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# NOVEL SILVER NANOPARTICLE COMPLEXES BASED ON BISACETYLACETONEETHYLENEDIAMINE AND CETYLTRIMETHYLAMMONIUM BROMIDE: SYNTHESIS AND STRUCTURE

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In the present work, binary and ternary complexes of silver nanoparticles (AgNPs) with bisacetylacetoneethylenediamine (bis-AAED) reagent and cetyltrimethylammonium bromide (CTAB) were synthesized. UV–Vis analysis showed that AgNPs exhibited a plasmon resonance peak at 410 nm, while bis-AAED displayed π→π* and n→π* absorption bands at 223, 270, and 299 nm. The Ag–bis-AAED complex revealed shifted bands at 227, 272, and 308 nm, whereas the Ag–bis-AAED–CTAB ternary complex exhibited sharper and more intense peaks at 227, 272, and 308 nm, confirming complex formation and changes in the electronic environment. According to XRD results, the bis-AAED reagent exhibited 2θ peaks within 9.90°–42.88° with an average crystallite size of 26.0 nm; the Ag–bis-AAED binary complex showed 2θ peaks at 37.78° and 43.91° with an average size of 10.9 nm; and the Ag–bis-AAED–CTAB ternary complex displayed 2θ peaks within 12.30°–43.95° with an average crystallite size of 9.0 nm. The broadening of peaks and decrease in intensity indicate the partially amorphous nature of the complexes.

**Keywords:** silver, nanoparticles, CTAB, complex, bisacetylacetoneethylenediamine, UV–Vis, XRD

## INTRODUCTION

With the rapid development of nanotechnology, research on the synthesis of metal nanoparticles and their complexes with various functional reagents has become increasingly relevant. Among them, silver nanoparticles (AgNPs) have attracted considerable attention due to their unique optical, electrical, and antibacterial properties [1,2]. Owing to the surface plasmon resonance (SPR) effect observed in these particles, they exhibit characteristic absorption bands in the visible region, which enables their widespread application in colorimetric analysis, sensor systems, and bioanalytical methods. Silver nanoparticles (AgNPs), owing to their high surface area, easily interact with different reagents to form stable complexes. These complexes are stabilized by the functional groups of organic reagents, and their structural characteristics can be investigated [5]. In particular, bisacetylacetoneethylenediamine (bis-AAED) is of special interest, as it effectively forms complexes with AgNPs, leading to stabilization and the creation of coordinated structures.

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This reagent is a condensation product of ethylenediamine and acetylacetone molecules, containing two β-diketone groups and two amino groups in its molecular structure. Such a configuration provides bis-AAED with multiple coordination centers, making it a reagent capable of forming stable complexes with metal ions, especially $Ag^+$ ions [6]. Both oxygen and nitrogen donor atoms of the reagent can coordinate with metal centers, resulting in diverse structures and functional properties of the complexes. The antibacterial effect, catalytic activity, electron transfer properties, and electrochemical stability of AgNPs further broaden their applications in medicine, environmental analysis, and materials science. To direct complex formation and enhance the stability of nanoparticles, a cationic surfactant, cetyltrimethylammonium bromide (CTAB), is introduced into the system. CTAB adsorbs onto the surface of AgNPs, preventing particle aggregation, ensuring colloidal stability, and facilitating the oriented interaction of the reagent with AgNPs [8,9]. The stabilization and surface modification of nanoparticles play a decisive role in controlling their dispersion and reactivity. Similar effects were reported for surface-engineered $Fe_3O_4$ nanoparticles, where functional coatings significantly enhanced colloidal stability and uniformity[10]. In this study, new complexes of AgNPs with bis-AAED and CTAB were synthesized, and their structural and morphological characteristics were investigated using UV–Vis, IR, and XRD analyses. The results obtained may expand the potential applications of such systems in analytical chemistry and materials science [11–12].

## EXPERIMENTAL

*Materials*

Silver nitrate (AgNO3, PLC 141459, 98% chemically pure), soluble starch ((C6H10O5)n, PLC 121096, 98% chemically pure), β-D glucose (C6H12O6, CAS No.50-99-7); sodium hydroxide (NaOH, PLC 1416x87), cetyltrimethylammonium bromide (CTAB, AB 117004), ethanol (C2H5OH, CAS No.64-17-5, 95%), ethylenediamine ($C_2H_8N_2$, CAS No. 107-15-3, 99%), acetylacetone ($C_5H_8O_2$, CAS No. 123-54-6, 99%), and ethanol ($C_2H_5OH$, CAS No. 64-17-5, 99.9%) were used as received.

