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ARTICLE

Interactions of the G-series organophosphorus chemical warfare agent sarin and various simulants with luminescent lanthanide complexes

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Fundamental supramolecular interactions of the G-series organophosphorus (OP) chemical warfare agent (CWA) sarin, and various simulants, with simple lanthanide complexes of the type $\text{Ln}(\text{phen})_2(\text{NO}_3)_3 \cdot (\text{H}_2\text{O})_x$ (where phen = 1,10-phenanthroline; **1**: Ln = Eu(III), $x = 3$ and **2**: Ln = Tb(III), $x = 2$) have been elucidated by spectroscopic investigations. Luminescent and UV-Vis results show only minimal fluorescence quenching occurring as a result of a dynamic mechanism. These results have been compared with previously presented V-series OP CWA data demonstrating that the luminescence quenching of the two series occurs with differing magnitudes and mechanisms. Agent-simulant correlations for use with lanthanide complexes are also discussed which are of critical importance for informing the design and construction of efficient, advanced and regenerable supramolecular sensing systems.

Introduction

The highly toxic G- and V-series organophosphorus (OP) chemical warfare agents (CWAs, Figure 1) are potent acetylcholinesterase inhibitors that are virtually undetectable to the human senses and can cause incapacitation and death within minutes of exposure.¹ Fast, efficient and selective detection of these compounds is therefore of paramount importance. Chemical sensors for OP CWAs have traditionally relied on the reactivity of the agent, however supramolecular based sensing approaches are receiving increased attention.²

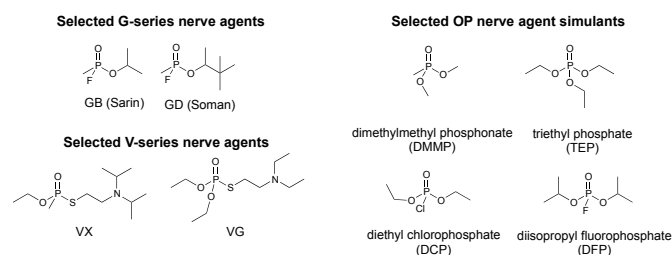


Figure 1: Structures of selected G- and V- Series OP CWAs and related simulants.

The literature is replete with chemically reactive molecularly based sensing systems for the detection of organophosphorus CWAs and their sensing mechanisms have been mechanistically and soundly elucidated.³⁻⁵ Whilst these sensors reactions produce highly visible signals, they predominantly

rely on phosphorylation via reactive moieties common to these agents which can lead to false positives and lack of sensor specificity. Many of the systems also suffer from drawbacks such as extended response rates due to rate limiting steps involving the breaking and formation of covalent bonds, irreversibly removing the possibility of regenerable systems. Hence supramolecular based systems, which exploit non-covalent interactions (such as metal-ion coordination) to drive the sensing event, are of particular interest. In addition to rapidity of response, advantages may be obtained in the possibility of 'off-on-off' sensing strategies, the realisation of next generation catalysts, and more generally in stimuli responsive materials. However, the literature in this area remains limited and presents an opportunity for novel research avenues to be explored and exploited.

Before the design, preparation and testing of new supramolecular sensors can be adequately achieved, the fundamental interactions of the different CWAs with potential sensing regimes needs to be elucidated. Such knowledge will be critical in the extension of recognition behaviour to achieve functional supramolecular systems and assemblies. A recent review highlighted some of the supramolecular strategies pursued to-date for both OP and other CWAs, including approaches that utilise cyclodextrins, hydrogen bond donors and transition metal complexes.²

Lanthanide based supramolecular sensors for OP CWAs and simulants

The formation of phosphoryl or phosphonyl coordinative bonds ($\text{P}=\text{O}\cdots\text{Ln}^{3+}$ where Ln = lanthanide ion) is well known, and has been investigated as a driving force in the design of novel ligands for the extraction of lanthanide ions from solution and the understanding of lanthanide coordination properties in general.⁶ The presence of P=O bonds in all OP nerve agents presents an opportunity to exploit this interaction for the G- and V-series agents. Furthermore, Ln^{3+} ions, such as Eu(III) and Tb(III), are characterised by narrow emission bands, long excited state lifetimes and marked increases in luminescence emission intensity in the presence of appropriate UV-light absorbing ligands *via* the antenna effect.⁷ Therefore, the combination of affinity for P=O bonds and the potential for modulation, or complete disruption, of the antenna effect *via* sensitising ligand displacement resulting in the loss of metal centred lanthanide luminescence emission makes such complexes attractive targets for organophosphorus CWA sensing systems.

