

A MIXED-ANION COMPLEX OF NICKEL(II) WITH MONOETHANOLAMINE

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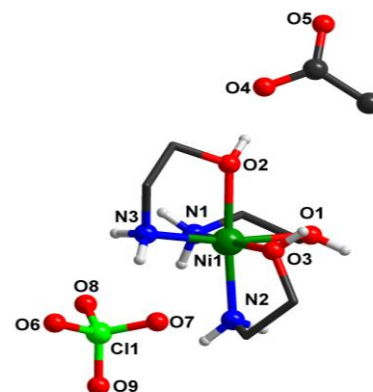
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Received June 16, 2023

Reaction of $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ with monoethanolamine (HMEA), in the presence of NaClO_4 , generates a mixed-anion complex, $\text{fac-}[\text{Ni}(\text{HMEA})_3](\text{ClO}_4)(\text{CH}_3\text{COO})$ (**1**). Compound **1** has been characterized by single crystal X-ray diffraction, IR and UV-VIS spectroscopy. The analysis of the crystal packing reveals the presence of an extended network supported by hydrogen bonds established between the anions and the complex cations.



INTRODUCTION

Monoethanolamine (2-aminoethanol, abbreviated HMEA), the first term of the aminoalcohol family, is a solvent frequently used in organic chemistry. Its popularity arises mainly from the ability to capture acid gases containing CO_2 and H_2S .^{1,2} Monoethanolamine is also a valuable ligand, as it was demonstrated by numerous compounds obtained for practical applications. For example, several complexes with monoethanolamine as a ligand were obtained from $\text{M}(\text{CH}_3\text{COO})_2$ ($\text{M} = \text{Ni}, \text{Co}, \text{Cu}, \text{Zn}$), in order to improve the CO_2

desorption capacity of HMEA; a solution containing the trivalent cobalt ion, $[\text{Co}(\text{HMEA})_3]^{3+}$, has remarkable CO_2 desorption properties as well.³ Other complexes with aminoalcohols as ligands have applications in catalysis, corrosion inhibition, or ion exchange processes.⁴

One of the first synthesis of metal aminoalcohol complexes was reported by Miller in 1940, namely the synthesis of sodium bismuth complex salts with triethanolamine and triisopropanolamine.⁵ Subsequently, complexes of various metals (*i.e.* $\text{Co}(\text{II})$, $\text{Co}(\text{III})$, $\text{Ni}(\text{II})$, $\text{Zn}(\text{II})$, $\text{Cd}(\text{II})$, $\text{Hg}(\text{II})$, $\text{Fe}(\text{III})$) with monoethanolamine

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were reported in literature starting with the 1960s. In the early period, these compounds were formulated, based on IR spectra and chemical analysis, as complex salts containing monoethanolamine and anions (Cl^- , Br^- , SO_4^{2-} , NO_3^- , ClO_4^-) as ligands. Based on IR spectra, monoethanolamine was assumed to be coordinated both in neutral (HMEA) and deprotonated (MEA^-) forms.^{4,6,7} The presence of the hydroxyl group prompted comparisons between the chelate effect of monoethanolamine and the one of ethylenediamine.⁸ An interesting feature of deprotonated monoethanolamine and other amino alcohols consists in their ability to act as bridges between two or three metal ions, forming alkoxido-bridged metal polynuclear complexes.^{9–13} Some binuclear species supported

by alkoxido bridges were employed as nodes, with *exo*-dentate ligands as spacers, for the construction of coordination polymers with various dimensionalities.^{14–16}

In this paper, we report on the synthesis and crystal structure of *fac*- $[\text{Ni}(\text{HMEA})_3](\text{ClO}_4)(\text{CH}_3\text{COO})$ (**1**), a new Ni(II) mixed-anion complex with chelating HMEA ligands.

RESULTS AND DISCUSSION

The crystal structure of complex **1** consists of cationic mononuclear Ni(II) species and two uncoordinated perchlorate and acetate anions (Fig. 1).

