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Role of Transition Metals in Coordinating with Heteroatom-Containing Organic Ligands

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Abstract: It is very insightful to synthesize and study copper subgroup metal complexes with organic ligands that include several heteroatoms in their structure. The resultant complex compounds will have a number of novel qualities that are useful in real-world applications because they have different physical and chemical features from the original organic components. 2-mercapto-4(3H)-quinazolinone and 2-mercaptonicotinic acid were used in this investigation. Complex compounds of copper subgroup metals were extracted from aqueous and water-alcohol solutions throughout the study. The chemicals that are produced resemble colorful powders. Instrumental analytical techniques were used to determine the organic reagent's coordination with metal ions. The impact of the added reagent (ammonia, alkali) on the organic reagent's coordination was examined.

Keywords: Transition metals, complexation, organic ligands, heteroatoms, coordination chemistry, metalligand interactions

I. INTRODUCTION

Using organic reagents, which the transition metals interact with to generate powerful complex compounds, the transition metals are separated, concentrated, and quantitatively determined. The most often employed organic reagents are compounds with functional-analytical groups that comprise almost all known donor atoms, including O, N, S, and P. These include thioacids, mercaptans, amines, phenolic and alcohol oxides, and other S-analogs of substances that include oxygen [1].

Furthermore, complex transition metal compounds have potential medical use. Gold, silver, and copper-based medicines (protargol, collargol, silver sulfadiazine, gold thiosulfate, auronofin, etc.) are employed in practical medicine. Because silver preparations may precipitate proteins and interfere with germs' enzyme systems, they have antibacterial, astringent, and cauterizing properties. Malignant tumors, lung TB, skin conditions, and autoimmune illnesses are all treated with gold compounds [2–4]. Gold nanoparticle-containing medications are often used to treat chronic arthritis [5]. Copper compounds are employed as cauterizing and antibacterial agents in medicine. Acute and chronic arthritis, chronic polyarticular gout, ankylosis and multiple spondylitis, rheumatoid fever, and erythema have all been successfully treated with medications that include copper (cupralene, dicupren or cuprimil, copper morruate, and permalon).

Metal ions of the copper subgroup with the electronic configuration d9 (oxidation state +2) may be classified as soft acids in accordance with Pearson's hard and soft acids and bases concept. Consequently, they combine soft bases to create the most stable molecules. These kinds of ligands include substances with electron-donating O, N, and S atoms. Because of the close proximity of their 3d orbitals to the metal ion orbitals and the diffusivity of the donor electron pair of the sulfur atom, ligands containing sulfur are the softest bases. Copper typically has this kind of structure among the metals in the copper subgroup. Numerous challenges accompany the manufacture and separation of gold (II) and silver (II) compounds due to their fragility. The majority of chemicals are only available as intermediate complexes [6].

As a "soft" metal center, gold (I) with the d10 configuration has a significant propensity to form stable complexes with soft donor atoms that are readily polarizable, such phosphorus and sulfur [3].

The N-heterocyclic coordination center of the ligands may coordinate silver (I), which is a stronger acid than Au (I), in accordance with Pearson's hard and soft acids and bases concept. P, N-coordination ar both heteroatoms is more

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common in silver (I) complexes than in gold (I), which has a much stronger propensity for coordination at the phosphoric coordination center. However, P-monodentate silver (I) complexes are also present. Silver in coordination compounds may have a linear or triangular geometry, and the most common coordination numbers for the silver ion in the oxidation state +1 are 2 and 3.

Compared to Au(I) and Ag(I), copper(I) is a stronger acid and has a greater propensity to coordinate at the Ncoordination center. Copper (I) has a coordination number of four and a tetrahedral or, less often, planar-square coordination geometry in complex compounds. The copper atom (I) has a linear shape with a coordination number of 2, which is less frequent than a potentially lower coordination number of 3. Because copper (I) may form cluster nuclei with halogen anions via the production of copper-halogen bridging bonds, its coordination number can be 6. Metallophilic interactions between copper atoms are achieved in a broad variety of Cu(I) complexes that are formed by polymer and oligomeric metal clusters. The complexes show luminous capabilities throughout a broad spectrum range, which reflects the extension of copper (I)'s coordination abilities and, therefore, the vast diversity of structures created [7].

Studies are required to ascertain the precise interaction of the transition metal with organic ligands, including heteroatoms, as well as the structure and characteristics of the resultant complex compounds because of the ambiguous behavior of the copper subgroup metals during complexation. 2-mercaptonicotinic acid and 2-mercapto-4(3H)-quinazolinone were selected as ligands to investigate the behavior of copper subgroup metals in complexation reactions with organic molecules. This is because the molecules in their composition contain donor atoms N, S, and O, which means that complexes of different structures and, consequently, the manifestation of different properties, are possible. The effort aimed to determine the coordination of the ligand to the metal atom and to generate complex compounds of the copper subgroup metals with organic ligands including heteroatoms.