This disruption to the antenna effect through the displacement of the sensitising ligand may be achieved in two ways. Firstly, by the interaction of the target analyte with the sensitising ligand either through reactivity or through competitive binding.⁸ Or, secondly, via the competitive binding of the target analyte to the lanthanide ion, thus displacing the sensitising ligand (Figure 2).^{9,10}

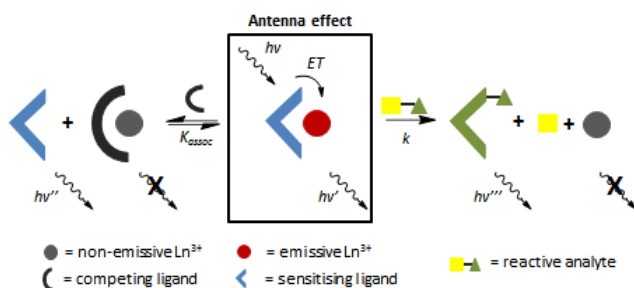


Figure 2: Potential mechanisms for the perturbation of the antenna effect resulting in quenching of metal centred luminescence.

Shumugam *et al.* have reported terpyridine (terpy) based lanthanide systems in which the addition of the G-agent simulants diisopropyl fluorophosphate (DFP) or diethyl chlorophosphate (DCP) are reported to quench the metal centred luminescence.⁸ The reported quenching mechanism was proposed to be via phosphorylation of the terpy nitrogen centres, resulting in decomplexation of the ligands and loss of the antenna effect. The mechanism was proposed to rely upon the susceptibility of the simulant phosphorus(V) electrophilic centre to nucleophilic attack by the terpyridine nitrogen atoms, thus chemical reactivity drives the sensing response.

In an example of competitive ligand binding Knapton *et al.* reported the luminescent detection of a CWA simulant by lanthanide 2,6-bis(1'-methylbenzimidazolyl)pyridine complexes of the type $[\text{Ln}(\text{L})(\text{NO}_3)_3]$ (Ln=La(III), Eu(III); L=MeBip).¹⁰ Upon addition of high equivalents of triethyl phosphate (TEP) to these complexes in CHCl_3 -MeCN (9:1) solution, the metal centred luminescence was quenched and the

emission of the free ligand was observed, indicating ligand displacement and competitive binding.

Due to international regulations and high toxicities, the use of OP CWA materials is restricted. Whilst testing with CWA simulants is critical to the development of new sensing approaches, it is imperative that differences in behaviour between commonly used simulants and CWAs are well understood in order to generate accurate agent-simulant correlations. In the case of molecular recognition, these correlations are less established than, for example, physical properties and chemical reactivity.

Despite the general interest in supramolecular approaches there are few fundamental studies into lanthanide complex-CWA interactions. Whilst theoretical studies into the coordination modes of V-series CWA (particularly VX) with Group I and II metal cations proposed that the most stable chelation mode to be via the formation of a seven membered $[\text{O}_p, \text{N}]$ chelate ring,¹¹ further experimentation is essential to inform future exploitation of such systems.

