Cluster of Hexamolybdenum \([\text{Mo}_6\text{Cl}_{14}]^{2-}\) for Sensing Nitroaromatic Compounds

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ABSTRACT: This contribution describes a novel method for the detection of trace amounts of trinitrotoluene (TNT) using a cluster of hexamolybdenum with general formula \([\text{Mo}_6\text{Cl}_{14}]^{2-}\). The molybdenum cluster was characterized by UV–visible, FT-IR, and fluorescence techniques, and the synthesis was efficient and reproducible. The evaluation of the molybdenum cluster by TNT detection was performed by fluorescence measurements, and the results were interpreted by the Stern–Volmer equation, obtaining \(K_{SV}\) values of 2.9 \(\times\) \(10^5\) and 1.6 \(\times\) \(10^4\) \(M^{-1}\) in different concentration ranges. Further, the results suggest that at TNT concentrations higher than 4 \(\times\) \(10^{-5}\) mM (0.01 mg L\(^{-1}\)) it is possible to measure the quenching of the cluster fluorescence. The DFT calculations indicate that the contribution of the TNT in the active lowest unoccupied molecular orbitals that are involved in the higher intensity transitions in the complex cluster–TNT are significant. This situation differs from all the luminescent \([\text{M}_6\text{X}_8\text{L}_6]^{2-}\) clusters (\(\text{M} = \text{Mo}; \text{X} = \text{facial bridging ligand, and } \text{L} = \text{labile axial ligands}\)), where most of the closely spaced excited states are located in the \(\{\text{M}_6\text{X}_8\}\)\(^{q+}\) core. Thus, the TNT switches off the cluster luminescence. The approach using a \([\text{Mo}_6\text{Cl}_{14}]^{2-}\)-based fluorescence sensor has the potential to be a sensing technology for the detection of nitroaromatic explosives.

1. INTRODUCTION

Substantial parts of modern solid-state inorganic chemistry may be identified with polynuclear coordination compounds of the well-known octahedral building block \([\text{M}_6\text{X}_8\text{L}_6]^{2-}\) clusters, where \(\text{M}\) is Mo, \(\text{X}\) is the facial bridging ligand, and \(\text{L}\) is labile axial ligands, have attracted substantial interest because of the luminescent characteristics displayed by the \(\{\text{M}_6\text{X}_8\}\)\(^{q+}\) core.\(^{1-3}\) In the past decade, numerous photophysical and computational studies of in view of the interest in the photophysics and photochemistry of these cluster complexes have shed light on their electronic structure and spectroscopic properties.\(^{2,5-7}\) Some recent applications of these luminescent clusters are known. For example, a the cluster \([\text{Mo}_6\text{Cl}_{14}]^{2-}\) is a promising fluorescent component and could be studied in animal models at therapeutic doses for potential use in tracking cancer cells in vivo and as an antiviral agent and show promise as bioimaging agents and also as metal-based X-ray contrast media.\(^{8-10}\)

Computational studies carried out by our research group indicate that the contribution of the axial pyridine ligands (py) in the active lowest unoccupied molecular orbitals that are involved in the higher intensity transitions in the \([\text{Mo}_6\text{Cl}_6(\text{py})_6]^{4+}\) cluster is significant.\(^4\) This situation differs from all the luminescent \([\text{M}_6\text{X}_8\text{L}_6]^{2-}\) clusters, where most of the closely spaced excited states are located in the \(\{\text{M}_6\text{X}_8\}\)\(^{q+}\) core.\(^4\) Moreover, the synthetic versatility of the \(\{\text{M}_6\text{X}_8\}\)\(^{q+}\) derived clusters has allowed the synthesis of extended new porous materials that can be used as molecular sieves or be used as starting material for designing versatile chemical sensors for the detection of a large variety of volatile organic contaminants.\(^{11,12}\) The detection of nitroaromatic compounds, best known as raw materials in explosives preparations, is important in many fields including environmental science, public security, and forensics.\(^{13-17}\)

This contribution describes the experimental and calculated electronic structure and the optical properties of the luminescent \([\text{Mo}_6\text{Cl}_{14}]^{2-}\) and not luminescent \([\text{Mo}_6\text{Cl}_{14}]^{2-}\)–TNT complex. To evaluate the use of the molybdenum cluster as a sensor, the study of the TNT impact on the emission spectra and its influence on their photophysics was carried out.

