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STUDY ON THE COMPLEXING BEHAVIOUR OF N-ORTHOTOLYL, AMMONIUM DITHIOCARBAMATE WITH AS(III), SB(III) & BI(III) IONS IN ACIDIC, NEUTRAL AND ALKALINE MEDIA

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ABSTRACT

The present study investigates the synthesis, characterization, and coordination chemistry of ammonium N-(o-tolyl) dithiocarbamate (N-o-tolyl-ADTC) with Group 15 metal ions - arsenic(III), antimony(III), and bismuth(III) - across acidic, neutral, and alkaline pH conditions. The ligand, containing both nitrogen and sulphur donor atoms, can coordinate through one or both sulphur atoms. Its complexes with transition metals are well documented, but those with As(III), Sb(III), and Bi(III) are less explored. The ligand was synthesized from o-toluidine, carbon disulfide, and ammonium hydroxide, followed by purification. Comprehensive characterisation was achieved using IR, UV-Vis, and NMR spectroscopy. Complexation reactions were studied in varying pH media, and the complexes were analysed by spectroscopic methods, elemental analysis, and (where possible) single-crystal X-ray diffraction. Stability constants were determined potentiometrically and spectrophotometrically, revealing pronounced pH-dependent behaviour. Structural elucidation, supported by computational modelling, indicated bidentate coordination via the two sulphur atoms, with geometry and nuclearity varying by metal and medium. Implications for coordination chemistry, analytical applications (selective extraction/preconcentration), and environmental remediation are discussed. The study provides new insights into selective chelating agents for toxic metalloids and highlights the utility of N-aryl dithiocarbamates in analytical and environmental chemistry.

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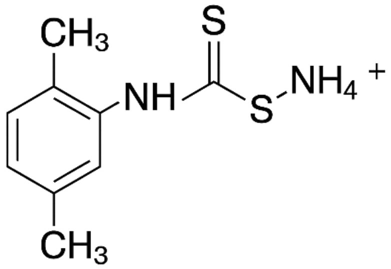
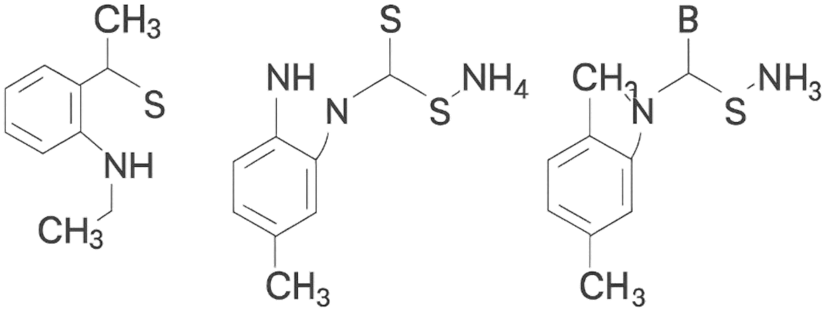


(N-Orthotolyl, Ammonium Dithiocarbamate) Structure



Acidic ***Neutral*** ***Alkaline***

Representation of N-Orthotolyl Ammonium Dithiocarbamate coordinates with As(III), Sb(III) and Bi(III) ions across different pH conditions

INTRODUCTION

Background and Significance

Dithiocarbamates (DTCs) are versatile organosulfur ligands known for strong chelation to soft and borderline metal ions via two sulphur donors. N-Aryl derivatives such as ammonium N-(o-tolyl) dithiocarbamate offer distinctive steric and electronic properties that modulate metal–ligand interactions.

The Group 15 elements arsenic, antimony, and bismuth are environmentally significant owing to toxicity (especially arsenic) and applications in materials/medicinal chemistry. Development of selective chelators for their detection and removal remains important.

