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The use of DOSY experiments to determine the solution structures of coinage metal pyrazolates: The case of $\{[3,5-(\text{CF}_3)_2\text{Pz}]\text{Ag}\}_3$

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Abstract

A series of DOSY experiments have been carried out to determine the solution stoichiometry of silver(I) 3,5-bis (trifluoromethyl)pyrazolate species. This compound exists as a trimer in the solid state ($n = 3$) but in solutions of chlorinated solvents, the DOSY data suggest the presence of a mixture of solvent stabilized monomer ($n = 1$) and dimer ($n = 2$) in equilibrium. Different approximations have been used including the Stokes–Einstein and the Stokes–Einstein–Gierer–Wirtz equations. Some methodological problems are discussed.

KEYWORDS

DOSY, fractal dimension, SEGWE, silver pyrazolates, stoichiometry, Stokes–Einstein

1 | INTRODUCTION

Coinage metal pyrazolates have an interesting history that structurally starts in 1984 when Bovio determined the crystal structure of a trimeric gold(I) 3,5-bis (trifluoromethyl)pyrazolate.^[1,2] In 1988, Fackler reported trimeric complexes of gold(I), copper(I), and silver(I) using 3,5-diphenyl-pyrazolate.^[3,4] Additionally, this study provided insight into the effects of the metallic ionic radius trend—Cu(I) < Au(I) < Ag(I)—and the

substituent groups on the pyrazole ring, as the latter greatly influences the coordination geometry of the complex.^[5] Careful consideration of these factors is of importance for the design of complexes with a particular nuclearity, that is, with a defined number of metal atoms.

In their review, La Monica and Ardizzio indicate the dependence of nuclearity on the substitution of the pyrazole ring for a series of copper(I) pyrazolates.^[6] Whereas no substitution at the 3- and 5-positions results in polymeric species, as seen for 1*H*-pyrazole and the

polymeric α - and β -phases of $[\text{Cu}(\mu\text{-Pz})]$, a simple methyl functionalization affords the trimeric complex $[\text{Cu}(\mu\text{-Pz})]$.^[7] Larger substituents, that is *tert*-butyl and phenyl, produces tetramers.^[8,9]

The study of trimeric gold(I) pyrazolate complexes started as elementary research in chemistry but quickly evolved into an applied field due to an increasing interest in their unique properties with recent applications in chemical sensing,^[10] medicine,^[11] liquid crystalline materials,^[12] and MOFs.^[13] Other coinage metals also lead to interesting applications, such as phosphorescence,^[14] emissive properties,^[15] catalysis,^[16] olefin-paraffin separation,^[17–19] and as Buckycatchers.^[20]

Pyrazolate anions with monovalent coinage metal cations form cyclic structures called metallocycles, $(\text{pzM})_n$ for $n = 2$ (with supporting ligands), 3, 4, 5 and 6 and $\text{M} = \text{Cu}(\text{I})$, $\text{Ag}(\text{I})$ and $\text{Au}(\text{I})$.^[21] In the solid-state trimers are the most common. The n numbers (the nuclearity) are determined in the solid state by X-ray crystallography. With very rare exceptions, in the experimental part of the corresponding publications, the NMR spectra in solution are reported (usually ^1H and ^{13}C) without any indication of the stoichiometry usually assuming that the X-ray structure is maintained.

This is by no way evident to the point that some conclusions based on NMR spectroscopy are, at least, inconclusive. Schmidbaur et al. concluded that the complex $[\text{PzH}_2\text{Ag}]^+\text{NO}_3^-$ is dynamic, with rapid site exchange of silver cations and pyrazole rings, by ^1H and ^{13}C NMR in water solution.^[22] This result was used to indicate that magnetic equivalence of R^3 groups (H , *t*-Bu) in tetrameric silver(I) 3,5-di-*tert*-butyl pyrazolate studied by ^1H NMR in CDCl_3 solution was a proof of fast tautomerization in the NMR timescale, without any proof of its nuclearity.^[23] To explain the different behavior of gold and silver pyrazolate trimers differ in solution, the authors assume as a possibility that in solution the trimers persist with a pyrazole-metal exchange through a coordination-decoordination process that is faster in silver than in gold complexes; again the nuclearity was assumed, not proved.^[24]

