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Complex compound of trinitrotriamminecobalt(III): in theoretical studies

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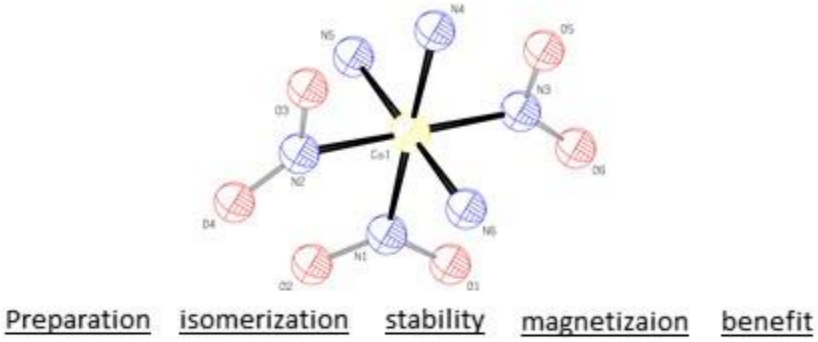
Abstract

$[Co(NH_3)_3(NO_2)_3]$ is an octahedral complex compound that can have several isomers. The complex compound has magnetic properties. Its stability has been explained. It can be easily synthesized and is known as a bioinorganic synthesis reagent, oxidant compound and base hydrolysis.



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3. trinitrotriamminecobalt(III).

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Highlights

- Trinitroamminecobalt(III) with its isomerization and magnetization theoretically.
- The stability of the complex compound is discussed theoretically.
- The complex compound has beneficial properties.

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1. Introduction

The recent development of complex compounds is increasingly changing along with its usefulness in everyday life. The applications of complex compounds, especially as catalysts (Alhafez *et al.*, 2022), continue to be developed. Complex compounds of d-block elements have an advantage over other compounds because they have empty d orbitals. This d orbital generally plays a role in the catalytic process (Feng *et al.*, 2022). In addition, potential applications in many areas include metal purification, photography, medicine, and colouring agents (Habiddin and Hartanto, 2023).

Complex compounds in the laboratory are synthesized by reacting a base ligand with a metal by donor-acceptor of the electron pair. Based on the number of electrons donated by the ligand, the ligands can be classified into monodentate, bidentate, and polydentate ligands (Effendy, 2013; Verma *et al.*, 2022). A monodentate ligand donates only one pair of electrons to the metal. A bidentate ligand donates its two pairs of electrons to a metal, and many electrons can be donated to a metal by a polydentate ligand. These polydentate ligands can also form chelate structures (Eivazihollagh *et al.*, 2019).

These metals are inert and stable in forming complex compounds with various ligands. One metal that has these properties is cobalt. These metals were used by Werner (Ernst *et al.*, 2011), the father of coordination chemistry who studied complex compounds (Deblitz *et al.*, 2014), the first to produce Werner's coordination theory, which lasted long enough and is still being introduced in the early days of studying coordination chemistry (Constable and Housecroft, 2013; Nguyen *et al.*, 2014).

One of the complex compounds with a cobalt central atom is trinitrotriamminecobalt(III) compound which has the chemical formula of $[Co(NH_3)_3(NO_2)_3]$ as shown in **Fig. 1** (Bąk *et al.*, 2013; Laing *et al.*, 1971). The trinitrotriamminecobalt(III) compound has a central atomic number 6 with an octahedral compound structure (**Fig. 1**). The objective of this work is to introduce $[Co(NH_3)_3(NO_2)_3]$ in theoretical studies and relate the potential application.

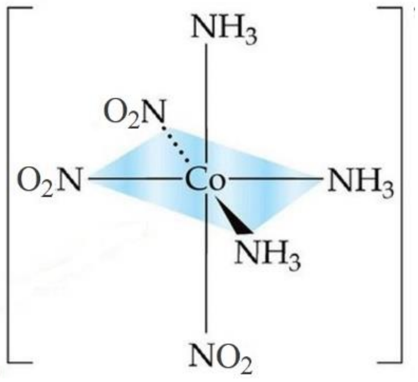


Figure 1. Molecular structure of $[Co(NH_3)_3(NO_2)_3]$.

2. Experimental

2.1. Reagents and solutions

The reagents and solutions used included cobalt carbonate ($CoCO_3$), glacial acetic acid, distilled water, cold solution mixture (10.6 g of sodium nitrate in 50 mL of ammonia), ice, and activated charcoal.