*Green synthesis of silver nanoparticles (AgNPs)*

An environmentally friendly synthetic approach was applied for the preparation of silver nanoparticles (AgNPs). Initially, 150 mL of 1% soluble starch solution was added to 100 mL of 0.01 M silver nitrate ($AgNO_3$) solution. In parallel, 100 mL of 0.07 M sodium hydroxide (NaOH) solution was mixed with 100 mL of 0.2 M β-D-glucose solution to obtain a homogeneous mixture. The prepared glucose–NaOH solution was then added dropwise to the $AgNO_3$–starch mixture, and the reaction mixture was stirred continuously for 30 minutes. During this stage, the color of the solution gradually turned dark brown, indicating the formation of metallic silver nanoparticles. The resulting colloidal solution was centrifuged at 12,000 rpm using an Eppendorf R 5430 ultracentrifuge, and the nanoparticles were repeatedly washed with a water–ethanol mixture to remove residual ions. In this synthesis process, starch acted both as a stabilizer and a partial reducing agent, while glucose functioned as the main reducing reagent, converting $Ag^+$ ions into metallic $Ag^0$. Sodium hydroxide provided an alkaline medium, which accelerated the reduction process [13,14].

*Synthesis of bis(acetylacetone)ethylenediamine (bis-AAED) reagent.*

For the preparation of the bis-AAED reagent, the following synthesis procedure was employed. Initially, 0.02 M acetylacetone (2,4-pentanedione) was completely dissolved in 50

mL of ethanol ($C_2H_5OH$), and the mixture was cooled in an ice bath. Subsequently, 0.01 M ethylenediamine ($NH_2CH_2CH_2NH_2$) was added dropwise to the system, and stirring was continued at room temperature for 2 hours. As a result of the condensation reaction, a colorless, needle-like crystalline product was formed in the reaction medium, which was collected by filtration after one day and then dried. Analytical studies indicated that the product exists in a protonated form in the solid state. It was established that intramolecular N–H···O hydrogen bonds are present within the molecule. In these interactions, the proton transfers from the oxygen atom of the enol form to the imine nitrogen, resulting in charge distribution between oxygen and nitrogen atoms. Schiff base-type ligands, formed by the condensation of ethylenediamine with β-diketones, are well known for their ability to form stable coordination complexes with transition metal ions—particularly $Ag^{+}$, $Cu^{2+}$, $Ni^{2+}$, and $Zn^{2+}$. Owing to these properties, the bis-AAED reagent has found wide application in coordination chemistry and structural analysis [16–17].

*Synthesis of $Ag^{+}$–bis-AAED–CTAB complexes.*

In this study, novel binary and ternary complex systems based on silver nanoparticles (AgNPs), bis-AAED reagent, and CTAB were synthesized. In the first step, a $10^{-3}$ M solution of bis-AAED reagent was prepared in a water–ethanol mixture. Then, 10 mL of a pre-synthesized 0.01 M AgNP dispersion was added to 50 mL of $10^{-3}$ M reagent solution, and the mixture was stirred magnetically at room temperature for 2 hours. A visible color change from deep red to light red was observed, indicating the formation of the binary $Ag^{+}$–bis-AAED complex. For the synthesis of the ternary complex, the same procedure was repeated: 10 mL of 0.01 M AgNP solution was added to 50 mL of $10^{-3}$ M bis-AAED solution and stirred for 2 hours. Afterwards, 5 mL of 0.5% 0.01 M CTAB solution was added dropwise, and the system was stirred again. Upon the addition of CTAB, a further lightening of the solution color was observed, which confirmed the formation of the ternary AgNP–bis-AAED–CTAB complex. CTAB plays a crucial role in ensuring the stability of the complex: this cationic surfactant prevents the aggregation of AgNPs, regulates the surface interactions of both the reagent and silver nanoparticles, and enhances the colloidal stability of the resulting complex.

Analytical Methods. X-ray diffraction (XRD) patterns of silver nanoparticles were recorded at room temperature using a Rigaku MiniFlex 600 diffractometer. Ultraviolet–visible (UV–Vis) spectra were obtained at room temperature in the wavelength range of 200–900 nm using a Specord 210 spectrophotometer.