Experimental Part

Copper (II) chloride crystallohydrate, "hg"; 2-mercaptonicotinic acid "ACROS ORGANICS" (CAS: 38521-46-9); silver fluoride made from silver carbonate by dissolving it in hydrofluoric acid; and copper (I) chloride, which was recently produced using the method [8], were utilized as starting compounds for the synthesis of complex compounds. A white precipitate of copper (I) chloride settled when a stoichiometric quantity of sodium sulfite was added to an aqueous solution of copper (II) sulfate, as per [8]. The following were also utilized: copper (II) chloride crystallohydrate, "hg"; 2-mercapto-4(3H)-quinazolinone ALDRICH (CAS: 13906-09-7); silver nitrate, which was made by dissolving silver in nitric acid; and an aqueous solution of the gold complex (H[AuCl4]), which was made by dissolving gold in a mixture of nitric and hydrochloric acids (in aqua regia, in a 4:1 ratio). Distilled water and ethyl alcohol were mixed 1:2 to create the water-alcohol solution.

Copper (I) is prepared using 2-mercaptonicotinic acid. In a 250 ml beaker, a sample weighing 1 g of 2-mercaptonicotinic acid and 17 ml of distilled water were added. Next, sodium hydroxide (0.25 g) was added while stirring, and ten minutes later, freshly precipitated copper (I) chloride (0.64 g) was added. Since the mixture was allowed to sit at ambient temperature, the development of There was a brown-orange (or "reddish") precipitate. After 30 minutes of stirring, the fluid thickened and the precipitate took on the consistency of gel. After adding 17 milliliters of distilled water, it was left for a day. The mixture was filtered through a glass filter the next day, and the precipitate was washed with distilled water and alcohol before being dried in a desiccator. The silt became dark brown, almost black, in the air. The mixture became orange (or "red") when water was added.

Making a compound of 2-mercapto-4(3H)-quinazolinone with gold (I). An aqueous solution of the H[AuCl4] gold complex (1 g) was added to a beaker containing 1.15 g of sodium chloride, 10 ml of pure water, and the mixture was stirred. The reaction mixture was then supplemented with 0.12 g of sodium sulfite. Everything was well combined until the mixture took on a stained appearance [9]. Immediately, 0.5 g of ligand in 30 ml of water-alcohol solution containing 2-mercapto-4(3H)-quinazolinone was added. While stirring, either an aqueous solution of sodium hydroxide (0.13 g in 5 ml of distilled water) or an aqueous solution of ammonia (up to pH = 9) was added to the reaction mixture. For sixty minutes, everything was fully blended. A glass filter was used to filter out the resultant precipitate, which was then washed with an aqueous alcohol solution and dried at 50 °C. The material that was obtained had a golden hue. Gold (II) complex formation using 2-mercapto-4 (3H)-quinazolinone. Five milliliters of ethanol were added to 0.1

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grams of the gold complex H [AuCl4] in an aqueous solution. After dissolving 0.4 g of chemical compounds in 30 ml of aqueous alcohol solution, an aqueous ammonia solution was added while stirring (to pH = 3) to create an aqueous-alcoholic solution of 2-mercapto-4 (3H) -quinazolinone. The gold complex solution was supplemented with the obtained organic ligand combination. After everything was well combined and heated to 50 °C, the reaction mixture was left for 60 minutes. After the precipitate was removed using a glass filter, it was washed with ethanol and dried at 40 °C. The material that was obtained had a pale golden hue.

Silver (I) complex formation using 2-mercapto-4 (3H)-quinazolinone. Ten milliliters of distilled water were added to a beaker containing seven milliliters of silver nitrate aqueous solution. Silver was dissolved in diluted nitric acid (2 g in 30 ml) to create a silver solution. The AgNO3 solution was stirred before an aqueous solution of ammonia (8 ml) and an aqueous-alcoholic solution of the ligand (0.5 g in 50 ml of an aqueous-alcoholic combination) were added. After being heated to 50°C for 10 minutes, the reaction mixture was left for 30 minutes. Mixing and heating were stopped. A glass filter was used to filter the resultant precipitate, which was then washed with an aqueous alcohol solution and dried at 50°C. The material that was obtained had a light brown hue.