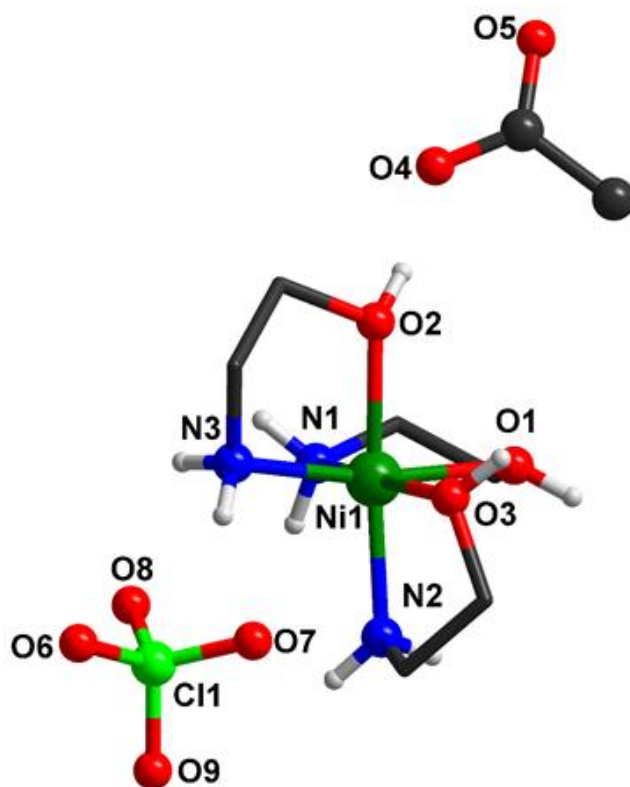


Fig. 1 – Perspective view of *fac*- $[\text{Ni}(\text{HMEA})_3](\text{ClO}_4)(\text{CH}_3\text{COO})$ (**1**), along with the atom numbering scheme.

The presence of these ions was also demonstrated by the IR spectrum of **1**, that illustrates vibrations modes characteristic for both acetate ($\nu_{\text{as}}(\text{COO})$: 1551 cm^{-1} and $\nu_{\text{s}}(\text{COO})$: 1413 cm^{-1}) and perchlorate ions ($\nu(\text{ClO}_4)$: 1051 cm^{-1} , 1021 cm^{-1} , 660 cm^{-1}).¹⁷ The metal ion shows a distorted octahedral stereochemistry with a N_3O_3 donor set. The donor atoms, three nitrogen and three oxygen atoms, are in facial arrangement.

Each HMEA ligand chelates to form three five-membered rings (NC_2ONi), with Ni-N bond distances ranging from $2.077(2)$ to $2.079(2)\text{ \AA}$, and Ni-O bond distances ranging from $2.0877(19)$ to $2.1214(17)\text{ \AA}$. The values of the three bite angles, for the chelating HMEA ligands, O-Ni-N, are: $80.32(9)$, $80.76(8)$, and $81.18(9)^\circ$. Structure refinement data are given in Table 1, and selected bond lengths and angles are given in Table 2.

Table 1

Crystallographic data, details of data collection and structure refinement parameters for compound **1**

Empirical formula	C ₈ H ₂₄ ClN ₃ NiO ₉
Formula weight	400.441
Temperature/K	293K
Crystal system	<i>monoclinic</i>
Space group	<i>P2₁/c</i>
<i>a</i> /Å	14.1823(5)
<i>b</i> /Å	8.1207(3)
<i>c</i> /Å	14.8385(7)
α /°	90
β /°	103.892(4)
γ /°	90
Volume/Å ³	1658.97(12)
Z	4
ρ_{calc} /cm ³	1.603
μ /mm ⁻¹	1.376
F(000)	842.7
Crystal size/mm ³	0.2 × 0.1 × 0.1
Radiation	(λ = 0.71073)
Independent reflections	3992 [R_{int} = 0.0351, R_{sigma} = 0.0388]
Data/restraints/parameters	3992/12/216
Goodness-of-fit on F^2	1.020
Final R indexes [$I > 2\sigma(I)$]	R_1 = 0.0404, wR_2 = 0.1061
Final R indexes [all data]	R_1 = 0.0533, wR_2 = 0.1153
Largest diff. peak/hole / e Å ⁻³	0.53/-0.54

$${}^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad {}^b wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}; \quad w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$$

where $P = [\max(F_o^2, 0) + 2F_c^2] / 3$.