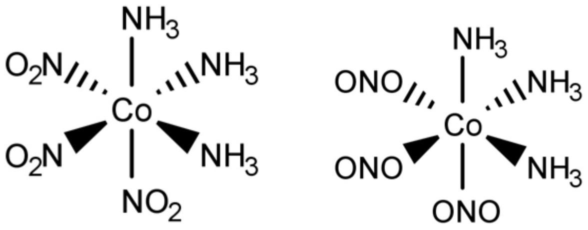
2.2. Synthesis of trinitrotriamminecobalt(III) compound

The trinitrotriamminecobalt(III) compound can be synthesized on a laboratory scale. The compound was synthesized by dissolving 5 g of $CoCO_3$ in 7 mL of a hot solution of glacial acetic acid and 14 mL of H_2O. After that, the solution was put in a cold solution mixture (10.6 g of sodium nitrate in 50 mL of ammonia) in an Erlenmeyer flask. The resulting mixture was cooled on ice and dripped with 28 mL of 30% water slowly for 5 – 20 min. Activated charcoal (0.5 g) was then added. In the next step, the mixture was heated for 30 min in a bath. In the last stage, the mixture was filtered, and the product compounds formed were on filter paper.

3. Results and discussion

3.1. Isomerization of trinitrotriamminecobalt(III) compound

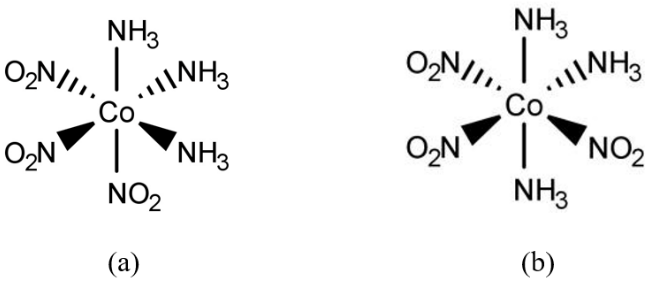
The trinitrotriamminecobalt(III) compound has several different atomic arrangements known as isomerization (Bąk *et al.*, 2013). The compound shows structural isomerism and spatial isomerism. The structural isomerism of the compound is linkage isomerism. The linkage isomerism occurs in the compound containing ambidentate ligands such as NO_2^-. The NO_2^- ligand can bind to the central atom via an N or O atom. In $[Co(NH_3)_3(NO_2)_3]$, the nitrite ion, NO_2^-, binds to the central atom via an N atom and a nitro complex is formed, whereas in $[Co(NH_3)_3(ONO)_3]$, nitrite ion binds to the central atom via the O atom and a nitrite complex is formed. The different types of donor atoms attached to the central atom in the two complex compounds produce different colours. The two-coloured compounds are because the central atom, Co^{3+}, has 3d orbitals that are not completely filled with electrons. The two compounds are linked isomer pairs (Effendy, 2013). The following is the structure of a linked isomer compound pair (**Fig. 2**).



(a) (b)

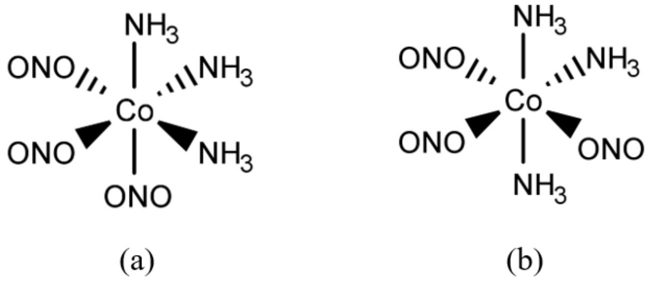
Figure 2. (a) trinitrotriamminecobalt(III) and **(b)** trinitritotriamminecobalt(III).

Spatial isomerization of the trinitrotriamminecobalt(III) compound is facial-meridional isomerism (fac-mer isomerism) (Bernal *et al.*, 1996; Nuber *et al.*, 1979; Palmer and Hill, 1993; Tanito *et al.*, 1952). This isomerism only occurs in octahedral complex molecules that have the same 3 ligands and the same 3 other ligands. The structures of the facial (fac-) and meridional (mer-) isomers of the trinitrotriamminecobalt(III) compound are given in Figs. 3 and 4.



