

A Novel Mixed Ligand Dinuclear Complex of Cobalt (II): Synthesis, Characterization and Magnetic Studies*

Emmanuel N. Nfor^{1#}, Luke L. Keenan², Justin Nenwa³, Peter T. Ndifon³, Romanus N. Njong¹, Christelle N. T. Dzesse¹, Offiong E. Offiong⁴

¹Department of Chemistry, University of Buea, Buea, Cameroon

²Department of Chemistry, University of Bath, Bath, UK

³Department of Inorganic Chemistry, Coordination Chemistry Laboratory, University of Yaounde I, Yaoundé, Cameroon

⁴Department of Pure and Applied Chemistry, University of Calabar, Calabar, Nigeria

Email: [#nforemman@gmail.com](mailto:nforemman@gmail.com)

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Abstract

A novel dinuclear complex $[\text{Co}_2(\text{atr})_3(\text{mal})_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}(\mathbf{1})$ (atr = 4-amino-1,2,4-triazole and mal = malonic acid) containing mixed N- and O-donor atoms has been prepared and structurally characterized. The structure is made up of the symmetrically 1, 2, 4-triazole bridged $[\text{Co}_2(\text{atr})_3(\text{mal})_2(\text{H}_2\text{O})_2]$ moiety and four lattice water molecules. The single crystal X-ray analysis reveals that the complex has a distorted octahedral structure. Magnetic susceptibility measurements reveals that antiferromagnetic interactions exists between the high spin Co(II) ions within the dinuclear unit.

Keywords

Dinuclear Complex; Cobalt (II) Complex; Magnetic Properties; Mixed Triazole-Malonate

1. Introduction

Magnetic materials constructed from the paramagnetic ions and mixed short mediators have received a great deal of attention due to their impressive structural diversities, complicated magneto-structural correlations, and

*Dedicated to Professor Offiong Efang Offiong on the occasion of his 50th birthday.

#Corresponding Author.

intriguing applications in high-density information storage and quantum computation [1] [2]. As compared with the differently magnetic nature of the spin carriers (magnetic anisotropy, spin-orbit coupling, and spin state transition), the mixed homo-/hetero-bridges that aggregate the spin carriers in various binding modes play more important roles in determining the sign and strength of the super-exchange couplings [3] [4]. Among the diverse choices of the mixed magnetic-active bridges (such as azido-, formato-, cyanato-, and dicyanamido-ligands), a combination of five-membered heterocyclic triazolate and three-atom nonlinear carboxylate heterobridges has recently become one of the promising candidates for the investigations of the magnetic systems with novel structures and appealing magnetic properties. Anionic triazolate and the expanded analogues can smartly hold the paramagnetic ions into various magnetic-active motifs [5] [6], such as oligonuclear clusters [7]-[9], polymeric chains with single or multiple mediators [10] [11], infinite broad ribbons [12], as well as corner-/edge-sharing triangular lattices [13] [14], which have exhibited diverse magnetic phenomena with canted, frustrated, and typically antiferromagnetic couplings. More interestingly, the magnetic behavior and the relevant solid structures of these diverse magnetic samples can further be tailored by the presence of the short carboxylate mediator with conformation dependent magnetic interactions (antiferromagnetic coupling with different strength transmitted by syn, syn-/anti, anti-COO⁻, and/or ferromagnetic interaction with syn, anti-COO⁻) [15]. In particular, rigid polycarboxylate coligands have been found to well extend the low-dimensional magnetic structures into high-dimensional ordered ones, in which the number and position of the carboxylate group toward the phenyl backbone can essentially dominate the connectivity of the magnetic subunits [7] [16]. Furthermore in continuation with our ongoing investigations on the magnetic studies of mixed-ligand complexes [17] [18], using triazoles and carboxylates mediators, herein, 4-amino-1,2,4-triazole (atr) and malonic acid (mal) were judiciously selected as mixed mediators to self-assemble with inorganic Co^{II} source under controllable conditions to establish and enrich the magneto-structural correlations.

