(m, 2H, *o*-H(Ph)), 7.29-7.26(m, 2H, H(t)), 7.23-7.18(m, 2H, *m*-H(Ph)), 6.95-6.91(m, 2H, *p*-H(Ph)+H(t)), 6.70(s, 1H, H4). Anal. Calc. for C$_{39}$H$_{27}$Ag$_3$N$_6$S$_3$ (MW, 999.47): C, 46.87; H, 2.72; N, 8.41. Found: C, 46.72; H, 2.83; N, 8.25 %.

[Ag$_3$(ttfpz)$_3$] (10)

The reaction completed in 20 minutes in both py and CH$_3$CN. Colourless crystals (0.281g, 86%, M.p.270-272°C) were obtained after recrystallization from CH$_2$Cl$_2$. **10** was recrystallized from many different solvents [CH$_2$Cl$_2$, CH$_2$Cl$_2$/CH$_3$CN and THF/Hexane]. All crystals gave the same unit cell, but all have either twinning or disorder problems. IR (Nujol) 1565w, 1524m, 1402s, 1317w, 1250s, 1225m, 1153s, 1120s, 1043m, 1002s, 932w, 900w, 843m, 794s, 745m, 698s cm^{-1}. Anal. Calc. for C$_{24}$H$_{12}$Ag$_3$F$_9$N$_6$S$_3$ (MW, 975.19): C, 29.56; H, 1.24; N, 8.62. Found: C, 29.48; H, 1.20; N, 8.59%.

[Ag$_2$(Me$_2$pz)(PPh$_3$)$_4$Cl] (11)

The reaction completed after stirring overnight, and a white precipitate formed (0.174 g, 86 %, M.p.>300°C). IR (Nujol) 1582w, 1522s, 1428s, 1343m, 1147s, 1046m, 976w, 761s cm^{-1}. The

product was taken up in CH_2Cl_2, and a small amount of PPh_3 (50 mg, 0.2 mmol) was added to facilitate the crystallization process. Colourless crystals (M.p.224°C) were obtained after recrystallizing at -20 °C for two weeks. IR (Nujol) 1513m, 1435s, 1314m, 1263s, 1182m, 1156m, 1093s, 1025s, 859w, 800m, 742s, 730s, 693s cm^{-1}.

References

[1]. W. Tyrra, M.S. Wickleder, *Z. Anorg. Allg. Chem.* **2002**, *628*, 1841.

[2]. Z. Guo, J. Luu, V. Blair, G. B. Deacon, P. C. Junk, Eur. J. Inorg. Chem. **2019**, 1018.,

[3]. (a) T. Simler, T. J. Feuerstein, R. Yadav, M. T. Gamer, P. W. Roesky, *Chem. Commun.* **2019**, *55*, 222; (b) N. Schwarz, X. Sun, R. Yadav, R. Koppe, T. Simler, P. W. Roesky, *Chem. Eur. J.* **2021**, *27*, 12857.

[4]. (a) Z. Guo, R. Huo, Y. Q. Tan, V. Blair, G. B. Deacon, P. C. Junk, *Coord. Chem. Rev.* **2020**, *415*, 213232; (b) G. B. Deacon, Md E. Hossain, P. C. Junk, M. Salehisaki, *Coord. Chem. Rev.* **2017**, *340*, 247.

[5]. C. L. Rowe, *Sci. Total. Environ.* **2014**, *485*, 490.

[6]. Z. Guo, V. Blair, G. B. Deacon, P. C. Junk, *Dalton Trans.* **2020**, *49*, 13588.

[7]. W. Bradley, I. Wright, *J. Chem. Soc.* **1956**, 640.

[8]. F. A. Cotton, X. Feng, M. Matusz, R. Poli, *J. Am. Chem. Soc.* **1988**, *110*, 7077.

[9]. (a) T. Ren, C. Lin, P. Amalberti, D. Macikenas, J. D. Protasiewicz, J. C. Baum, T. L. Gibson, *Inorg. Chem. Commun.* **1998**, *1*, 23; (b) S. J. Archibald, N. W. Alcock, D. H. Busch, D. R. Whitcomb, *Inorg. Chem.* **1999**, *38*, 5571; (c) S. Radak, Y. Ni, G. Xu, K. L. Shaffer, T. Ren, *Inorg.Chim.Acta.* **2001**, *321*, 200.

[10]. A. C. Lane, M. V. Vollmer, C. H. Laber, D. Y. Melgarejo, G. M. Chiarella, J. P. Fackler Junior, X. Yang, G. A. Baker, J. R. Walensky, *Inorg. Chem.* **2014**, *53*, 11357.