A more penetrating discussion was found in a paper by Yang et al. where for silver pyrazolate complexes existing in tetramer/hexamer equilibrium ($n = 4/6$) it is written: "Because only one set of signals was observed in the NMR spectra, it is inferred that either there is only one major species present in the solution or two or more species exist simultaneously at a fast dynamic equilibrium."^[25] In addition, NMR as well as vapor pressure osmometry data of some copper tetramers like $\{[3,5-(\text{Pr}^i)_2,4-(\text{Br})\text{Pz}]\text{Cu}\}_4$ suggest the possible existence of trimer-tetramer equilibrium in solution depending on the concentration.^[26,27]

A hypothesis concerning the nuclearity of pyrazole-metal complexes^[28,29] is that it is the same as the structure of the corresponding NH-pyrazoles (cyclamers and catemers).^[30–32]

It was decided to use DOSY spectroscopy to explore the possibility to determine the n value in silver pyrazolate complexes. The compound selected $\{[3,5-(\text{CF}_3)_2\text{Pz}]\text{Ag}\}_3$ (MW = 932.8 g/mol) was a compound recently studied by some of us,^[33] **12Ag₃** or (**12Ag**)₃ (Figure 1), **12** being the anion of 3,5-bis(trifluoromethyl)pyrazole, although previously known,^[34] and much cited afterwards.^[21,35,36]

Utility and problems of using DOSY to determine the molecular mass (m , units $\text{g}\cdot\text{mol}^{-1}$).

There is an abundant bibliography about DOSY, including obviously the use of the Stokes–Einstein equation.^[37,38] For equilibrium mixtures, the problem is analog to that for 1D spectra in solution which corresponds of the fact that if the equilibrium rate is slow and there are several species simple integration determine their relative abundance; the determination is possible even if the signals are broad.

The use of weighted chemical shift average of free species and aggregates is recommended.^[39,40] In general, since the rate of exchange between the free species and the aggregates is fast with respect to the NMR time scale, the observed resonances are found by a weighted chemical shift average of free species and aggregates. Thus, the observed (measured) diffusion coefficient (D_{obs}) is a weighted average of the free and bound diffusion coefficients (D_{free} and D_{bound} , respectively) and can, therefore, be used to calculate the bound fraction x : $D_{\text{obs}} = x D_{\text{bound}} + (1 - x) D_{\text{free}}$.^[41] In the case of fast exchange on the NMR timescale, K_a can be evaluated through diffusion NMR titrations as the bound guest fraction (x) can be calculated from a simple equation where the observed D of the guest ($D_{\text{obs}}^{\text{guest}}$) is a weighted average of its free and bound D , $D_{\text{free}}^{\text{guest}}$, and $D_{\text{bound}}^{\text{guest}}$, respectively,

FIGURE 1 The structure of the silver(I) 3,5-bis(trifluoromethyl)pyrazolate complex $\{[3,5-(\text{CF}_3)_2\text{Pz}]\text{Ag}\}_3$ (MW = 932.8 g/mol)

which has the same form as that employed for obtaining K_a from changes in chemical shifts in titration experiments.^[38]

In the case of slow exchange on the NMR timescale, K_a can be determined by simple integration of their respective characteristic signals in a solution of known concentrations. In this case, diffusion measurements can only be used to probe the association between the species involved but not to obtain numerical values of K_a .