Table 2

Selected bond lengths (Å) and angles (°) for compound **1**

Distances (Å)			Angles (°)			
Ni1	O1	2.1214(17)	O3	Ni1	O1	91.66(7)
Ni1	O3	2.0986(17)	O2	Ni1	O1	89.73(7)
Ni1	O2	2.0877(19)	O2	Ni1	O3	87.56(7)
Ni1	N2	2.077(2)	N2	Ni1	O1	92.95(9)
Ni1	N3	2.078(2)	N2	Ni1	O3	80.76(8)
Ni1	N1	2.079(2)	N2	Ni1	O2	168.08(9)
			N3	Ni1	O1	169.32(9)
			N3	Ni1	O3	91.79(8)
			N3	Ni1	O2	80.32(9)
			N3	Ni1	N2	97.58(10)
			N1	Ni1	O1	81.18(9)

The complex exists in two enantiomeric forms (Λ and Δ), both being present in the crystal lattice

by virtue of the crystallographic inversion center (Fig. 2).

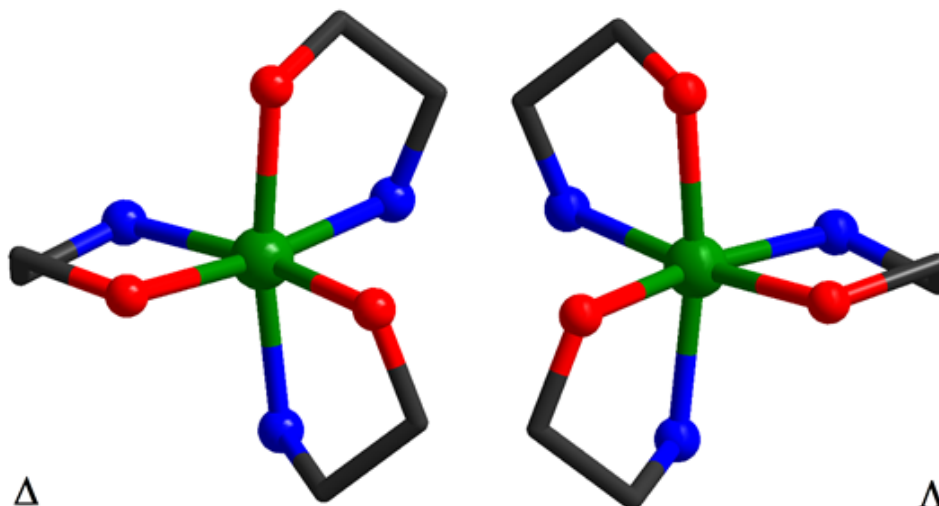


Fig. 2 – Perspective view of the two enantiomeric forms (Δ and Λ) for complex 1.