Recently, we reported that V-series agents (VX and VG) quenched the lanthanide luminescence emission in complexes of the type $\text{Ln}(\text{phen})_2(\text{NO}_3)_3 \cdot (\text{H}_2\text{O})_x$ (where phen = 1,10-phenanthroline; 1: Ln = Eu(III), $x = 3$ and 2: Ln = Tb(III), $x = 2$) (Figure 3).⁹ In particular, rapid and complete luminescence quenching with under 10 molar equivalents of V-series agent was achieved and a competitive binding mechanism through formation of a bidentate chelate seven-membered ring was proposed.⁹

Analogous UV-Vis titrations demonstrated the displacement of the phen ligand from the lanthanide ion, resulting in the disruption of the antenna effect. Analysis of Stern-Volmer (SV) plots of emission quenching indicated not only the presence of the static quenching mechanism suggested by the ligand displacement, but also an excited state dynamic quenching mechanism. Quantitative UV-Vis titrations allowed the determination of association constants for VX and VG with both lanthanide complexes and the consideration of putative mono-dentate ligands based on the structure of VX ($(\text{RO})_2\text{MeP}=\text{O}$, R_2S , R_3N) allowed for the proposal of a bidentate seven-membered chelate between VX/VG and the lanthanide complexes.

In this new study we turn our attention to the fundamental interactions of the G-series agent sarin (GB) with lanthanide complexes 1 and 2 and contrast this to the behaviour of V-series agents. Related OP simulants DMMP and DCP, and the fluoride ion as a potential hydrolysis product of the phosphonofluoridate agents, are also investigated with regard to their interactions with lanthanide complexes. This allows for the formulation of supramolecular agent:simulant correlations in the context of lanthanide coordination.

Results

The structure of the two lanthanide complexes used in this study are shown in Figure 3, the synthesis and characterisation of which have been previously described.^{9,12} Solutions of these complexes ($1 \times 10^{-3} \text{ mol dm}^{-3}$) were prepared in 1:9 DMF:MeCN, and further diluted in MeCN to give a complex

concentration of $1 \times 10^{-5} \text{ mol dm}^{-3}$. These solutions were then used directly in all spectroscopic experiments.

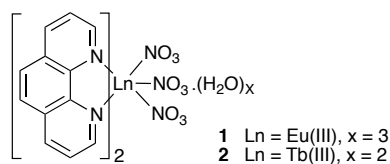


Figure 3: Structure of the Eu(III) and Tb(III) 1,10-phenanthroline complexes used in this study.

Interaction with the OP CWA Sarin (GB)

Upon addition of up to ten molar equivalents of GB in acetonitrile to the solutions of **1** and **2**, the emission intensity was observed to decrease by only *ca.* 15%. This contrasts distinctly with our previous studies with VX.⁹ The titration profiles of GB and VX are shown in Figure 4 and demonstrate the stark differences in luminescence emission quenching behaviour between the two agents. Only at high GB concentrations in excess of 300 molar equivalents is complete luminescence quenching observed.

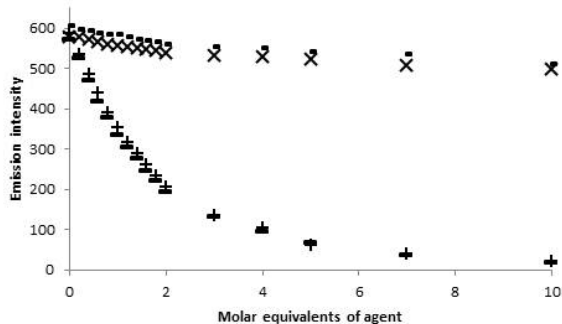


Figure 4: The luminescent emission intensity quenching ($\lambda_{em} = 617 \text{ nm}$) observed upon titration of $\text{Eu}(\text{phen})_2(\text{NO}_3)_3$ with GB (x and -) and VX (+ and -). Two quenching experiments were conducted per agent-complex combination. The VX data is taken from our previous work.⁹ Reproduced from reference 9 with permission from The Royal Society of Chemistry.

Unlike the V-agent data discussed previously, analysis of the UV-Vis spectral data from the GB titration indicates no perturbations in the absorption spectrum up to the addition of ten molar equivalents of GB (see ESI). This indicates the absence of a static quenching mechanism, and that the system is dominated by dynamic, collisional quenching processes. At higher concentrations of GB (approx. 40 molar equivalents) a red-shift is observed in the absorption maximum and a charge transfer band centered around 310 nm is noted (see ESI). It is postulated that this is a result of the increase in electron density concentration in solution, which is supported by the luminescence data (*vide infra*).