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2. EXPERIMENTAL SECTION

2.1. Reagents and Apparatus. Reagents were purchased of analytical grade and used without further purification. All procedures were carried out under a nitrogen atmosphere by using a vacuum atmosphere drybox equipped with a Model HE 493 Dri-Train purifier. Fourier transform infrared spectroscopy (FT-IR) spectra were measured using a JASCO FT-IR 4100 spectrometer in the frequency range 500−4000 cm\(^{-1}\). UV−visible spectra were recorded with a JASCO V-630 UV−visible spectrophotometer. Elemental analyses were made with a Fisons EA 1108 microanalyzer. Photoluminescence measurements were recorded with a JASCO FP-8200 spectrophotometer using an excitation of 312 nm and an emission range of 250−700 nm, with an integration time of 0.1 s and a slit of 5 nm. Samples were contained on 1 cm path length quartz cuvettes.

2.2. Synthesis of Molybdenum Cluster. A slightly modified preparation method was used to produce molybdenum cluster \([\text{Mo}_6\text{Cl}_{14}]^{2−}\), with a higher yield and a more straightforward protocol. Briefly, an ampule with MoCl\(_5\) (5.00 g, 18.3 mmol) and bismuth (3.825 g, 18.3 mmol) was sealed under a vacuum and left in the receiver chamber of the oven. The ampule was placed in the center of a horizontal tube furnace, and the temperature was slowly raised to 230 °C over 2 h and then to 350 °C for an additional 2 h. Subsequently, the ampule was heated at 350 °C for 2.5 days. In the final stage, it was allowed to cool and then placed in the glovebox.

As a result, we obtained 4.066 g (theory for Mo\(_6\)Cl\(_{12}\), 3.053 g) of a homogeneous crystalline olive green/brown nonvolatile product. A portion of this solid (2 g) was treated with concentrated HCl and recrystallized to yield 1.456 g of an orange-yellow chloromolybdic acid, \((\text{H}_3\text{O})_2[\text{Mo}_6(\mu_3-\text{Cl})_8\text{Cl}_6]\)·6H\(_2\)O (extended formula of \([\text{Mo}_6\text{Cl}_{14}]^{2−}\)), 80% yield, based on MoCl\(_5\). Anal. Calc: Mo, 55.50 (average of three trials); UV−vis (DMSO), \(\lambda_{\text{max}}\) 330 nm; FT-IR, \(\nu(\text{OH})\) 3200−3600 water cluster.

A concentrated 5 mM stock solution of \([\text{Mo}_6\text{Cl}_{14}]^{2−}\) was prepared with 61 mg of molybdenum cluster dissolved in 10 mL of DMSO. Concentrated 22 mM stock TNT solution was prepared with 50 mg of TNT (purchased from Sigma-Aldrich) dissolved in 10 mL of DMSO. For photoluminescent measurements, the molybdenum cluster was transferred (500 μL) to a 5 mL calibrated flask with TNT solution aliquots containing from \(4 \times 10^{-5}\) to 18 mM, and then the fluorescence spectra were recorded.

2.3. Computational Details. The computational calculations were carried out by using Amsterdam Density Functional (ADF) code.\(^{19}\) The scalar and spin−orbit relativistic effects were incorporated by using the zero-order regular approximation (ZORA).\(^{20}\) All the real cluster structures were fully optimized via analytical energy gradient method implemented by Verluis and Ziegler, employing the local density approximation (LDA) within the Vosko−Wilk−Nusair parametization for local exchange correlations. We also used the GGA (Generalized Gradient Approximation) PW91 functional.\(^{21}\) The excitation energies were estimated by time-dependent perturbation density functional theory including relativistic scalar and spin−orbit effects (TDDFT). Solvation effects were modeled by a conductor-like screening model for real solvents (COSMO)\(^{22}\) using dichloromethane as solvent. The cluster geometry optimization and the excitation energies were calculated using a standard Slater-type-orbital (STO) basis sets with triple-ζ quality double plus polarization functions (TZ2P) for all atoms.\(^{19}\) We carried out harmonic frequency calculations on each cluster to confirm that the converged geometries were equilibrium structures.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization of Molybdenum Cluster. Several synthetic routes to chloromolybdic acid have
been reported, and one has been developed by our research group in high temperature solid-state inorganic synthesis by reduction with bismuth under a vacuum and heating at 350 °C for 2.5 days. Subsequently, a portion of this solid was treated with concentrated hydrochloric acid and recrystallized to yield of orange-yellow chloromolybdic acid, solid was treated with concentrated hydrochloric acid and recrystallized to yield of orange-yellow chloromolybdic acid, (H2O)2[Mo6(μ-Cl)4Cl8]·6H2O with a 80% of yield. The stable molybdenum cluster was characterized using analysis elemental, FT-IR and UV–vis as are detailed below.