However, if the equilibrium is fast it is very difficult to differentiate a single component from a mixture. This has been recognized by several authors that indicate that interpolation methods should be used. Below are some sentences from the literature:

“Since the rate of exchange between the free species and the aggregates is fast with respect to the NMR time scale, the observed resonances are found by a weighted chemical shift average of free species and aggregates.”^[39] “In the event of fast exchange, only average signals will be seen, whose upfield shifts depend on the relative amount of complexed and free guest.”⁴⁰ “For any other case, assuming fast exchange on the NMR time scale, the observed (measured) diffusion coefficient (D_{obs}) is a weighted average of the free and bound diffusion coefficients (D_{free} and D_{bound} , respectively) and can, therefore, be used to calculate the bound fraction x , as shown in Equation (18), in the same way that chemical shifts are used. $D_{obs} = x D_{bound} + (1-x) D_{free}$.”⁴¹ “In the case of slow exchange on the NMR timescale, K_a can be determined by simple integration of their respective characteristic signals in a solution of known concentrations. In this case, diffusion measurements can only be used to probe the association between the species involved but not to obtain numerical values of K_a . In the case of fast exchange on the NMR timescale, K_a can be evaluated through diffusion NMR titrations as the bound guest fraction (x) can be calculated from eqn. (6) where the observed D of the guest (D_{obs}^{guest}) is a weighted average of its free and bound D (D_{free}^{guest} and D_{bound}^{guest} , respectively), which is the same as that employed for obtaining K_a from changes in chemical shifts in titration experiments.”^[38]

Interpolation methods usually need to make some assumptions. It is easy to interpolate a diffusion coefficient D between two diffusion coefficients one lower and one higher. Following Occam razor principle, we have assumed that there are only two stoichiometries present; besides, with three or more entities, interpolation is not possible, that is, there are an infinite number of solutions. Therefore, interpolation is only possible between two n -mers, for instance, monomer/dimer, monomer/trimer, and dimer/trimer.

If the D s of pure species are not known, as in our case, then it is necessary to transform the D_{obs} into mass using

an empirical equation and then interpolate M_{obs} into M_n ($n = 1, 2, 3$). Note that in the solid state the free monomers (i.e., metal pyrazoles with coordination number = 1) are not observed in the absence of other supporting ligands. For example, it is possible to isolate mono-nuclear species such as $[3,5-(CF_3)_2Pz]Au(PPh_3)$ by breaking the trinuclear metal pyrazolate framework using secondary donors.⁴²

One of us has used vapor-pressure osmometry (VPO) to determine the structure in solution of **(12Ag)**₃.⁴³ In heptane they observed only the trimer but in toluene on increasing the concentration (between 2 and 43 mmol·kg⁻¹, 43 being the limit of solubility) they observed the monomer, the dimer, the trimer and the hexamer (i.e., likely dimer of trimers). It is expected that some of these species (monomers) are stabilized by the solvent coordination.

2 | RESULTS AND DISCUSSION

We decided to use two approaches. Section 2.2 describes measurements on separate samples, while Section 2.3 uses the SEGWE software. We started using two related solvents, CDCl₃ and CD₂Cl₂, but obtaining similar results we have completed the work using CDCl₃ and these will be the sole results reported in this work.

2.1 | The structure of silver pyrazolates in chlorinated solvents

In the solid state, chlorinated solvent stabilized silver structures are known. For example, a search in the Cambridge Structural Database (CSD)⁴⁴ affords 24 structures of CH₂Cl₂ coordinated silver complexes in two situations, linked by only one Cl atom (Ag-Cl-CH₂-Cl) and linked by both chlorine atoms [Ag < Cl₂CH₂]. Of the first kind are, for instance, XELHOL45 and XUCNIT46 and of the second class, for instance, CUQLIK47 and JABVIR.48 There are no structures containing CHCl₃ probably due to the fact that dichloromethane is a more common solvent in organometallic chemistry than chloroform. We cannot exclude monomers bearing two chlorinated ligands with MWs of 485 and 552 g/mol (Figure 2).

These molecular weights will be used in the following interpolations.