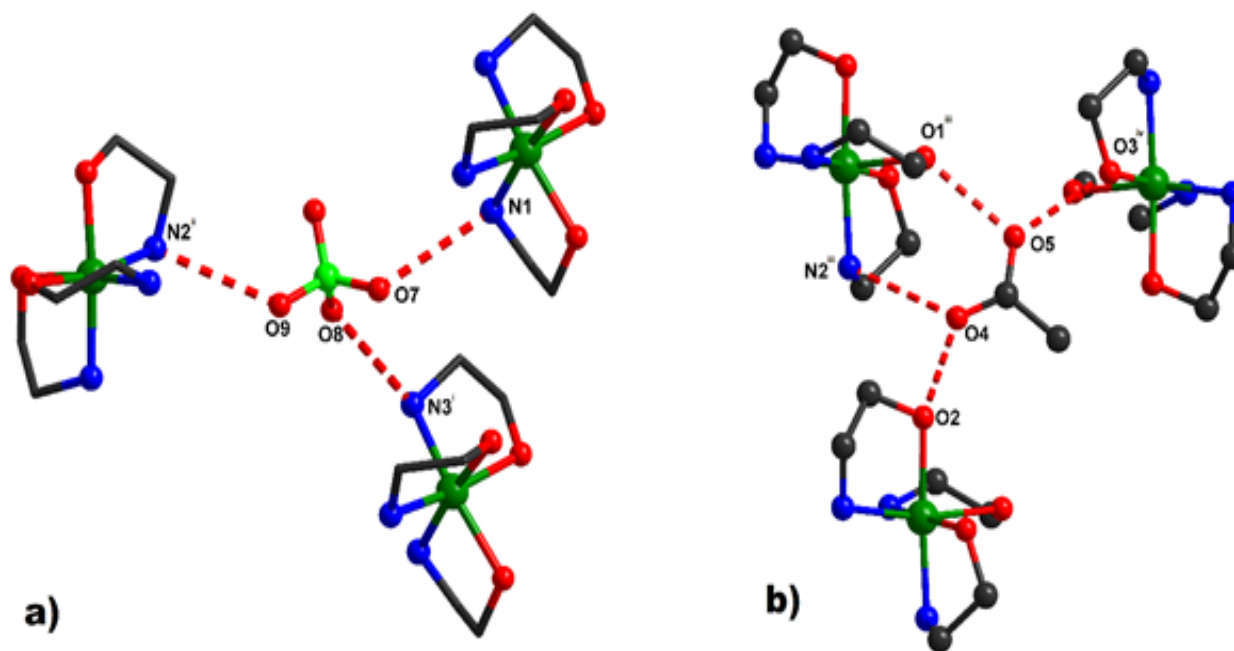


Fig. 3 – The hydrogen bonding interactions of perchlorate (a) and acetate (b) anions with the mononuclear Ni(II) units ($i = x, 1+y, z$, $ii = 1-x, 1/2+y, 1/2+z$, $iii = x, 1/2-y, 1/2+z$, $iv = 2-x, 1/2+y, 3/2-z$).

The crystal packing of compound **1** is governed by only hydrogens bonds. All of the nitrogen atoms are involved as donors to oxygen atoms on the perchlorate anions (Fig. 3a) with average N \cdots O distances of 3.03 Å (N1 \cdots O7 = 3.011 Å, N2 ii \cdots O9 = 3.034 Å, N3 i \cdots O8 = 3.025 Å, $i = x, 1+y, z$, $ii = 1-x, 1/2+y, 1/2+z$).

The carboxylate anion connects through hydrogen bonds three mononuclear Ni(II) units (Fig. 3b), as follows: (a) the O4 atom is strongly hydrogen bonded to one nitrogen atom

and one oxygen atom from two adjacent Ni(II) complex cations (O4 \cdots O2 = 2.601 Å, O4 \cdots N2 iii = 3.034 Å, $iii = x, 1/2-y, 1/2+z$); (b) the O5 atom is involved in two hydrogen bonds with two oxygen atoms arising from HMEA ligands belonging to two neighboring mononuclear Ni(II) cationic units (O5 \cdots O1 iii = 2.653 Å, O5 \cdots O3 iv = 2.637 Å, $iii = x, 1/2-y, 1/2+z$, $iv = 2-x, 1/2+y, 3/2-z$). The propagation of the hydrogen bonds leads to an extended supramolecular network (Fig. 4).