2. Experimental

2.1 Materials and Methods

All reagents were purchased commercially and used without further purification. Doubly deionized water was used for conventional synthesis. Elemental analysis was performed on a Thermo Flash EA-1112 Series CHNS-O Elemental Analyzer. The IR spectra were obtained from KBr pellets in the range 4000 - 400 cm⁻¹, using a Perkin-Elmer Spectrum 100 FT-IR spectrometer. TGA measurements were performed at the heating rate 10°C·min⁻¹ in the temperature range 25 - 600°C, under dry nitrogen flow of 60 mL·min⁻¹ on a TGA Q500 instrument. Approximately 2 - 5 mg of sample was placed in an open aluminum crucible. Magnetic susceptibilities were acquired on a Quantum Design SQUID MPMS-XL-7 magnetometer with polycrystalline samples, in which the phase purity of the sample was determined by PXRD experiments. The magnetic susceptibility was corrected for the contribution of the gel capsule and for the core diamagnetism (using Pascals constant).

2.2. Synthesis of [Co₂(atr)₃(mal)₂(H₂O)₂]₂·4H₂O (**1**)

A methanolic solution (10 cm³) of 4-amino-1,2,4-triazole (210 mg; 2.5 mmol) was added to a warm aqueous solution (20 cm³) of cobalt (II) nitratehexahydrate (356 mg; 2.5 mmol). Potassium malonate (generated *in situ* by reacting stoichiometric amounts of malonic acid and potassium carbonate) dissolved in water (2.5 mmol; 10 cm³) was added to the previous warm reddish-orange solution under continuous stirring for two hours and filtered, the filtrate was allowed to slowly evaporate at room temperature and complex separated as reddish-orange crystals suitable for X-ray diffraction analysis after one week. *Yield* 85%. *Anal. Calcd*: C, 59.92; H, 3.95; N, 19.97. *Found*: C, 59.57; H, 4.00; N, 19.75%. IR (KBr, cm⁻¹): 1594.5, 1505.1, 1471.1, 1345.1, 917.2, 789.7, 669.3.

2.3. Crystallographic Data Collection and Structure

Suitable single crystals of Compound **1** was mounted on a Bruker SMART APEX CCD diffractometer equipped with a graphite-monochromated MoK α radiation source ($k = 0.71073 \text{ \AA}$) at 150 K. All absorption corrections were performed with SADABS program [19]. All the structures were solved by direct methods and refined with full-matrix least-squares and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in the calculate positions. All calculations were performed using SHELXTL-

97 program [20]. The crystal parameters, data collection, and refinement result for Compound **1** is summarized in **Table 1**. Selected bond lengths and angles are listed in **Table 2**.

3. Results and Discussion

3.1. Infrared Spectrum

In the infrared spectrum, complex **1** exhibit multiple weak bands at *ca*, 3466, 3413 and 3350 cm^{-1} , corresponding to the O-H/N-H stretching vibrations of hydroxyl group and exocyclic amino group of the atr ligand [21]. Instead, broad bands centered at *ca* 3300 cm^{-1} in **1** suggest the presence of water molecule which heavily mask the weak absorptions of hydroxyl group and exocyclic amino group of atr ligand. Symmetric stretching vibrations of the malonate are observed at 1616, 1557, 1431 and 1366 cm^{-1} for **1**. Thus, the IR spectrum of **1** is in agreement with the single-crystal X-ray diffraction.

Table 1. Crystal data and structure refinement for Compound **1**.

Empirical formula	$\text{C}_{12}\text{H}_{28}\text{Co}_2\text{N}_{12}\text{O}_{14}$
FW	682.32
T (K)	150(2) K
Space group	$P2_12_12_1$
Wavelength (\AA)	0.71073
Crystal system	Orthorhombic
Unit cell dimensions	
<i>a</i> (\AA)	9.2550(1)
<i>b</i> (\AA)	13.9920(2)
<i>c</i> (\AA)	19.7580(3)
α (deg)	90
β (deg)	90
γ (deg)	90
<i>V</i> (\AA^3)	2558.58(4)
<i>Z</i>	4
D_x (g/cm^{-3})	1.771
μ (mm^{-1})	1.386
F (000)	1400
Crystal size (mm^3)	$0.10 \times 0.08 \times 0.05$
θ range (deg)	27.485
Index range (h, k, l)	$-12 \leq h \leq 12, -18 \leq k \leq 17, -25 \leq l \leq 25$
Reflection collected	5840
Independent reflections (R_{int})	5153 (0.0328)
Absorption correction	none
Data/restraints/parameter	5840/23/416
Goodness-of-fit on F^2	1.043
Final R indices [$I > 2\sigma > (I)$]	$R1 = 0.0328, wR2 = 0.0702$

Table 2. Selected Bond lengths (Å) and Bond angles (°) of **1**.