[11]. A. Mohamed, L. Perez, J. Fackler Jr, *Inorg. Chim. Acta.* **2005**, *358*, 1657.

[12]. (a) Y. Morishima, D. J. Young, K. Fujisawa, *Dalton Trans.* **2014**, *43*, 15915; (b) K. Fujisawa, Y. Ishikawa, Y. Miyashita, K. Okamoto, *Inorganica Chim. Acta.* **2010**, *363*, 2977; (c) N. Masciocchi, P. Cairati, A. Sironi, *Powder Diffr.* **1998**, *13*, 35.

[13]. R. Galassi, S. Ricci, A. Burini, A. Macchioni, L. Rocchigiani, F. Marmottini, S. M. Tekarli, V. N. Nesterov, M. A. Omary, *Inorg. Chem.* **2013**, *52*, 14124.

[14]. G. Yang, P. Baran, A. Martinez, R. Raptis, *Cryst. Growth Des.* **2013**, *13*, 264.

[15]. (a) C. V. Hettiarachchi, M. A. Rawashdeh-Omary, D. Korir, J. Kohistani, M. Yousufuddin, H. V. Rasika Dias, *Inorg. Chem.* **2013**, *52*, 13576; (b) H. V. Rasika Dias, C. S. Palehepitiya Gamage, J. Keltner, H. V. K. Diyabalanage, I. Omari, Y. Eyobo, N. R. Dias, N. Roehr, L. McKinney, T. Poth, *Inorg. Chem.* **2007**, *46*, 2979; (c) H. V. Rasika Dias, H. V. K. Diyabalanage, *Polyhedron* **2006**, *25*, 1655; (d) H. V. Rasika Dias, S. A. Polach, Z. Wang, *J. Fluor. Chem.* **2000**, *103*, 163; (e) Y. Chi, E. Lay, T. Chou, Y. Song, A. J. Carty, *Chem. Vap. Deposition* **2005**, *11*, 206; (f) L. Soria, M. Cano, J. A. Campo, M. R. Torres, C. Lodeiro, *Polyhedron* **2017**, *125*, 141.

[16]. G. Yang, R. Raptis, *Inorg. Chim. Acta.* **2007**, *360*, 2503.

[17]. K. Fujisawa, Y. Ishikawa, Y. Miyashita, K. Okamoto, *Inorg. Chim. Acta.* **2010**, *363*, 2977.

[18]. F. G. Bordwell, G. Z. Ji, *J. Am. Chem. Soc.* **1991**, *113*, 8398.

[19]. (a) Bordwell pKa table https://www.chem.wisc.edu/areas/reich/pkatable/ Oct. 26, **2017**; (b) E. S. Petrov, M. I. Terekhova, V. M. Basmanova, A. I. Shatenshtein, *J. Org. Chem.* USSR, **1980**, *16*, 2089; (c) J. Catalan, M. Menendez, J. Elguero. *Bull. Soc. Chim. Fr.* **1985**, I-30; (d) Evans pKa table. https://evans.rc.fas.harvard.edu/pdf/evans_pKa_table; (e) J. Elguero, G. I. Yranzo. *J. Org. Chem.* **1991**, *36*, 3942; (f) J. Catalan, J. Elguero. *Adv. Heterocycl. Chem.* **1987**, *41*, 187.

[20].   (a) D. Dolman, R. Stewart, Can. J. Chem. **1967**, *45*, 911; (b) M. R. Chakrabarty, C. S. Handloser, M. W. Mosher, *J. Chem. Soc., Perkin Trans. 2*, **1973**, 938; (c) A. Borghese, F. Laurent, J.-J. Tondeur, G. Vandendunghen, Bull. Soc. Chim. Belg. **1992**, *101*, 923.

[21].   A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441.

[22].   Z. Guo, V. Blair, G. B. Deacon, P. C. Junk, *Dalton Trans.* **2020**, *49*, 13588.

[23].   (a) K. Singh, J. R. Long, P. Stavropoulos, *J. Am. Chem. Soc*. **1997**, *119*, 2942; (b) S.E. Kabir, M.A. Mottalib, G.M.G. Hossain, E. Nordlander, E. Rosenberg, *Polyhedron* **2006**, *25*, 95.

[24].   A. Cassel, *Acta. Cryst.* **1979,** *B35*, 177.

[25].   N. P. Cowieson, D. Aragao, M. Clift, D. J. Ericsson, C. Gee, S. J. Harrop, N. Mudie, S. Panjikar, J. R. Price, A. Riboldi-Tunnicliffe, R. Williamson and T. Caradoc-Davies, *J. Synchrotron Radiat.* **2015**, *22*, 187.