## RESULTS AND DISCUSSION

Figure 1 presents the X-ray diffraction (XRD) patterns of the bis-AAED reagent (1), the Ag–bis-AAED (2) binary complex, and the Ag–bis-AAED–CTAB (3) ternary complex. The analysis indicates significant differences in crystallinity and phase structure among the samples. In the diffractogram of the reagent (red line), sharp and high-intensity diffraction peaks were observed at 2θ angles of 9.90°, 13.72°, 15.03°, 16.99°, 20.27°, 21.71°, 24.79°, 26.71°, 29.88°, 35.01°, and 42.88°, reflecting its polycrystalline nature. These signals are associated with a stable crystalline lattice formed through hydrogen bonding and intramolecular coordination involving the carbonyl and imine groups present in the molecule. The sharpness and intensity of the peaks are attributed to the regular and stable arrangement of the molecules. The XRD pattern of the Ag–bis-AAED complex (blue line) exhibits peaks at 2θ = 37.78° and 43.91°, indicating a phase change due to complexation. Peak broadening and reduced intensity are related to partial amorphization and decreased crystallinity, as the reagent molecules coordinate to the surface of AgNPs.

Similar observations regarding the correlation between diffraction peak broadening and amorphous character were reported for LDH-based nanocomposites synthesized by Balayeva et al., confirming that surface modification leads to a decrease in crystallite size

and an increase in disorder [18]. The formation of the complex can be attributed to the coordination of Ag ions with the donor atoms (N and O) of the reagent. In the Ag–bis-AAED–CTAB ternary complex (green line), broader, weaker, and somewhat irregular peaks were observed at 2θ = 12.30°, 19.66°, 37.64°, and 43.95°. This effect is explained by CTAB acting as a surfactant, surrounding AgNPs and preventing their aggregation, while simultaneously increasing molecular freedom. As a result of CTAB's influence, the complex exhibits a more amorphous structure.

To determine the average crystallite size of the complexes, the Debye–Scherrer equation was applied, taking into account the observed peak broadening in the XRD analysis. A similar analytical approach to determine crystallite size and structural parameters was applied by Ahmadov et al. during the synthesis and thermodynamic study of $SiO_2$ nanoparticles, confirming the reliability of the Debye–Scherrer equation for nanoscale materials [19]. In this equation, parameters include the X-ray wavelength of the source (Cu Kα, λ = 1.5406 Å), the shape factor K, the full width at half maximum (FWHM, β), and the diffraction angle (θ).

$$D = \frac{K}{\beta COS\theta}$$

Based on the calculations, the average crystallite sizes were determined to be 26.0 nm for the reagent, 10.9 nm for the binary complex, and 9.0 nm for the $Ag^+$–bis-AAED–CTAB ternary complex.

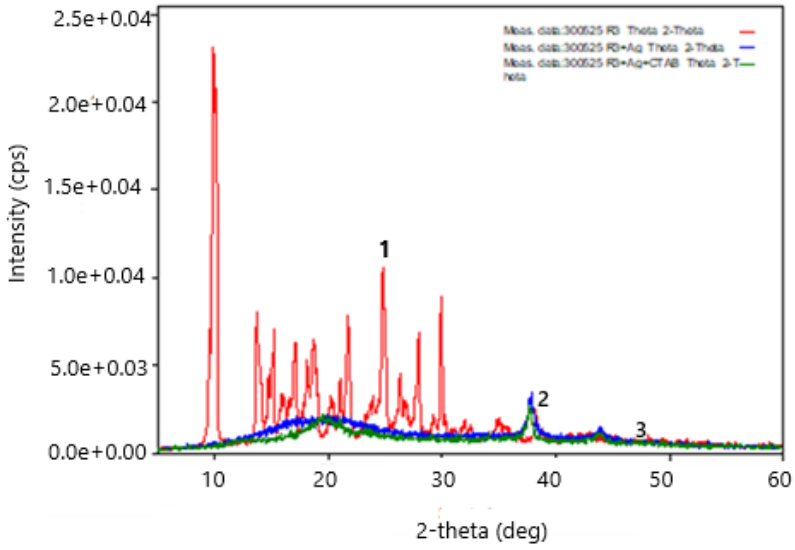


Figure 1. XRD diffractograms of the R reagent (1), Ag+R (2), and Ag+R+CTABr (3) complexes.