Copper (II) complex formation using 2-mercapto-4 (3H)-quinazolinone. In a beaker, 0.8 g of copper (II) chloride (CuCl2 \cdot 2H2O) was dissolved in 10 milliliters of pure water. After dissolving 0.5 g of 2-mercapto-4 (3H)-quinazolinone in 30 ml of aqueous alcohol solution, an aqueous ammonia solution (up to pH=9) was added, and everything was well combined. After mixing the organic compound solution with an aqueous solution of copper chloride and heating it to 50°C, a precipitate was seen to develop. The heating and mixing were stopped after half an hour. A glass filter was used to filter the resultant precipitate, which was then washed with a water-alcohol combination and dried at 50°C. The resulting material had a dark green (malachite) hue.

IR spectroscopy was used to confirm the structure of the coordination compounds that were produced. Using samples in the form of tablets containing KBr, the Nicolet 6700 IR Fourier spectrometer recorded the IR absorption spectra of the produced compounds in the 400–4000 cm-1 range with a resolution of 4 cm-1. Using solutions of the examined substances prepared by dissolving them in dimethyl sulfoxide (DMSO), the UV spectra of the synthesized compounds were recorded on the Shimadzu (Japan) UV spectrometer UV-1800 in the range of 190-600 cm-1. By using X-ray fluorescence analysis (XRF), the presence of metal in the complex compounds that were produced was verified. An ARL QUAN^TX X-ray energy-dispersion spectrometer from Thermo Scientific in the United States was used to conduct the study. Sixty seconds was the shooting time.

II. RESULTS AND DISCUSSION

Characteristic absorption bands of the S-H group at 2546 cm-1, N-H at 2156-1945 cm-1, and C=N groups at 1563-1496 cm-1 were discovered in the ligand (2-mercaptonicotinic acid)'s infrared spectra. The COO-group's valence vibrations were found in the 1680–1621 cm-1 range.

The presence of a COO-Na bond is indicated by changes in the position of symmetric valence vibration absorption bands for the COO-group in the ligand and its complexes' IR spectra when compared to the Cu(I). These bands shift towards higher frequencies by 29 cm-1 as the ligand transitions to the complexes. Furthermore, the ligand's spectra shows the band at 2546 cm-1 disappearing, indicating the SH-group's involvement in the complex's creation. The valence vibrations of the O-Na and S-Cu bonds are likely responsible for the appearance of absorption bands at 602-522 cm-1 and 496-475 cm-1 in the IR spectra of complexes that are not present in the ligand spectrum. This suggests that the sulfur atom of the benzene cycle is responsible for coordinating the organic ligand to the transition metal ion. Therefore, it can be inferred from the IR spectroscopic analysis of the produced complexes that the sulfur atom coordinates the metal atoms to the ligand that has heteroatoms in its structure.

The absorption bands in the UV spectrum of 2-mercaptonicotinic acid dissolved in DMSO have the following values: λ max: 312, 250 nm. The following values are found in the UV spectra of copper complexes with 2-mercaptonicotinic acid dissolved in DMSO: Complexes of Cu (I): λ max: 241, 285 nm. When the UV spectra of the acquired complex compounds were studied, a hypsochromic shift and a drop in transmission values were detected for copper complexes. These findings seem to be related to the complex compound's luminescence ability.

There are two bands in the infrared spectra of 2-mercapto-4 (3H)-quinazolinone: one at around 3400 cm-1 and another at 3400 cm-1. Thus, the enol tautomeric form (B) is presumed for 2-thioxoquinazolone in the instance. There is an

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average intensity band that corresponds to v(SH) in the infrared spectrum at about 2600 cm-1. The HN-C=S grouping was identified by four thioamide bands at 1549 (I), 1300 (II), 972 (III), and 760 cm-1 (IV). It is hypothesized that the coordination of the 2-mercapto-4(3H)-quinazolinone anion via the sulfur and the nitrogen atom of the thioamide group is present in the infrared spectrum of the gold (I) complex that was produced using alkali. The band v(SH) at 2670 cm-1 vanishes, whereas the band v(NH) at 3086 cm-1 shifts to the low-frequency zone at 15 cm-1. The addition of the sodium atom to the oxygen atom of the C=O group is most likely the cause of the shift of the band v (C=O) at 1710 cm-1 to 19 cm-1 to the low-frequency region. The band v(C=N) in the 1630 cm-1 area is still present, indicating that there is no interaction between the gold atom and the nitrogen amide. Although thioamide bands can be seen in the 159 (I), 1307, 977, and 789 cm-1 area, the initial band is moved to the low-frequency region at 35 cm-1, most likely as a result of the Au-N bond forming. Both the v(Au-S) and v(Au-N) absorption bands can be seen at 593 cm-1 and 646 cm-1, respectively.