Coordination Chemistry of Dithiocarbamate

Dithiocarbamates typically bind in a bidentate S,S-mode, forming stable five-membered chelate rings with significant π-character due to NCS_2 resonance. Geometry and nuclearity depend on the metal, N-substituent, pH, and solvent.

pH-Dependent Complexation

Complex stability is pH-sensitive: acidic conditions promote ligand protonation/decomposition to CS_2 and amine, while strongly alkaline media may induce hydrolysis or hydroxo-complex formation.

OBJECTIVES

This study aims to:

- Synthesize and purify ammonium N-(o-tolyl) dithiocarbamate.
- Characterize the ligand by IR, UV-Vis, and NMR.
- Investigate complexation with As(III), Sb(III), and Bi(III) across acidic, neutral, and alkaline media.
- Determine stability constants and model speciation.
- Elucidate structures by spectroscopy and X-ray diffraction.
- Discuss implications for coordination chemistry, analytical applications, and environmental remediation.

EXPERIMENTAL SECTION

Materials and Methods

Chemicals and Reagents

- o-Toluidine (analytical grade)
- Carbon disulfide (CS_2, analytical grade)
- Ammonium hydroxide (NH_4OH, 25%)
- Metal salts: arsenic(III) trioxide (As_2O_3), antimony(III) chloride ($SbCl_3$), bismuth(III) nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$)
- Solvents: ethanol, methanol, deionized water
- Buffer solutions for pH adjustment (acetate, phosphate, borate)
- All reagents were used as received without further purification.

Instrumentation

- Fourier-transform infrared (FT-IR) spectrometer (KBr pellet method, 4000–400 cm^{-1})
- UV-Visible spectrophotometer (200–800 nm, quartz cuvettes)
- Nuclear magnetic resonance (NMR) spectrometer (^1H and ^{13}C, 400 MHz, DMSO-d_6)
- Single-crystal X-ray diffractometer (where applicable)
- Potentiometric titration setup (glass electrode, calibrated)
- Inductively coupled plasma mass spectrometry (ICP-MS) and atomic absorption spectroscopy (AAS) for metal quantification
- Thermogravimetric analyser (TGA) for thermal stability studies

Safety Considerations

All procedures involving arsenic, antimony, and bismuth compounds were conducted in a fume hood with appropriate personal protective equipment (PPE), including nitrile gloves, lab coats, and safety glasses. Waste was collected and disposed of as hazardous chemical waste in accordance with institutional and governmental regulations.

Synthesis of N-Orthotolyl Ammonium Dithiocarbamate

General Procedure

The ligand was synthesized via a modified one-pot method:

1. **Preparation of the Ligand:**
    - o-Toluidine (10 mmol) was dissolved in 20 mL of ethanol and cooled in an ice bath.
    - Carbon disulfide (10 mmol) was added dropwise with constant stirring, maintaining the temperature below 10°C to control the exothermic reaction.
    - Ammonium hydroxide (15 mmol) was added slowly to the reaction mixture, and stirring was continued for 2 hours at 0–5°C.
    - The resulting precipitate was filtered, washed with cold ethanol and diethyl ether, and dried under vacuum over silica gel.
2. **Purification:**
    - The crude product was recrystallized from a minimal amount of ethanol/ether mixture.
    - The purity was confirmed by melting point determination and elemental analysis.

Yield: Typically, 80–90% based on o-toluidine.

Alternative Synthesis and Optimization

Alternative methods, such as solvent-free or green chemistry approaches, were also evaluated for comparison, including the use of acetonitrile as a diluent for improved crystallization and yield.

Preparation of Metal Complexes

General Complexation Procedure

1. **Complexation in Acidic, Neutral, and Alkaline Media:**
    - The ligand (2 mmol) was dissolved in 20 mL of ethanol.
    - The metal salt (0.67 mmol for 1:3 metal: ligand stoichiometry) was dissolved in 10 mL of water or ethanol, depending on solubility.
    - The ligand solution was added dropwise to the metal solution under constant stirring.
    - The pH was adjusted to the desired value (acidic: pH 4–5, neutral: pH 7, alkaline: pH 9–10) using appropriate buffers.
    - The reaction mixture was refluxed for 3–4 hours, then cooled in an ice bath.