The hydration has been studied in numerous reactivity and spectroscopy experiments, mainly elucidating the structure of clusters. The FT-IR spectrum exhibits broad absorption features that were assigned to rapid fluctuation of isomeric structures. This observation agrees with theoretical calculations and experimental results described in literature.

As shown in Figure 1, the FT-IR spectrum of the molybdenum cluster is similar to that observed in published works, and it is possible to assign the broad absorption feature (3200–3600 cm⁻¹) to the O–H stretching associated with the water present in the cluster chemistry structure.

The UV–vis absorption spectrum of the molybdenum cluster was recorded in DMSO and is shown in Figure 2. Comparison of the absorption spectra of several clusters of the general formula [Mo6X14]²⁻ suggest that the nature of the HOMO and LUMO, the lowest energy electronic transitions arise from metal to metal charge transfer (MMCT). The UV–vis spectrum shows the maximum absorption at 330 nm, and that value is comparable to the optical energy band gaps found from absorption spectra of reported previously for similar clusters [Mo6X14]²⁻, [Mo6X4(NCS)6]²⁻ (X = Cl⁻, Br⁻, I⁻), and [Mo6X4(CF3COO)6]²⁻. These optical energy gaps, obviously, refer to spin-allowed (i.e., singlet state to singlet state) transitions.

3.2. Detection of Nitroaromatic Compounds. Detection of explosive materials is necessary in a variety of complex environments, including munitions storage facilities, wastewater treatment facilities, transportation areas, blast sites, and mine fields. In each of these settings, sensitive and timely detection of explosive materials is necessary to ensure the safety and security of the surrounding area. For this reason, the molybdenum cluster capacity of TNT sensing at low concentrations was evaluated by photophysics studies. The photoluminescent emission spectrum of molybdenum cluster in DMSO (excitation at 312 nm) is characterized by a broad band in the 330–600 nm range with a maximum at 409 nm (Figure 3).

Nitroaromatic explosives, despite having an aromatic structure, do not fluoresce as result of the strong electron-withdrawing nature of the nitro substituents. Despite this lack of native fluorescence, many methods have been proposed in recent years for their detection using luminescence-based techniques. In this respect, fluorescence-based sensors are very promising.

The quenching of the molybdenum cluster fluorescence by nitroaromatic compound was described using the Stern–Volmer equation:

\[
\frac{I}{I_0} = 1 + K_{SV}[TNT]
\]

where \(I_0\) is the fluorescence intensity without nitroaromatic compound, \(I\) is the fluorescence intensity observed in the presence of the nitroaromatic compound, and \(K_{SV}\) is the Stern–Volmer constant.

### Table 1. Stern–Volmer Parameters for the Quenching of the Molybdenum Cluster by TNT

| compound                  | \(K_{SV}\) [M⁻¹] | intercept | \(R^2\) | points | [TNT] [mM] |
|---------------------------|------------------|-----------|---------|--------|------------|
| [Mo6Cl14]²⁻               | 2.9 × 10⁴        | 1.158     | 0.923   | 7      | (0–3) × 10⁻³ |
|                           | 1.6 × 10⁴        | 2.043     | 0.990   | 7      | 3 × 10⁻³ to 0.13 |

### Table 2. Quenching Constants (\(K_{SV}\)) for Different Compounds with Nitrocompounds

| compound                  | \(K_{SV}\) [M⁻¹] | concn range [mM] | ref |
|---------------------------|------------------|------------------|-----|
| [Mo6Cl14]²⁻               | 2.9 × 10⁴        | TNT (0–3) × 10⁻³  | this work |
|                           | 1.6 × 10⁴        | 3 × 10⁻³ to 0.13  |     |
| pyrene                    | 394              | TNT              | 43  |
| DAB-CdS                   | 25               | nitromethane 8.8–52.8 | 44  |
| polyethyleneimine capped carbon quantum dots | 8.39 × 10⁴ | TNT 0–0.04 | 45  |
| conjugated polymer (carbazole and tetraphenylethylene units) | 8.5 × 10⁴ | TNT 0–0.07 | 46  |
The linear Stern–Volmer plot was obtained in two sections (Figure 4a,b and Table 1) and the calculated parameters show sensibility for the nitroaromatic compound by the molybdenum cluster with a relatively large quenching ($K_{SV} = 1.6 \times 10^4$ to $2.9 \times 10^5$ M$^{-1}$). Also, this result suggests that at TNT concentrations higher than $4 \times 10^{-5}$ mM it is possible to measure the quenching of the cluster fluorescence.