It is thought that the 2-mercapto-4(3H)-quinazolinone anion is coordinated via the nitrogen atom of the thioamide group in the infrared spectrum of the gold (I) complex that was produced using an ammonium hydroxide. The low-frequency region shifts the band v(NH) 3086 cm-1 to 6 cm-1. The positions of the bands v(SH) at 2670 cm-1 and v(C=O) at 1706 cm-1 remain unchanged. The band v(C=N) in the 1630 cm-1 area is still present, indicating that there is no interaction between the gold atom and the nitrogen amide. At 1307, 977, and 789 cm-1, thioamide bands are visible; at 1549 cm-1, the band vanishes. At 646 cm-1, the absorption band v (Au-N) is seen.

The anion of 2-mercapto-4(3H)-quinazolinone is thought to be coordinated by a nitrogen atom of the thioamide group and a sulfur atom in the infrared spectrum of the gold (II) complex that was produced using an ammonium hydroxide. A band at 3511 cm-1 is seen in the valence vibration zone; it seems that this band represents the coordinated water molecule's v (OH). The low-frequency zone is reached by shifting the band v(NH) 3086 cm-1 to 15 cm-1. The highfrequency zone is reached by shifting the band v(SH) at 2670 cm-1 to 14 cm-1. The addition of the NH4+ ion to the oxygen atom of the C=O group is most likely the cause of the shift of the band v(C=O) at 1706 cm-1 to 19 cm-1 to the low-frequency region. The band v (C=N) at 1630 cm-1 is still present, indicating that there is no interaction between the gold atom and the nitrogen amide. The thioamide band vanishes at 1549 cm-1, most likely as a result of the Au-N bond forming. There is no change in the remaining thioamide bands in the 1307, 979, and 789 cm-1 area. At 593 and 646 cm-1, respectively, the absorption bands v(Au-S) and v(Au-N) are visible.



Figure 1. a – IR spectrum of 2-mercapto-4 (3H)-quinazolinone; b – IR spectrum of the gold (I) complex with 2mercapto-4 (3H)-quinazolinone obtained with the use of alkali.

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Figure 2. c – IR spectra of the silver (I) complex with 2-mercapto-4 (3H)-quinazolinone; d – IR spectra of the copper (I) complex with 2-mercapto-4 (3H)-quinazolinone.

The absorption bands of the group v(NH) 3086 cm-1 are displaced to 9 cm-1 to the low-frequency region, and the band v(SH) vanishes at 2670 cm-1, according to a comparison of the infrared spectra of 2-mercapto-4 (3H)-quinazolinone and its complexes with Ag(I) and Cu(II). There is no change in the band v(C=O) at 1706 cm-1. For the Ag(I) complex, the thioamide bands in the range of 1549, 1307, 977, and 789 cm-1 do not change, whereas for the Cu (II) complex, the band vanishes at 1549 cm-1, signifying the establishment of the Cu-N bond. At 668 cm-1, the absorption band v(Ag-S) is seen. At 457(445) and 690 cm-1, respectively, the absorption bands v(Cu-N) and v(Cu-S) are visible. Therefore, the coordination of the sulfur atom's organic ligand and, in the case of the copper (II) complex, the sulfur and nitrogen atoms of the thioamide group, results in the formation of the complex with silver(I) ions. The metals present in the produced complexes with ligands 2-mercaptonicotinic acid and 2-mercapto-4 (3H)-quinazolinone are confirmed by the X-ray fluorescence analysis results.

III. CONCLUSION

The following findings were from an investigation on the behavior of copper subgroup metals in complexation reactions with organic molecules that include many heteroatoms in their structure. 2. The sulfur atom coordinates with the metal atoms Cu (I) to form mercaptonic acid. 2-Mercapto-4(3H)-quinazolinone is likely coordinated by sulfur and the nitrogen atom of the thioamide group in the gold (I) complex that is obtained with the use of alkali, and only by the nitrogen atom of the thioamide group in the same complex that is obtained with the use of ammonium hydroxide. Sulfur and a nitrogen atom of the thioamide group are thought to coordinate the anion of 2-mercapto-4(3H)-quinazolinone in the gold (II) complex that is produced using an ammonium hydroxide. It was shown that the sulfur atom in the Ag(I) and Cu(II) complexes with 2-mercapto-4(3H)-quinazolinone and the sulfur and nitrogen atoms of the thioamide group in the Cu(II) complex coordinate the organic ligand with silver (I) ions. The existence of these metals in the complexes' composition was verified by examining the generated complex compounds for their presence using the X-ray fluorescence technique of analysis.

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