Bond lengths		Bond angles			
Co(1)-N(1)	2.116(2)	N1-Co1-N10	91.28(9)	N9-Co2-N5	92.36(9)
Co(1)-N(6)	2.141(2)	N1-Co1-N6	90.75(9)	N9-Co2-N2	88.46(9)
Co(1)-N(10)	2.130(2)	N10-Co1-N6	90.59(9)	N5-Co2-N2	90.80(9)
Co(2)-N(2)	2.166(3)	O5-Co1-O3	87.25(8)	N9-Co2-O2	175.40(9)
Co(2)-N(5)	2.106(2)	O5-Co1-O1	91.11(8)	N5-Co2-O2	88.52(9)
Co(2)-N(9)	2.102(2)	O3-Co1-O1	94.19(8)	O8-Co2-O7	86.81(8)
Co(1)-O(1)	2.128(2)	O5-Co1-N1	174.53(8)	O8-Co2-O2	91.35(9)
Co(1)-O(3)	2.074(19)	O3-Co1-N1	87.36(8)	O7-Co2-O2	96.78(8)
Co(1)-O(5)	2.062(19)	O3-Co1-N10	88.05(9)	O7-Co2-N9	87.79(9)
Co(2)-O(2)	2.107(2)	O1-Co1-N10	177.33(9)	O8-Co2-N5	173.25(8)
Co(2)-O(7)	2.097(2)	O1-Co1-N6	87.21(9)	O2-Co2-N2	87.01(8)
Co(2)-O(8)	2.085(19)	O5-Co1-N6	94.60(8)	O8-Co2-N2	95.94(8)
		N1-Co1-O1	90.27(9)	O7-Co2-N5	86.50(8)

Symmetry transformation used to generate equivalent atoms for **1**: $1/2 -x, -y, 1/2 +x, 1/2 +x, 1/2 -y, -z, -x, 1/2 +y, 1/2 -z$.

3.2. Thermal Stability and PXRD Patterns

Thermal stability of the complex was measured from room temperature to 600°C (**Figure 1**). The TG analysis of the complex shows that the weight loss of 16.83% takes place in the temperature range 70°C - 250°C (**Figure 1**), corresponding to the loss of coordinated and uncoordinated water molecules (theoretical weight loss 15.83%). The phase purity of the bulk product of **1** was further confirmed by PXRD technique. The experimental and computer-simulated PXRD patterns were in good agreement with each other, indicating the phase purity of the as-synthesized product.

3.3. Description of the Structure

The molecular structure of the complex **1** with atom numbering scheme is shown in **Figure 2**. The crystal structure refinement data for the compound is shown in **Table 1**, while selected bond lengths and bond angles are listed in **Table 2**.

The complex crystallizes in the orthorhombic system with space group $P2_12_12_1$. The Co(II) coordination environment is a distorted octahedron with each Co atom linked to one another by means of triple $\mu\text{-}\kappa^2\text{N}^1, \text{N}^2$ -1,2,4-triazole bridge having C-N bond distances ranging from 2.102(2) to 2.166(3) Å, one terminal malonate ligand with Co-O_{malonate} bond distances of 2.062(2) to 2.097(2) Å. The octahedral coordination is completed by one water molecule with bond distance of Co-O_{water} ranging from 2.107(2) to 2.128(2) Å. The Co-N bond distances in the range 2.101(2) - 2.166(2) Å (**Table 2**) are comparable to previously reported values [22]. The Co-Co separation of 3.80546(5) Å is consistent with the value reported for a similar dinuclear Co (II) complex linked by $\mu\text{-}\kappa^2\text{N}^1, \text{N}^2$ -1,2,4-triazole bridges [23].

The cobalt atom is positioned in a highly distorted octahedron where the angles subtended at the cobalt atom vary from 87.25° to 177.65°. So the environment around the cobalt (II) atom can be described as a distorted octahedron. The distorted octahedral configuration of Co (II) can be explained by Jahn-Teller effect for the d^7 configuration.

The high spin $3d^7$ ion of cobalt (II) gives $^4F_{9/2}$ ground term in octahedral ligand fields. Since it is a Jahn-Teller configuration, the distorted octahedron is expected. As shown in **Figure 2**, intermolecular hydrogen bonds exist extensively in the crystal. The intermolecular hydrogen bonds exist between the lattice water molecules (O13-H13A-O14 = 2.807 Å), coordinated carboxylate and lattice water (O11-H11A-O6 = 2.711 Å), coordinated water and lattice water (O2-H2B-O1 = 2.904 Å) as well as the carboxylate oxygen and the 1,2, 4-triazole nitrogen atoms (N8-H8A-O4 = 2.866 Å) leading to an extended three-dimensional hydrogen-bonded structure as depicted in **Figure 3**.