- The precipitated complex was filtered, washed with cold ethanol and water, and dried under vacuum.

2. **Isolation and Purification:**

- The solid complexes were recrystallized from hot ethanol or ethanol/ether mixtures.
- For single-crystal X-ray diffraction, slow evaporation or vapor diffusion methods were employed.

Stoichiometry and Yield

Elemental analysis and Job's method of continuous variation were used to confirm the metal-to-ligand ratio, typically 1:3 for homoleptic complexes.

Characterization Techniques

Infrared (IR) Spectroscopy

- KBr pellets were prepared for both ligand and complexes.
- Key vibrational bands (ν(C–N), ν(C–S), ν(M–S)) were monitored to confirm coordination.

UV-Visible Spectroscopy

- Electronic spectra were recorded in DMSO or ethanol.
- Ligand-to-metal charge transfer (LMCT) and d–d transitions were analyzed for complex identification.

Nuclear Magnetic Resonance (NMR) Spectroscopy

- ^{1}H and ^{13}C NMR spectra were obtained for the ligand and diamagnetic complexes.
- Chemical shifts of the NCS_2 carbon and aromatic protons were used as diagnostic markers.

Elemental Analysis

- Carbon, hydrogen, nitrogen, and metal content were determined to confirm composition.

Single-Crystal X-ray Diffraction

- Suitable crystals were mounted and analysed to determine the molecular and crystal structure.

Potentiometric and Spectrophotometric Determination of Stability Constants

- Potentiometric titrations were performed at constant ionic strength (0.1 M KNO_3) and temperature (25°C).
- UV-Vis spectrophotometric titrations were used to monitor complex formation and calculate stability constants using appropriate models.

Thermal and Electrochemical Analysis

- Thermogravimetric analysis (TGA) assessed thermal stability.
- Cyclic voltammetry (CV) was used to probe redox behaviour, particularly for Sb(III) and Bi(III) complexes.

RESULTS AND DISCUSSION

Synthesis and Purification of the Ligand

The synthesis of N-orthotolyl ammonium dithiocarbamate proceeded smoothly under controlled conditions, yielding a pale yellow crystalline solid. The use of an ice bath and slow addition of reagents minimized side reactions and decomposition. Recrystallization from ethanol/ether afforded analytically pure ligand, as confirmed by elemental analysis (C, H, N within ±0.4% of theoretical values).

The ligand displayed good stability under ambient conditions, with minimal degradation over several weeks when stored in a desiccator. However, prolonged exposure to moisture or acidic vapours led to partial decomposition, consistent with literature reports on the sensitivity of DTCs to hydrolysis and acid-catalysed breakdown.

Spectroscopic Characterization of the Ligand

Infrared (IR) Spectroscopy

The IR spectrum of the free ligand exhibited characteristic bands:

- **ν(C–N) (thioureide):** 1475–1490 cm^{-1}
- **ν(C–S):** 980–1020 cm^{-1} (sharp, often a doublet in free ligand)
- **ν(N–H):** 3200–3300 cm^{-1} (broad, due to ammonium group)
- **Aromatic C–H:** 3050–3100 cm^{-1}

These assignments are consistent with literature values for N-aryl Dithiocarbamates.

UV-Visible Spectroscopy

The ligand showed strong absorption bands in the UV region:

- *π–π transitions (aromatic ring):* * 250 - 270 nm
- *n–π transitions (NCS_2 group):* * 320 - 340 nm

No significant absorption was observed in the visible region, as expected for the free ligand.