(a) (b)

Figure 3. (a) *fac*-trinitrotriamminecobalt(III) and **(b)** *mer*-trinitrotriamminecobalt(III).



(a) (b)

Figure 4. (a) *fac*-triaminetrinitrito-O-cobalt(III) and **(b)** *mer*-triaminetrinitrito-O-cobalt(III).

In the same fac- isomer the three ligands are located on an equilateral triangle which is one of the octahedral faces, whereas in the mer- isomer the three ligands are in an isosceles triangle.

3.2. Magnetism of trinitrotriamminecobalt(III) Compounds

Based on the energetic principle, the energy level of $[Co(NH_3)_3(NO_2)_3]$ is lowest when the repulsion between the three NH_3 ligands and three NO_2^- ligands is minimal. This happens when the position is as far as possible, namely at the octahedral corners (Kilic *et al.*, 2015), so that the complex has an octahedral structure (Alhafez *et al.*, 2022; Kilic *et al.*, 2017). Besides that, $[Co(NH_3)_3(NO_2)_3]$ is diamagnetic in that its magnetism is equivalent to the pairing of all the electrons present. This property indicates that the formation of the compound occurs electron excitation. Therefore, the formation of this compound involves d^2sp^3 hybridization. The following is an explanation with the electron configuration shown in **Fig. 5**.

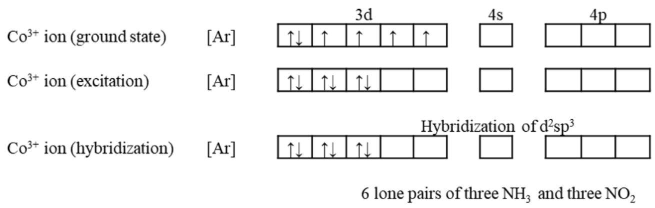


Figure 5. Electron configuration of Co^{3+} ion in $[Co(NH_3)_3(NO_2)_3]$.

Meanwhile, based on the crystal field theory, the complex compound of $[Co(NH_3)_3(NO_2)_3]$ is also diamagnetic. The compound is octahedral in shape and has a central atom (Kılıç *et al.*, 2017), namely Co^{3+} with an electron configuration in the ground state of Co^{3+} = [Ar] $3d^6$. The ligand attached to the central Co^{3+} atom is a strong field, so it is energetically more advantageous if the six electrons occupy the t_2g orbital, paired with the electrons already in the orbital so that a configuration is obtained as shown in **Fig. 6**.

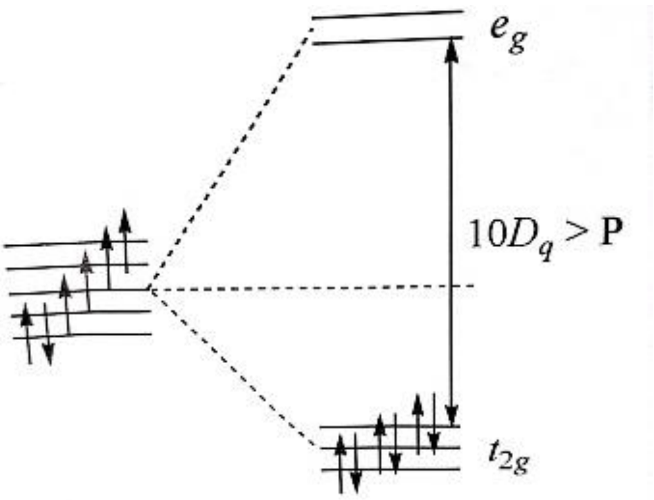


Figure 6. Electron configuration of strong field octahedral complex compound of $[Co(NH_3)_3(NO_2)_3]$ with d^6 central atom.

According to molecular orbital theory, the complex compound of $[Co(NH_3)_3(NO_2)_3]$ is also diamagnetic. The compound is octahedral in shape and has a central atom (Kılıç *et al.*, 2017), namely Co^{3+} with an electron configuration in the ground state of Co^{3+} = [Ar] $3d^6$. The number of electrons in the 3d orbital of the central atom and the electrons donated by three NH_3 ligands and three NO_2^- ligands is 18 electrons. The 18 electrons are filled in the molecular orbitals of the octahedral complex compound as shown in **Fig. 7**.