3.4. Magnetic Properties

The magnetic susceptibility of **1** (**Figure 4**) was measured on a polycrystalline sample under an applied field of 1000 Oe. The χ mT value at 300 K is 2.80 $\text{cm}^3\text{mol}^{-1}\text{K}$ (μ_{eff} per Co(II) = 4.73 μB), which is higher than that expected for a high-spin Co(II) ion through the spin-only formula, *ca.* 1.87 $\text{cm}^3\text{mol}^{-1}\text{K}$ with $g = 2.0$ ($\mu_{\text{eff}} = 3.87 \mu\text{B}$)

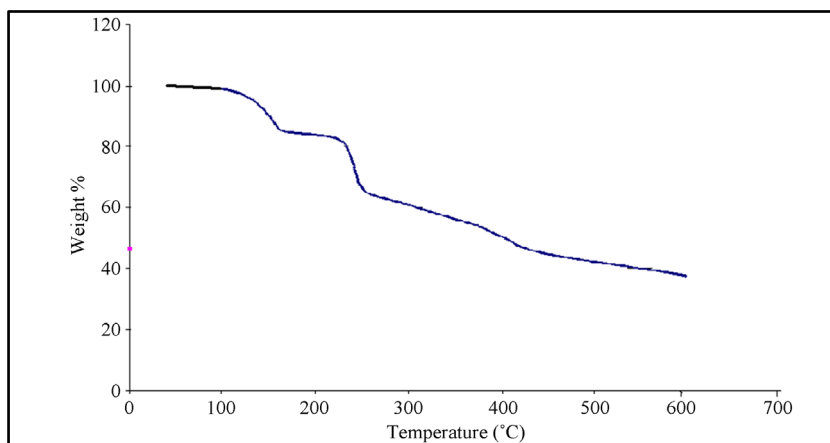


Figure 1. TGA curve of the complex 1 under N_2 .

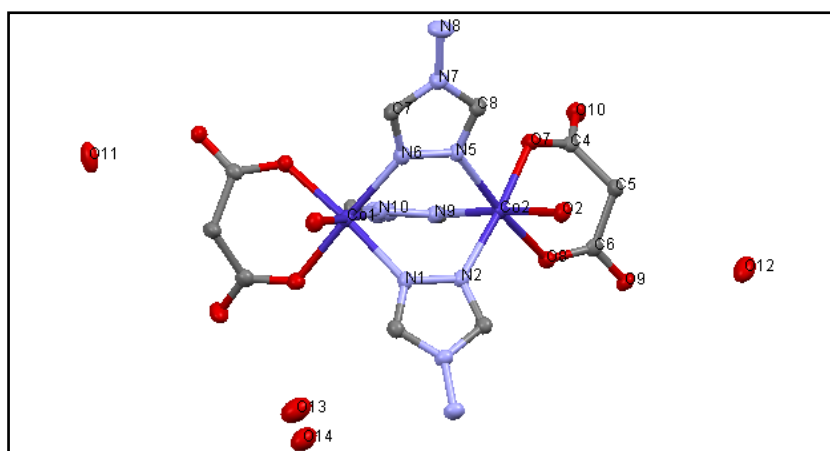


Figure 2. Perspective view of the dinuclear Co(II) complex showing the atom numbering scheme (Hydrogen atoms are omitted for clarity).

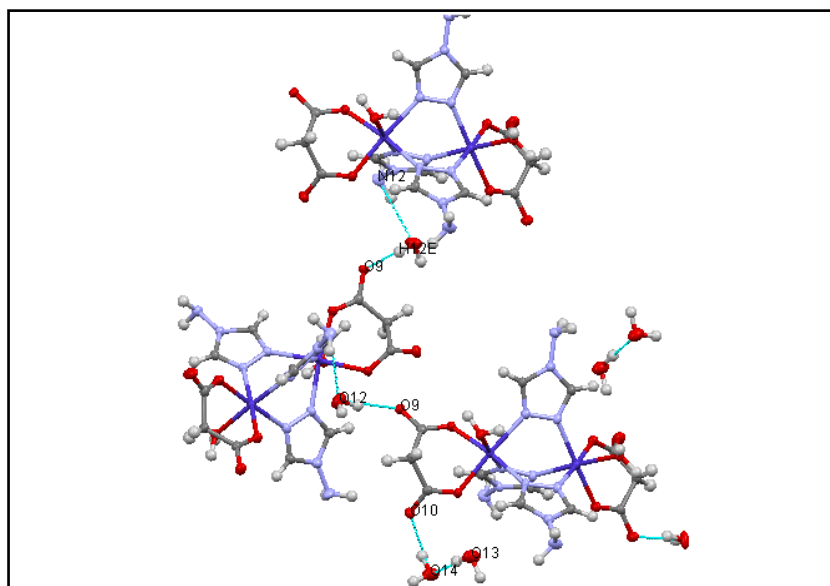


Figure 3. Intermolecular hydrogen bonds occurring in the crystal lattice of **1**.