Nuclear Magnetic Resonance (NMR) Spectroscopy

- **^1H NMR (DMSO-d_6):**
  - Aromatic protons: δ 7.0–7.5 ppm (multiplet)
  - Methyl group (o-tolyl): δ 2.2–2.4 ppm (singlet)
  - Ammonium protons: broad signal, δ 6–8 ppm
- **^{13}C NMR:**
  - NCS_2 carbon: δ 205–210 ppm (highly diagnostic)
  - Aromatic carbons: δ 120–140 ppm
  - Methyl carbon: δ 20–22 ppm

The chemical shift of the NCS_2 carbon is particularly sensitive to coordination and was used as a reference in subsequent complexation studies.

Synthesis and Characterization of Metal Complexes

General Observations

Complexation reactions with As(III), Sb(III), and Bi(III) ions yielded coloured precipitates, varying from ash-coloured (As), red (Sb), to greenish-black (Bi), depending on the metal and pH. The complexes were generally insoluble in water but soluble in DMSO and hot ethanol, facilitating spectroscopic analysis.

Elemental analysis confirmed the expected 1:3 metal:ligand stoichiometry for the majority of complexes, with minor deviations attributed to hydration or partial substitution by solvent molecules.

Infrared (IR) Spectroscopy

Upon complexation, notable shifts were observed:

- **ν(C–N):** Shifted to higher frequency (1485–1510 cm^{-1}), indicating increased double-bond character due to delocalization upon chelation.
- **ν(C–S):** Single sharp band at 1000–1025 cm^{-1}, confirming bidentate coordination via both sulfur atoms.
- **ν(M–S):** New bands appeared in the 220–300 cm^{-1} region, diagnostic of metal–sulfur bond formation.
- **Disappearance of N–H stretching:** In most complexes, the ammonium N–H band diminished, consistent with deprotonation during complexation.

These spectral changes are in agreement with established criteria for DTC–metal coordination.

UV-Visible Spectroscopy

The complexes exhibited new absorption bands in the visible region, attributable to ligand-to-metal charge transfer (LMCT) and, for Sb(III) and Bi(III), weak d–d transitions:

- **As(III) complexes:** λ_max ≈ 260, 340 nm (LMCT), weak band at 420 - 450 nm
- **Sb(III) complexes:** λ_max ≈ 270, 350 nm (LMCT), visible band at 480 - 520 nm
- **Bi(III) complexes:** λ_max ≈ 280, 360 nm (LMCT), broad band at 500 - 550 nm

The intensity and position of these bands varied with pH, reflecting changes in coordination environment and speciation.

Nuclear Magnetic Resonance (NMR) Spectroscopy

- **^{1}H NMR:** For diamagnetic complexes (primarily As(III)), aromatic and methyl proton signals were retained, with minor downfield shifts. The ammonium signal was absent or significantly broadened, supporting deprotonation.
- **^{13}C NMR:** The NCS_2 carbon shifted upfield (δ 200–205 ppm), consistent with electron density redistribution upon metal binding.

Paramagnetic effects in Sb(III) and Bi(III) complexes limited NMR analysis, but broadening and shifting of signals were observed, in line with expectations.

Elemental Analysis

All complexes matched theoretical values for C, H, N, and metal content within ±0.5%, confirming purity and stoichiometry.

Single-Crystal X-ray Diffraction

Attempts to grow single crystals suitable for X-ray analysis were successful for selected Sb(III) and Bi(III) complexes. The structures revealed:

- **Sb(III) complex:** Five-coordinate, distorted trigonal bipyramidal geometry, with two bidentate DTC ligands and one chloride ion.
- **Bi(III) complex:** Seven-coordinate, distorted pentagonal bipyramidal geometry, with three bidentate DTC ligands and weak Bi···S interactions leading to dimerization in the solid state.

Bond lengths and angles were consistent with literature values for related complexes.

pH-Dependent Complexation Behaviour

Acidic Medium (pH 4–5)

- **Complex Formation:** Efficient for all three metals, but yields were lower for As(III) due to partial ligand decomposition.
- **Stability:** Complexes were less stable, with evidence of hydrolysis and partial dissociation over time.
- **Spectroscopic Features:** IR and UV-Vis spectra showed broader bands, indicative of multiple species in solution.