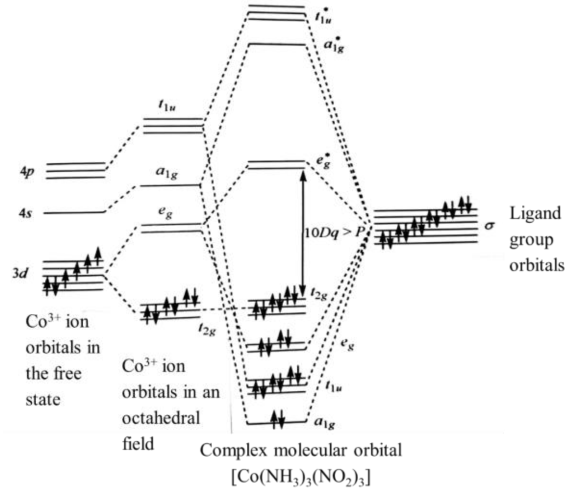


Figure 7. Molecular orbital diagram of $[Co(NH_3)_3(NO_2)_3]$.

The way of filling the 18 electrons in the molecular orbitals of the complex is as follows. First, fill the six pairs of electrons in the a_1g, t_1u, and e.g. orbitals. Second, filling the remaining six electrons in the t_2g orbital in pairs because $[Co(NH_3)_3(NO_2)_3]$ is a complex with a strong field, the value is 10 Dq > P. Its diamagnetic properties are indicated by the pairing of all the electrons present in the molecular orbitals of the compound.

3.3. Stability and colour of [$Co(NH_3)_3(NO_2)_3$]

The stability of [$Co(NH_3)_3(NO_2)_3$] is based on the central atom with a certain oxidation number. The oxidation number of the central atom of [$Co(NH_3)_3(NO_2)_3$] is +3, where in the Co^{3+} complex with d^6 configuration, the e.g. orbitals are not filled with electrons so that the complex formed will be stable. This could happen due to the influence of strong ligands.

The colour that appears in a complex depends on the strength of the crystal field. The greater the strength of the crystal field of a complex, the transition will require radiation with smaller wavelengths, and the absorbed colour shifts from red to purple with the complementary results seen by the eye shifting from dark colours (green-blue) to more vibrant colours, namely pale (lemon yellow). Because the strength of the crystal field depends on the strength of the existing ligands, for complex compounds with the same central atom the colour of the complex tends to get paler with increasing ligand strength. If we compare the colour of [$Co(NH_3)_3(NO_2)_3$] which is pale yellow and the colour of [$Co(H_2O)_6]^{3+}$ which is blue. This colour change is due to the influence of the ligand where the NH_3 and NO_2^- ligands are stronger than the H_2O ligands so that [$Co(NH_3)_3(NO_2)_3$] has a paler colour.

3.4. Benefits of [$Co(NH_3)_3(NO_2)_3$]

[$Co(NH_3)_3(NO_2)_3$] has several benefits, including as a reagent in the synthesis of bioinorganic complex compounds and as an oxidant compound ferredoxin in parsley extract (Adzamli *et al.*, 1982) or therapeutic potential as reduction-activated complexes, or can be applied in imaging by MRI (Renfrew *et al.*, 2018). In addition, [$Co(NH_3)_3(NO_2)_3$] can also react as base hydrolysis (Singh and Shanker, 1989).

4. Conclusions

[$Co(NH_3)_3(NO_2)_3$] can be explored in the future about the potency as medicinal agent such as therapy and imaging instruments. The chemical characteristics of the complex show the unique compound as diamagnetic compound, and stable. Deep understanding of the complex may encourage us to apply it in many fields.

Authors' contributions

Conceptualization: Rokhim, D. A.; **Data curation:** Rokhim, D. A.; **Formal Analysis:** Rokhim, D. A.; **Funding acquisition:** Not applicable; **Investigation:** Rokhim, D. A.; **Methodology:** Rokhim, D. A.; **Project administration:** Rokhim, D. A.; **Resources:** Rokhim, D. A.; **Software:** Not applicable; **Supervision:** Wijaya, H. W.; **Validation:** Wijaya, H. W.; **Visualization:** Asrori, M. R.; **Writing – original draft:** Rokhim, D. A.; **Writing – review & editing:** Asrori, M. R.

Data availability statement

All data sets were generated or analyzed in the current study.

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