SV analysis (Figure 5) of the emission intensity data for the GB titration yields K_{SV} constants of 3800 and 4100 M^{-1} for complexes **1** and **2**, respectively (Table 1). At high concentrations of GB the SV plot is observed to undergo upward curvature away from the x-axis (not shown). Given the high concentrations of GB needed to achieve this (>10 molar equivalents relative to the complex, $[\text{GB}] > 0.0002 \text{ M}$), and the associated red shift in the UV-Vis absorption spectral data, it is

suggested that this deviation from linearity is as a result of a sphere of effective quenching mechanism in which the concentration of the quencher is high enough that diffusion of species in solution is not required to allow for collisional deactivation.

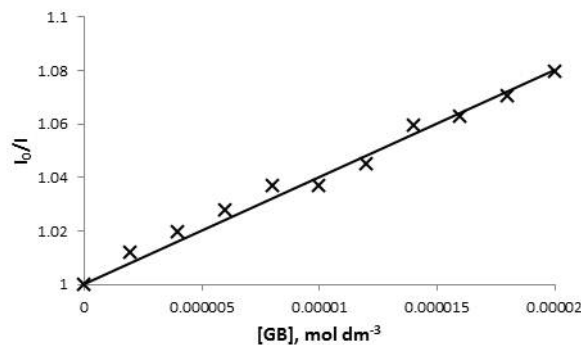


Figure 5: SV plot generated from the titration of $\text{Eu}(\text{phen})_2(\text{NO}_3)_3$ with GB in acetonitrile. The quenching constant K_{SV} was determined as 3800 M^{-1} as a mean of the two titration data sets.

OP CWA simulants DCP and DMMP

As might be expected considering their structural commonalities to GB, similar spectroscopic interactions with **1** and **2** were observed for the simulants DCP and DMMP. In all cases, emission quenching upon the addition of less than 10 molar equivalents was limited. This indicates, in combination with UV-Vis analysis, the absence of a static quenching mechanism. SV plots for all complex-simulant combinations are presented in the supporting information and the calculated K_{SV} constants are collated in Table 1. For DCP, a negative curvature (towards the x-axis) was apparent even at low concentrations, indicating a limited accessibility to the emissive species. This observation was also made for DMMP and GB, but with higher concentrations of the OP compound. The reason for this behaviour is unknown, but may be a result of steric hindrance preventing all collisional non-radiative decay processes.¹³

Table 1: K_{SV} constants (M^{-1}) for GB and OP simulants with complexes $\text{Ln}(\text{phen})_2(\text{NO}_3)_3(\text{H}_2\text{O})_x$ (where **1** Ln = Eu, x = 3 or 2 Ln = Tb, x = 2), $1 \times 10^{-5} \text{ mol dm}^{-3}$, 293 K.

	$\log K_{SV} (\text{M}^{-1})$	
	1	2
GB	3.56 ± 0.01^d	3.62 ± 0.02
DMMP	3.66 ± 0.02	3.77 ± 0.01
DCP	3.70 ± 0.01	3.91 ± 0.02
TBAF ^a	5.0 ± 0.014	4.7 ± 0.018
VX ^{a,c}	5.1 ± 0.12^d	5.2 ± 0.12
VG ^{a,c}	4.5 ± 0.03	5.2 ± 0.13

^a $K_{assoc} = K_{SV}$. ^b Standard deviation of the refined parameters from the least squares fitting of binding isotherms. ^c Values reproduced from from reference 9 with permission from The Royal Society of Chemistry. ^d Errors estimated from the average of two titrations.