Regarding Table 1, on the one hand, a good fit is observed for both concentration ranges studied. However, the intercept value obtained in the $(0-3) \times 10^{-3}$ mM range is closer to the theoretical value presented in the Stern–Volmer equation. On the other hand, the behavior observed in the $3 \times 10^{-3}$ to 0.13 mM range can be attributed to the appearance of significant collisional quenching between the molybdenum clusters (intercept different from 1).

The analysis of the Stern–Volmer calculated parameters shows that, besides the expected collisional quenching, there is probably the formation of a ground-state complex between the nitroaromatic compound and molybdenum cluster (vide infra). Indeed, the comparison of these constants with others corresponding to the quenching of fluorophores by nitrated substances shows that the now calculated values are several orders of magnitude higher (Table 2).

For example, Goodpaster and McGuffin$^{43}$ studied the fluorescence quenching of pyrene and related compounds by nitrated explosives and obtained maximum Stern–Volmer constants of nearly four hundred. Also, they have found that nitroaromatic compounds are more efficient quenchers than their aliphatic counterparts, with higher quenching constants. They have also found that the quenching constants increased with the increasing number of electron withdrawing nitro groups in the benzene ring. In another study using a CdS-DAB dendrimer nanocomposite by nitromethane, a $K_{SV}$ of 25 M$^{-1}$ was observed.$^{44}$ The results obtained are promising, but it is necessary to study the selectivity of the sensor in the future to validate a real application.

The theoretical calculations suggest that in the $[\text{Mo}_6\text{Cl}_{14}]^{2-}$ luminescent cluster, the HOMO is mainly metallic and most of the lowest unoccupied molecular orbitals are located in the $[\text{Mo}_6\text{Cl}_{14}]^{2-}$ core.$^{3,5}$ Thus, most of the allowed electronic transitions are of the MMCT type and the closely spaced excited states are all localized in the $[\text{Mo}_6\text{Cl}_{14}]^{2-}$ core with no participation of the axial ligands.$^{3,4}$ However, for the $[\text{Mo}_6\text{Cl}_{14}]^{2-}$–TNT complex, the HOMO is mainly metallic, but most of the lowest unoccupied molecular orbitals are made from $[\text{Mo}_6\text{Cl}_{14}]^{2-}$–TNT complex contributions and are not located in the $[\text{Mo}_6\text{Cl}_{14}]^{2-}$ core. The participation of the TNT...
ligands in the closely spaced excited states is significant (see Figure 5), whereas the participation of the bridging Cl ligand is minor.

The excitation energies were calculated using the TDDFT formalism including scalar relativistic and solvent effects. Thus, this value shows that the participation of the TNT ligand in the active lowest unoccupied molecular orbitals that are involved in the higher intensity transitions in the [Mo6Cl14]2− cluster is minor. The TNT antennas are deactivated practically instantaneously after being excited since the quencher molecule is situated in the proximity of the excited molecules and interacts with them. Thus, the TNT switches off the cluster luminescence.

4. CONCLUSION

The characterization and application for TNT sensing were studied using a [Mo6Cl14]2− cluster. The synthesis of the molybdenum cluster was efficient and reproducible. The quenching of the molybdenum cluster luminescence by nitroaromatic compound was described using the Stern–Volmer equation, obtaining a good fit in two concentration ranges. The obtained $K_{SV}$ values in both concentration ranges were similar or superior to those measured using other fluorescent sensors. Also, concentrations higher than $4 \times 10^{-5}$ mM (0.01 mg L$^{-1}$) of the TNT were possible to measure the quenching of the cluster fluorescence.

The DFT calculations indicate that the contribution of the TNT in the active lowest unoccupied molecular orbitals that are involved in the higher intensity transitions in the complex cluster−TNT are significant. This situation differs from all the luminescent $[M_6X_8]^{2−}$ clusters, where most of the closely spaced excited states are located in the $[M_6X_8]^{9+}$ core. The interaction of TNT with molybdenum clusters was reported by theoretical and experimental methods. The TNT switches off the $[Mo_6Cl_{14}]^{2−}$ cluster luminescence.

The approach using a cluster fluorescence sensor has the potential to be a sensing technology for the detection of nitroaromatic explosives. The results obtained are promising, but in the future it will be necessary to evaluate the sensor capacity in real samples with other interferents.

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Notes

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