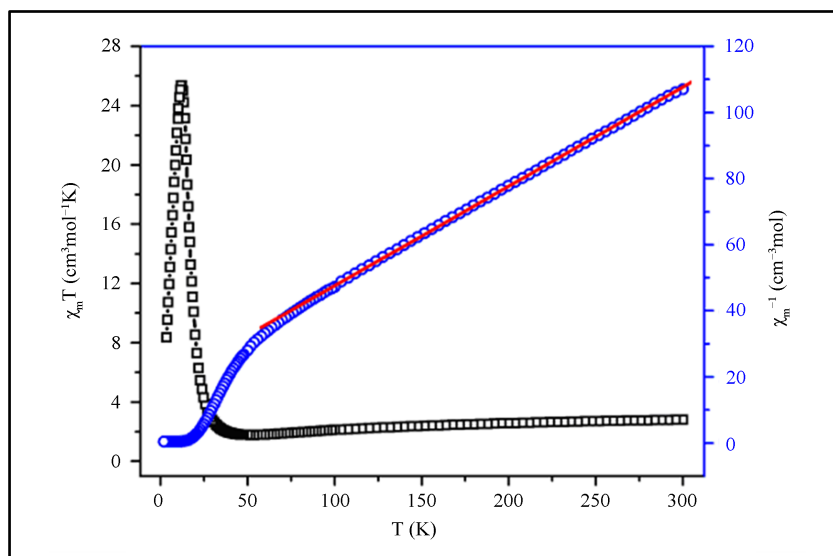


Figure 4. Temperature dependence of magnetic susceptibility ($\chi_m T$) and inverse susceptibilities (χ_m^{-1}) versus T plots. Red line indicates theoretical fitting for **1**.

[24], thus indicating that an important orbital contribution due to the distorted octahedral Co^{II} ion exists. The $\chi_m T$ value decreases gradually as the temperature is lowered from 300 K to 51 K, reaching a minimum of $1.77 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 51 K, which is attributed to spin-orbit coupling effects and indicates the presence of dominant antiferromagnetic interaction between two $\text{Co}(\text{II})$ paramagnetic centers. As the temperature is lowered the $\chi_m T$ value increases abruptly to a maximum of $25.31 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 12 K, and then drops sharply to a minimum of $8.0 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 2 K. This low temperature behaviour suggests a ferromagnetic phase transition. The dominant antiferromagnetic coupling mainly mediates through the $\mu\text{-}\kappa^2\text{N}^1$, N^2 -1,2,4-triazole pathway between two $\text{Co}(\text{II})$ centers in **1** at high temperature. Furthermore, the reciprocal molar magnetic susceptibility data (Figure 4) obey the Curie-Weiss law in the high temperature region of 75 - 300 K with a Curie constant of $C = 3.31 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ (close to the value of 2.8 - 3.4 $\text{cm}^3 \text{ mol}^{-1} \text{ K}$ expected for an octahedral $\text{Co}(\text{II})$ ion) and a Weiss constant of $\theta = -53.89 \text{ K}$. This large negative value of the Weiss constant supports the antiferromagnetic interaction between the $\text{Co}(\text{II})$ ions.

4. Conclusion

A novel mixed-ligand dinuclear $\text{Co}(\text{II})$ complex $[\text{Co}_2(\text{atr})_3(\text{mal})_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ has been synthesized and characterized. The complex crystallizes in an orthorhombic system and space group $\text{P}2_12_12_1$ with the $\text{Co}(\text{II})$ ion exhibiting a distorted octahedral coordination. Magnetic susceptibility measurements of the complex reveal an antiferromagnetic interactions between the $\text{Co}(\text{II})$ ions within the dinuclear units.

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Appendix A. Supplementary Material

CCDC 940976 contains the supplementary crystallographic data for **1**. This data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax (44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).