2.2 | Establishing an empirical model in CDCl₃

We will use the Stokes-Einstein equation, $D = k_B T / 6\pi\eta R_H$, (D diffusion coefficient, k_B the

FIGURE 2 Possible solvates of silver(I) pyrazolate complexes. Note that the likely interactions with solvents are between the silver sites and the chlorides MWs given in g/mol

Boltzmann constant, T temperature in K, R_H hydrodynamic radius, η solvent viscosity) assuming that the form of all molecules is similar. In this case $\text{Ln}(\text{MW})$ should be proportional to $\text{Ln}(D)$ in the form $\text{Ln}(\text{MW}) = a_0 + a_1 \text{Ln}(D)$. Obviously, decimal logarithms can be used instead of natural ones.

Our first attempt was to establish an empirical plot that relies MW and DOSY. To do this we select four organic compounds (Figure 3) having masses about those of $(\mathbf{12Ag})_n$ [MW ($n = 3$) = 1194 to 1258 g/mol], three lower and one similar.

Then, following the indication of a reviewer according to which it is well established that when DOSY is used to characterize compounds that contain heavy elements, the reference compounds should also contain one heavy element, we selected the five compounds of Figure 4.

Table 1 and Figure 5 reported all the results.

These lines correspond to the following three equations:

$$\text{Organic: } \text{Ln}(\text{MW}) = -(13.9 \pm 2.0) - (1.7 \pm 0.2) \text{Ln}(D), n = 4, R^2 = 0.981$$

(1)

$$\text{Organometallic: } \text{Ln}(\text{MW}) = -(9.9 \pm 2.0) - (1.4 \pm 0.2) \text{Ln}(D), n = 4, R^2 = 0.956$$

$$\text{Both series: } \text{Ln}(\text{MW}) = -(12.0 \pm 2.5) - (1.5 \pm 0.2) \text{Ln}(D), n = 9, R^2 = 0.883$$

We measured the D value of $(\mathbf{12Ag})_n$ in CDCl_3 that results to be 8.07×10^{-6} and $\text{Ln}(D) = -11.73$. To this value correspond three molecular weights (in g/mol):

Equation 1

$$\text{Ln}(\text{MW}) = 5.935, \text{MW} = 378$$

Equation 2

$$\text{Ln}(\text{MW}) = 6.228, \text{MW} = 507$$

Equation 3

$$\text{Ln}(\text{MW}) = 6.108, \text{MW} = 450$$

Since the MW of solvated monomer ($n = 1$), dimer ($n = 2$), and trimer ($n = 3$) are 431, 863, and 1258 g/mol,

FIGURE 3 The structures and names of the four selected organic molecules

FIGURE 4 The structures and names of the five selected organometallic compounds

respectively (Figure 2), the 507 mass cannot be a mixture of dimer and trimer but must contain a large amount of monomer. Simple interpolation leads to 82% of monomer/18% of dimer. The monomer with two ligands has a mass, 552 g/mol, higher than that measured.

Evans, Morris et al. published two papers where they reported that D is proportional to $MW^{-\alpha}$ and that $\alpha = 1/3$ in the case of a full sphere (fractal dimension three).^[49,50] **(12Ag)_n** molecule is discotic, that is, has a fractal dimension of two, consequently an $\alpha = 1/2$ is

Compounds	Ln(D)	Ln (MW) organic	Ln (MW) organometallic
1	−11.249792	5.236974	
2	−11.555833	5.576290	
3	−11.840042	6.006821	
4	−12.370947	7.110321	
5	−11.312437		5.677815
6	−11.636224		6.043820
7	−11.642692		6.124640
8	−11.803278		6.280265
9	−11.815383		6.434595

TABLE 1 Ln(D) and Ln (MW) of the compounds used to establish Figure 5

FIGURE 5 Regression line of organic (red squares) and organometallic (blue circles) compounds

expected. The reciprocal equation corresponding to Equation 3 has a slope of -0.57 , close to $1/2$.