Interactions with fluoride ion

Titration with up to five molar equivalents of tetrabutylammonium fluoride (TBAF) into solutions of the

lanthanide complexes resulted in rapid and complete luminescence quenching. Analogous to the UV-Vis results obtained with the V-series CWA, titration of TBAF also demonstrated an absorbance blue shift (Figure 6) indicating the presence of free phen and a competitive binding mechanism. This contrasts significantly with the results obtained for GB and the OP simulants DCP and DMMP.

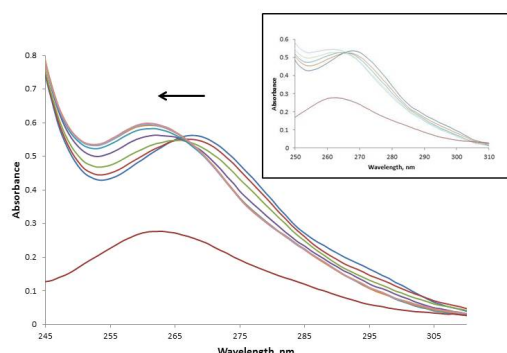


Figure 6: Selected spectra from the titration of **1** with TBAF: complex, 1.0, 2.0, 3.0, 4.0, 5.0, 7.0 and 10.0 mol. equiv. TBAF. The low absorbance red trace is the spectrum of free phen; $[complex]_{initial} = 1 \times 10^{-5} \text{ mol dm}^{-3}$, 293 K. Inset shows VX data for comparison. Reproduced from reference 9 with permission from The Royal Society of Chemistry.

Fitting of the TBAF UV-Vis titration data to a 1:1 binding isotherm using HypSpec¹⁴ allowed the determination of association constants ($\log K_{assoc}$) of 5.0 and 4.7 for the Eu(III) and Tb(III) complexes, respectively. As with our previous results for VX,⁹ there was no indication of higher stoichiometry complexes being formed, in agreement with the observations of a single isosbestic point during the titrations. This suggests a stepwise displacement of the phen ligands by the fluoride ions, and a lack of cooperativity effects between the two phen ligands in the complex. As such, the concentration of the binding site was treated as $2[complex]$, effectively $[phen]_{bound}$. As noted previously,⁹ the addition of phen to solutions of complex **1** resulted in a linear increase in absorption at 268 nm, indicating formation of $\text{Eu(phen)}_x(\text{NO}_3)_3$, where $x > 2$. This suggests that the intermediate complex $\text{Eu(phen)(F)(NO}_3)_3$ has an absorption spectrum similar to **1**, but at approximately half the extinction coefficient. This further supports the lack of cooperativity effects between bound phen ligands.

These results suggest that hydrolysis of the P-F bond of GB is not occurring under the conditions studied and that the limited luminescence quenching that is observed with the titration of GB is not the result of anion coordination. The lack of fluoride related quenching coupled with the similarity between the DMMP, DCP and GB results also indicates that phosphorylation of the N-centres of the phen ligands is unlikely.

Discussion

The data in Table 1 suggest a much weaker interaction of the CWA GB and the simulants DMMP and DCP with the lanthanide complexes as compared to the V-agents studied previously. The luminescence and UV-Vis data suggest a

purely dynamic (collisional) excited state quenching mechanism with the absence of any static quenching. The latter suggests the absence of any Ln-G complexes (where G = GB, DMMP, DCP) being formed in solution. This allows us to postulate two key reasons for this weaker interaction. First, in the case of GB a decrease in the Lewis basicity of the phosphonyl group due to the electron withdrawing nature of the fluorine substituent decreases the coordinative strength of the group. Second, the absence of secondary coordinating sites, as seen in the V-series agents, precludes the possibility of forming bidentate chelates. The displacement of bidentate phen ligands by mono-dentate OP compounds is clearly not occurring under the low molar equivalent conditions studied, and yet monodentate $\text{P=O} \cdots \text{Ln}$ complexes are known. Clearly, the relative affinity of the phen ligands and the OP ligands for the lanthanide ions determines the successful displacement of the former by the latter. The extent of complex stability enhancement due to the chelate effect is well known, and this can be as great as several orders of magnitude in association constants.¹⁵ Examples of seven-membered chelates with lanthanide ions, such as those previously proposed for VX, can be found in the literature,¹⁶ and this clearly drives the phen displacement. In the case of GB and the other monodentate ligands, the relative ligand affinities favour the retention of chelation of phen by the lanthanide ion.