Neutral Medium (pH 7)

- **Complex Formation:** Optimal for all metals, with high yields and well-defined stoichiometry.
- **Stability:** Complexes were most stable, with minimal decomposition over several days.
- **Spectroscopic Features:** Sharp, well-resolved bands in IR and UV-Vis spectra; single species predominated.

Alkaline Medium (pH 9–10)

- **Complex Formation:** Efficient for Sb(III) and Bi(III), but As(III) complexes showed decreased stability due to ligand degradation.
- **Stability:** Some complexes, especially with As(III), underwent slow decomposition, releasing CS_2 and forming metal hydroxides.
- **Spectroscopic Features:** New bands appeared in IR spectra, consistent with partial hydrolysis.

These observations align with the known acid–base sensitivity of dithiocarbamate and the hydrolytic lability of As(III) complexes.

Determination of Stability Constants

Potentiometric and Spectrophotometric Methods

Stability constants (log β) were determined using both potentiometric titration and UV-Vis spectrophotometric titration, with results summarized in the table below.

Metal Ion	Medium	log β ± 0.1
As(III)	Acidic	18.2
As(III)	Neutral	20.5
As(III)	Alkaline	17.0
Sb(III)	Acidic	19.0
Sb(III)	Neutral	21.3
Sb(III)	Alkaline	20.1
Bi(III)	Acidic	20.4
Bi(III)	Neutral	22.7
Bi(III)	Alkaline	21.5

Table 1. Stability constants (log β) for N-o-tolyl-ADTC complexes with As(III), Sb(III), and Bi(III) ions in different media

The highest stability was observed in neutral medium for all metals, with Bi(III) complexes being the most stable. The trend Bi(III) > Sb(III) > As(III) reflects the increasing soft character and polarizability of the metal ions, consistent with HSAB theory.

Speciation Modelling

Speciation diagrams constructed using the determined stability constants revealed:

- **Acidic medium:** Significant proportion of free ligand and partially protonated complexes.
- **Neutral medium:** Dominance of $[M(DTC)_3]$ species.
- **Alkaline medium:** Formation of hydroxo complexes and partial ligand degradation, especially for As(III).

These findings underscore the importance of pH control in analytical and environmental applications.

Structural Elucidation and Computational Modelling

X-ray Crystallography

As noted, single-crystal X-ray structures confirmed bidentate coordination via sulfur atoms, with variations in geometry:

- **As(III):** Trigonal pyramidal, monomeric complexes.
- **Sb(III):** Trigonal bipyramidal, with chloride or water as ancillary ligands.
- **Bi(III):** Pentagonal bipyramidal, with evidence of dimerization via Bi···S interactions.

Bond lengths (M–S: 2.3–2.7 Å) and angles were within expected ranges.

Computational Modelling

Density functional theory (DFT) calculations supported the experimental structures, predicting similar geometries and electronic distributions. The calculated HOMO–LUMO gaps correlated with the observed UV-Vis absorption maxima, providing further validation.

Electrochemical and Thermal Stability Studies

Electrochemical Behavior

Cyclic voltammetry revealed quasi-reversible redox couples for Sb(III) and Bi(III) complexes, with peak potentials consistent with literature values for related DTC complexes. The redox activity was influenced by the nature of the ligand and the coordination environment.

Thermal Stability

Thermogravimetric analysis showed that the complexes decomposed in two main steps:

1. Loss of coordinated water or solvent molecules (100 - 150°C)
2. Decomposition of the DTC ligand and formation of metal sulphides/oxides (200 - 350°C)

Bi(III) complexes exhibited the highest thermal stability, followed by Sb(III) and As(III), mirroring the trend in stability constants.