2.3 | Using the Stokes–Einstein–Gierer–Wirtz Estimation software

The SEGWE (Stokes–Einstein–Gierer–Wirtz Estimation) method allows the estimation of the MW of a compound directly from the D value without using any empirical equation. Only the solvent, the temperature, and the estimated viscosity are necessary.

From a D value of 8.07×10^{-6} using CDCl_3 as the solvent, with 0.5429 cPa as viscosity and 298.15 K as temperature, the SEGWE program affords $\text{MW} = 650$ g/mol.

We have reported together with $(12\text{Ag})_n$ values, those of compounds **1–9** in Table 2. Considering the nine reference compounds, **1–9**, it appears that the SEGWE values are largely overestimated, an increase of about 49% in average.

In average, the ratio $\text{SEGWE}/\text{MW} = 1.78$ that corresponds to 57% of increase, roughly half the value but with large variations from -5% to 125% . The values for $(12\text{Ag})_n$, 72, 22 and 31%, are intermediate. The mandatory conclusion is that for the compounds and solvent used SEGWE overestimated the molecular weights, although fortunately, using organometallic compounds, the variations (1.28, 22%) are modest.

3 | EXPERIMENTAL

3.1 | Origin of compound $(12\text{Ag})_3$

Compound $(12\text{Ag})_3$ was prepared according to reference Dias et al.^[34] Antipyrine **1** is a commercial compound. 1-(2,4-dinitrophenyl)-3,5-dimethyl-4,5-dihydro-1H-pyrazole **2** and tris(2-methyl-1H-benzimidazolyl) methane were reported in references,^[51,52] respectively. Compound **4** was synthesized by Ana San-Félix's research group according to reference San-Félix et al.⁵³ The origin of the compounds of Figure 4, except **5** and **6** that are commercial, were prepared for this work according to literature procedures: **7**,⁵⁴ **8**⁵⁵ and **9**.⁵⁶

3.2 | Nuclear magnetic resonance

Structural characterization was carried out by a multinuclear NMR study (^1H , ^{13}C , ^{15}N , and ^{109}Ag). NMR spectra were recorded at 298 K, using CD_2Cl_2 or CDCl_3 as the solvent, on a JEOL JNM-ECZ 400R spectrometer (^1H 399.83 MHz, ^{13}C 100.54 MHz, ^{15}N 40.52 MHz, ^{109}Ag 18.61 MHz) equipped with a 5-mm Auto Tune Royal HFX probe.

1D ^1H spectra were measured with eight scans, and a relaxation delay of 5 s. The FID was acquired with 16 k complex data points and was processed with zero-filling and Fourier Transformation (FT) to obtain a spectrum

TABLE 2 Molecular weight (in g/mol) known or estimated previously and calculated by the SEGWE method (solvent CDCl_3)

Compound	$D \text{ (cm}^2\text{/s)}$	MW	SEGWE	Ratio	Increase (%)
(12Ag)_n	8.074×10^{-6}	378 ^a	650	1.72	72
	8.074×10^{-6}	507 ^b	650	1.28	22
	8.074×10^{-6}	450 ^c	650	1.44	31
1	1.301×10^{-5}	188.1	247	1.31	31
2	9.58×10^{-6}	264.1	455	1.72	73
3	7.21×10^{-6}	406.1	820	2.02	102
4	4.24×10^{-6}	1224.5	2753	2.25	125
5	1.222×10^{-5}	292.31	279	0.95	-5
6	8.84×10^{-6}	420.52	537	1.27	28
7	8.78×10^{-6}	456.98	545	1.19	19
8	7.48×10^{-6}	533.93	765	1.43	43
9	7.39×10^{-6}	623.03	785	1.27	26

^aCalculated from the line of the first four compounds (**1–4**).

^bCalculated from the line with compounds with metals (**5–9**).

^cCalculated from the line with all compounds (**1–9**).