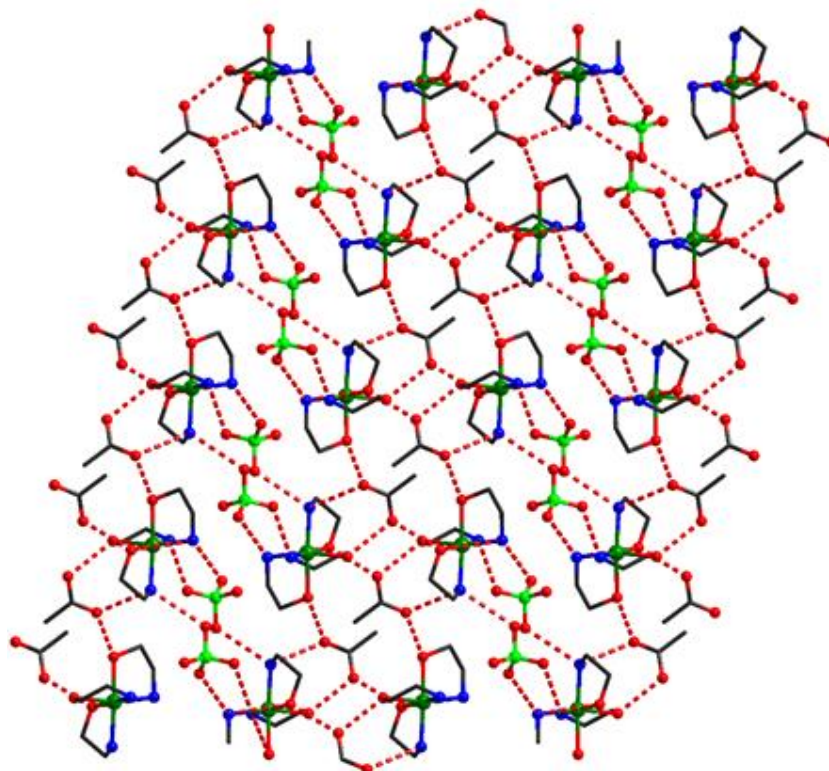


Fig. 4 – Perspective view of the extended hydrogen bonds network in crystal **1**.

The electronic spectrum, in solid state, using the diffuse reflectance technique (Fig. 5) shows the characteristic features for an octahedral nickel(II) ion, with three *d-d* bands assigned to the following transitions: ${}^3A_2 \rightarrow {}^3T_2$ (970 nm), ${}^3A_2 \rightarrow {}^3T_1$ (3F) (591 nm) and ${}^3A_2 \rightarrow {}^3T_1$ (3P) (369 nm), assuming the *O* symmetry group. The band with the maximum at 970 nm gives the value of the 10Dq parameter: 10310 cm^{-1} . The weak and sharp band at 767 nm is due to the spin forbidden transition, ${}^3A_2 \rightarrow {}^1E$.¹⁸⁻²⁰ The band located at 214 nm is probably due to one of the anions or to a metal-to-ligand charge transfer.

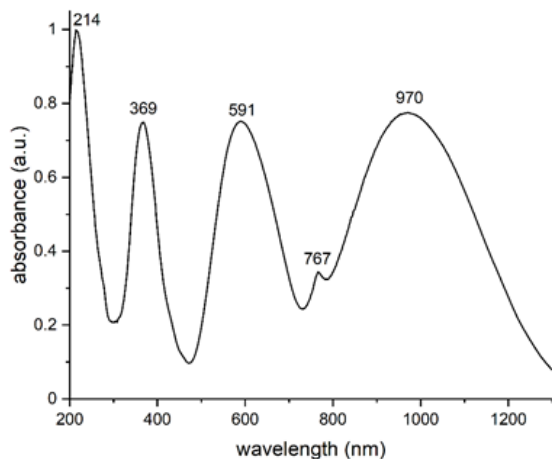


Fig. 5 – Electronic spectrum for compound **1**.

EXPERIMENTAL

Materials and methods

Nickel(II) acetate tetrahydrate, sodium perchlorate, monoethanolamine, and ethanol were purchased from commercial sources (Sigma-Aldrich) and used as received.

fac-[Ni(HMEA)₃](ClO₄)(CH₃COO) (**1**). In a solution obtained by solving 0.5456 g (2.2 mmol) Ni(CH₃COO)₂·4H₂O in 30 mL EtOH, 0.309 g (2.2 mmol) NaClO₄ was added. The obtained green solution was magnetically stirred for 15 min and then, a solution of 0.4026 g (6.6 mmol) monoethanolamine in 10 mL EtOH was added. The resulting blue solution was magnetically stirred for another 15 min. Blue single crystals were obtained by slow evaporation of the filtrate at room temperature. IR data (ATR mode, cm^{-1}): 660m, 853m, 883m, 950w, 1003s, 1021vs, 1051vs, 1111s, 1264vw, 1338w, 1413m, 1446w, 1472w, 1551m, 2598vw, 2702w, 2751w, 2822w, 2904w, 2933w, 2963w, 3172vw, 3246vw, 3287w, 3314w, 3351vw).

Physical measurements

The FTIR spectrum was recorded on Agilent Cary 630 FTIR spectrometer with a ZnSe ATR, in the wave number range of 4000–650 cm^{-1} . Electronic spectrum has been recorded on a Jasco V 670 spectrophotometer, in solid state, in the range 200–1300 nm, using the diffuse reflectance technique and Spectralon as standard.

X-Ray crystallography

Single X-ray studies were performed on a STOE IPDS II diffractometer using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$). The structures were solved by

direct methods and they were refined with the ShelXL refinement package. CCDC reference number: 2270213.

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