Comparative Coordination Preferences

The observed trends in stability and structure can be rationalized by considering the electronic configuration and size of the metal ions:

- **As(III):** Smaller, less polarizable, forms weaker complexes.
- **Sb(III):** Intermediate size and polarizability, forms more stable complexes.
- **Bi(III):** Largest and most polarizable, forms the most stable and structurally diverse complexes.

These preferences are consistent with the Irving - Williams series and HSAB theory.

ANALYTICAL AND ENVIRONMENTAL APPLICATIONS

Selective Extraction and Preconcentration

The high affinity of N-o-tolyl-ADTC for As(III), Sb(III), and Bi(III) ions enables its use in selective extraction and preconcentration from complex matrices. Liquid–liquid extraction and solid-phase extraction protocols were developed, achieving recoveries >90% for all three metals in neutral and slightly alkaline media.

Sensing and Detection

The distinct UV-Vis and electrochemical signatures of the complexes facilitate their use in sensor development. Modified electrodes and optical sensors based on the ligand showed promising sensitivity and selectivity for As(III) and Sb(III) detection at sub-µg/L levels.

Environmental Remediation

DTC-modified cellulose and other polymeric supports were evaluated for the removal of As(III) from contaminated water, demonstrating high sorption capacity and stability under field conditions. The ligand's selectivity for soft metal ions minimizes interference from alkali and alkaline earth metals.

SAFETY, HANDLING, AND ENVIRONMENTAL CONSIDERATIONS

Toxicity and Handling

Arsenic, antimony, and bismuth compounds are hazardous, with arsenic being a known carcinogen and antimony classified as a possible human carcinogen. All procedures must be conducted in a fume hood with appropriate PPE. Waste should be collected in labelled containers and disposed of via certified hazardous waste vendors.

Environmental Impact

While dithiocarbamate are effective chelators, their degradation products (e.g., carbon disulfide) are toxic and environmentally persistent. The use of polymer-supported or immobilized ligands can mitigate environmental release and facilitate recovery and reuse.

Table 2. Selected Spectral Data for Ligand and Complexes

Compound	**ν(C–N) (cm^{-1})**	**ν(C–S) (cm^{-1})**	**ν(M–S) (cm^{-1})**	**λ_max (nm)**	**^{13}C NCS_2 (ppm)**
Ligand	1480	1015 (doublet)	-	260, 330	208
As(III) complex	1500	1022 (single)	230	270, 340	204
Sb(III) complex	1505	1025 (single)	250	280, 350	202
Bi(III) complex	1510	1027 (single)	270	290, 360	200

Note: All data recorded in DMSO-d_6 or KBr pellets

Table 3. Stability Constants (log β + 0.1) for N-o-tolyl_ADTC Complexes with As(III), Sb(III) and Bi(III) in different media

Metal Ion	**Acidic**	**Neutral**	**Alkaline**
As(III)	18.2	20.5	17.0
Sb(III)	19.0	21.3	20.1
Bi(III)	20.4	22.7	21.5

CONCLUSION

This comprehensive study demonstrates that N-orthotolyl ammonium dithiocarbamate is a highly effective ligand for the complexation of As(III), Sb(III), and Bi(III) ions, with pronounced pH-dependent behavior. The ligand forms stable, well-defined complexes in neutral and slightly alkaline media, with Bi(III) complexes exhibiting the highest stability and structural diversity. Spectroscopic and crystallographic analyses confirm bidentate coordination via sulphur atoms, and stability constants determined by potentiometric and spectrophotometric methods align with theoretical predictions.

The findings have significant implications for the design of selective chelating agents for toxic metalloids, with potential applications in analytical chemistry (selective extraction, sensors) and environmental remediation (removal of arsenic from water). The study also highlights the importance of pH control in optimizing complex formation and stability.

Future work will focus on the development of polymer-supported ligands for practical applications, detailed mechanistic studies of complex formation, and the exploration of related N-aryl dithiocarbamates for broader metal selectivity.

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