FIGURE 6 Four spectra of compound **(12Ag)_n** in CD_2Cl_2 : (a) ^1H (400 MHz); (b) ^{13}C (100 MHz); (c) ^{15}N (40 MHz); and (d) ^{109}Ag (18 MHz)

FIGURE 7 Diffusion decay curve and best-fit curve of compound 4

with 52 k data points. Chemical shifts were referenced respect to TMS.

1D ^{13}C spectra were measured with 20,000 scans, and a relaxation delay of 1.0 s. The FID was acquired with 32 k complex data points and was processed with zero-filling and Fourier Transformation (FT) to obtain a spectrum with 52 k data points. Chemical shifts were referenced respect to TMS.

1D ^{15}N spectra were measured using a decoupled gated NOE sequence with 70,000 scans, and a relaxation delay (d_1) of 2.0 s. The FID was acquired with 32 k complex data points and was processed with zero-filling and Fourier Transformation (FT) to obtain a spectrum with 52 k data points. Chemical shifts were referenced respect to CH_3NO_2 .

1D ^{109}Ag spectra were measured with 100 scans, and a relaxation delay of 1000s. The spectral width was 700 ppm with center at 254 ppm. The FID was acquired with 32 k complex data points and was processed with zero-filling and Fourier Transformation (FT) to obtain a spectrum with 52 k data points. Chemical shifts were referenced externally with the ^{109}Ag NMR spectrum of a saturated sample of AgNO_3 in D_2O ($\delta^{109}\text{Ag}$ 0 ppm).

DOSY ^1H -NMR measurements were carried out on a Bruker Avance III HD-400 NMR spectrometer, operating at 399.86 MHz for ^1H , equipped with a 5 mm BBFO probe. The pulse sequence used was a longitudinal eddy current delay bipolar gradient pulse (ledbpgp2s). One hundred twenty-eight gradient increments were used for each spectrum and all were acquired at a temperature of 298 K. TD = 16,384. FIDRES F2 = 0.585 FIDRES F1 = 62.478. Each spectrum was acquired with eight scans, δ of 2.0 ms, Δ of 200 ms, and a relaxation delay of 3 s. The maximum gradient strength was 5.35 G/mm. All experiments were run without spinning to avoid convection. The DOSY spectra acquired on BreNO_2 ; 407.87 ppm (^{109}Ag) were processed with the MestreNova program (version 14.1.2, Mestrelab Research S.L.), using the DOSY Bayesian transformation.

In CD_2Cl_2 the signals of $(\mathbf{12Ag})_n$ appear at 7.09 ppm (H4) (^1H); 144.4 (C3, C5), 103.30 (C4), 120.50 (CF_3) ppm (^{13}C); -161.77 ppm (^{15}N , reference internal MeNO_2); 407.87 ppm (^{109}Ag) (Figure 6). The ^{19}F NMR chemical shift, -61.1 ppm, was reported in previous reference.³³

In Figure 7 are shown the best-fit curves that yield the reported value of the diffusion coefficient of compounds 4 and 8. The remaining diffusion decay curves and best-fit curves for the rest of the compounds are to be found in the supporting information.

4 | CONCLUSIONS

We have used two approaches to determine the nuclearity of $(\mathbf{12Ag})_n$ in CDCl_3 (incomplete, nonreported results, in CD_2Cl_2 yield similar results). Linear models using five organometallic compounds as external references yield MW = 507 g/mol. The direct method, SEGWE, has proved to yield a MW value too large, 650 g/mol. An interpolation using monomer with one ligand and dimer with two ligands (1:2 model) yield 82% monomer/18% dimer in CDCl_3 . Using monomer with two ligands and dimer with two ligands (2:2 model) yield more than 100% of monomers pointing to the possibility of a near 50/50 mixture of monomers with one and two chlorinated ligands. These results in chlorinated solvents are different than those obtained by osmometry in hydrocarbons, heptane and toluene.^[43] However Cu and Ag pyrazolate trimers breakup to yield monomers by toluene^[26,27] and chloroform have been established.

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