Table 1. Data of binary R, Ag+R and ternary Ag+R+CTABr complexes estimated by XRD method.

| R | | | Ag– bis-AAED | | | Ag– bis-AAED –CTAB | | |
|---|---|---|---|---|---|---|---|---|
| 2θ | β | D, nm | 2θ | β | D, nm | 2θ | β | D, nm |
| $9.897^0$ | 0.32 | 26.04 | $37.78^0$ | 0.68 | 12.9 | $12.30^0$ | 1.5 | 5.57 |
| $13.722^0$ | 0.474 | 17.64 | $43.91^0$ | 1.01 | 8.86 | $19.66^0$ | 2.90 | 2.91 |
| $15.030^0$ | 0.17 | 49.25 | | | | $37.64^0$ | 0.47 | 18.66 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $16.993^0$ | 0.27 | 31.1 | | | | $43.95^0$ | 0.99 | 9.04 |
| $20.273^0$ | 0.42 | 20.08 | | | | | | |
| $21.713^0$ | 0.414 | 20.4 | | | | | | |
| $24.793^0$ | 0.375 | 22.66 | | | | | | |
| $26.709^0$ | 0.38 | 22.45 | | | | | | |
| $29.876^0$ | 0.136 | 63.17 | | | | | | |
| $35.01^0$ | 1.22 | 7.13 | | | | | | |
| $42.88^0$ | 1.5 | 5.95 | | | | | | |

Figure 2 presents the UV–Vis spectra of silver nanoparticles (1), the bis-AAED reagent (2), the Ag–reagent (Ag–R) complex (3), and the Ag–R–CTAB ternary complex (4). For Ag nanoparticles (spectrum 1), a broad maximum peak is observed at approximately 410 nm. This signal corresponds to surface plasmon resonance (SPR), confirming the formation of AgNPs in colloidal solution and their stable dispersion.

The bisacetylacetoneethylenediamine reagent (spectrum 2) exhibits sharp absorption bands in the 250–330 nm range, which are associated with π→π* and n→π* transitions within the molecule. In particular, the absorptions at 223 nm, 270 nm, and 299 nm reflect electronic transitions of the β-diketone and imine functional groups. For the Ag–R complex (spectrum 3), an increase in absorption intensity and slight shifts of the bands are observed at 227 nm, 272 nm, and 308 nm compared to the free reagent. These changes indicate complex formation between silver nanoparticles and the bis-AAED reagent, as well as a modification of the electronic environment resulting from the coordination. In the Ag–R–CTAB ternary complex (spectrum 4), further enhancement in absorption intensity and sharper, more defined bands are noted. The addition of CTAB increases the absorption intensity and spectral stability, indicating that the surfactant enhances both the stability of the complex and the colloidal stabilization of the nanoparticles. This observation suggests that the ternary complex possesses a more coordinated and homogeneous structure. The obtained spectra clearly demonstrate coordination interactions between the components and changes in intramolecular electronic transitions.

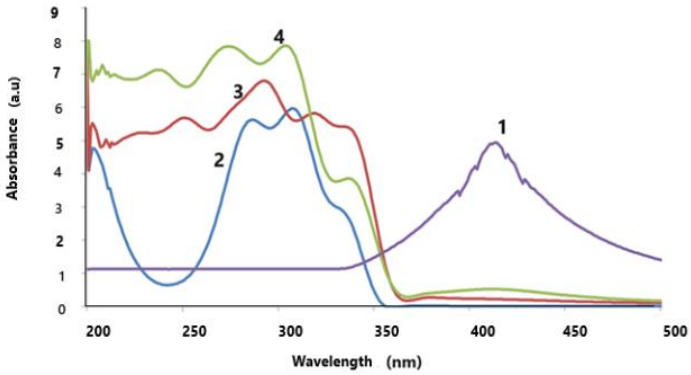


Figure 2. UV–Vis spectra of 1 – silver nanoparticles (AgNPs), 2 – bisacetylacetoneethylenediamine (R), 3 – Ag–R complex, and 4 – Ag–R–CTAB complex.

## CONCLUSION

In this study, novel complexes of silver nanoparticles (AgNPs) with bisacetylacetoneethylenediamine (bis-AAED) and CTAB were successfully synthesized. UV–Vis analysis showed a surface plasmon resonance (SPR) peak of AgNPs at 410 nm, while the absorption bands of bis-AAED at 223, 270, and 299 nm shifted to 227, 272, and 308 nm upon complex formation. These changes are associated with an increase in electron density and modification of the local environment. According to XRD results, the crystallite

size of the bis-AAED reagent was 26.0 nm, which decreased to 10.9 nm in the Ag–bis-AAED complex and further to 9.0 nm in the Ag–bis-AAED–CTAB ternary complex. The broadening and weakening of the peaks indicate an increase in the amorphous phase. The addition of CTAB enhanced the colloidal stability of the complexes, leading to more stable dispersed systems. Overall, the comparison of UV–Vis and XRD results demonstrates that complexation induces changes at both the electronic and structural levels, suggesting that the synthesized systems hold promising potential for applications in materials science and analytical chemistry.

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