Comparisons between agents and simulants

The results demonstrate differing luminescence quenching mechanisms between the G- and V-series OP CWAs in our system and allow us to postulate mechanisms by which the two different series of CWA and their simulants interact with model lanthanide complexes (Figure 7).

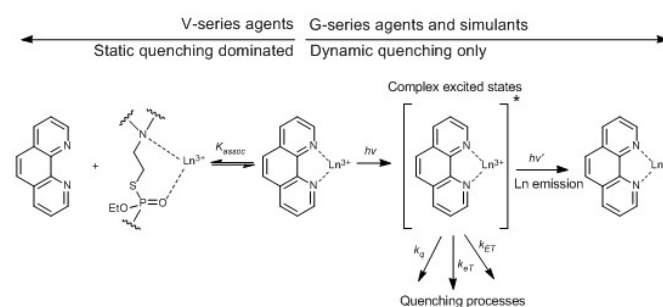


Figure 7: Illustrative schematic of the quenching regimes observed for tested lanthanide complexes in the presence of V- and G-series agents and simulants. V-series mechanisms are dominated by static quenching as a result of competitive binding of the V-agent and displacement of the phen ligand (K_{assoc} is defined earlier under Table 1). G-series agents follow a collisional dynamic quenching mechanism. Ligand and lanthanide excited states and related processes are omitted for clarity and intermediate excited states are represented as a single species. k_q = excited state collisional quenching mechanisms, k_{eT} and k_{ET} represent excited state electron and energy transfer processes, respectively.¹⁷

Evidently, the phosphorus containing, monodentate simulants DMMP and DCP provide analogous results to GB and can therefore be used to provide adequate representation of the dynamic mechanism of lanthanide luminescence quenching

with G-series CWA. However, DMMP and DCP, which have been frequently used in the literature to simulate V-series CWA, do not generate lanthanide luminescence quenching via the same mechanism as the V-series agents in our system. Therefore, they cannot always be relied upon as simulants in supramolecular studies with V-series CWAs. Simulants for V-series agents need to have the potential for multivalent interactions as part of a bidentate chelation. Accordingly, VG is commonly used as a V-series simulant due to its structural and chemical similarities to VX. Whilst VG is a structurally ideal simulant, it is still extremely toxic and access to it is tightly controlled (Schedule 2 under the Chemical Weapons Convention). Other commercially available V-series simulants, such as the pesticides malathion and parathion, do not adequately represent the coordinative functionalities and geometries present in the V-series agents.

Conclusions

We have successfully demonstrated that luminescent lanthanide complexes of the type $\text{Ln}(\text{phen})_2(\text{NO}_3)_3 \cdot (\text{H}_2\text{O})_x$ (where phen = 1,10-phenanthroline; **1**: Ln = Eu(III), $x = 3$ and **2**: Ln = Tb(III), $x = 2$) proceed through markedly different mechanisms of luminescence quenching when exposed to G- or V-series OP CWAs. Which mechanism occurs is largely dependent on the Lewis basicity of the potential coordinative site(s) and the ability of the CWA to undergo bidentate chelation. It has been previously demonstrated that the V-series CWA sensing response occurs through rapid disruption of the antenna effect by competitive binding driven by a bidentate [O_p, N] chelate effect, resulting in displacement of the sensitising phen ligand. This is in contrast to the G-series CWAs which we have shown to have no interaction with the ground state of the lanthanide complexes, where luminescence quenching proceeds via interaction with the excited state of the lanthanide complex.

Elucidation of these quenching mechanisms will inform the selection of appropriate CWA simulants for investigations with lanthanide complexes and will contribute to the future construction of more specific, efficient and potentially regenerable CWA sensing systems.

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Notes and references

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