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Note

The synthesis and crystal structure of ethylenedinitrilotetraacetamidoxime nickel(II) sulfate trihydrate

George A. Pearse, Jr. [a,*], Clarence E. Pfluger [b]

[a] *Department of Chemistry, Le Moyne College, Syracuse, NY 13214, USA*
[b] *Department of Chemistry, Pittsburg State University, Pittsburg, KS 66762, USA*

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Abstract

The synthesis of the first reported complex formed between a transition metal ion and the potentially hexadentate ligand, ethylenedinitrilotetraacetamidoxime (EDTAO), is presented. The crystal structure of a nickel(II) complex with EDTAO, $C_{10}H_{24}N_{10}O_4$, has been determined. The intensities of 2183 reflections (2030 observed) for $[Ni(EDTAO)]SO_4 \cdot 3H_2O$ were collected by diffractometer methods using Cu Kα radiation. The space group is $P2_12_12_1$ (No. 19). Cell dimensions are $a = 11.407(2)$, $b = 11.820(2)$, $c = 15.937(2)$ Å and $\alpha = \beta = \gamma = 90°$ with 4 molecules in the unit cell. The observed density is 1.710 g cm^{-3}. Refinement was by full-matrix least-squares methods to a conventional R value of 0.025. The complex consists of discrete $Ni(EDTAO)^{2+}$ cations and sulfate anions; the cation existing as a distorted octahedral complex with bonding through to amine and four oxime nitrogen atoms. Neither the sulfate nor the water molecules are involved in the coordination. The Ni–N(amine) distances are 2.123(2) and 2.134(2) Å, while the Ni–N(oxime) distances are 2.099(2), 2.074(2), 2.078(2) and 2.077(2) Å.

Keywords: Crystal structures; Nickel complexes; Amidoxime complexes

1. Introduction

Although transition metal complexes of aldoximes have attracted considerable attention [1–5], amidoximes, which have been known for over 100 years and are related to aldoximes, have not received the same degree of study with respect to their chelating abilities. Research on amidoximes, especially those containing the −N=C−C=N− diimine structure, has generally been in the area of solution chemistry of their transition metal complexes [6–8]. Crystal structures have been reported for some amidoxime ligands [9–15], however a search of the literature revealed only a few references to the determination of the molecular structure of the transition metal complex of an amidoxime by single crystal X-ray diffraction [15–18].

The synthesis of ethylenedinitrilotetraacetamidoxime, EDTAO (Fig. 1), was summarily reported over 30 years ago [19], and since then the only other reference to EDTAO was some transition metal ion–EDTAO solution spectra [20]. Of the amidoxime complexes investigated so far, none can function as a hexadentate ligand through the formation of five five-membered chelate rings involving nickel(II) in octahedral coordination. In order to determine the mode of coordination, the crystalline complex, $[Ni(EDTAO)]SO_4 \cdot 3H_2O$ was synthesized and its structure determined. The results of this investigation are compared to other reported ligands with similar structural features.

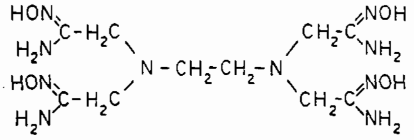

Fig. 1. Block diagram of ethylenedinitrilotetraacetamidoxime.

2. Experimental

2.1. Materials

Ethylenedinitrilotetraacetonitrile was obtained from Eastman Kodak Co. and used as received. All other chemicals were of reagent grade. Melting points were

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* Corresponding author.

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obtained using a Kofler micro hot stage. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Density measurements were made by the floatation method using a mixture of benzene and 1,2-dibromoethane at 22 °C.

2.2. Preparation

Ethylenedinitrilotetraacetamidoxime (**I**) was prepared by the slow addition of 150 ml of an aqueous solution containing 34.8 g (0.50 mol) of hydroxylammonium chloride and 20.0 g (0.50 mol) of sodium hydroxide to a slurry of 21.6 g (0.10 mol) of ethylenedinitrilotetraacetonitrile in 100 ml of 50% aqueous ethanol. The resulting exothermic reaction mixture was stirred overnight, filtered, and the white crystalline product washed with absolute ethanol and diethyl ether and then air-dried to give **I**: yield 28.2 g (81%); m.p. 191–192 (dec.). *Anal.* Calc. for $C_{10}H_{24}N_{10}O_4$: C, 34.38; H, 6.94; N, 40.21. Found: C, 34.23; H, 6.77; N, 40.06%.

Mono-(ethylenedinitrilotetraacetamidoxime)nickel(II) sulfate trihydrate (**II**) was prepared by the addition of 10.5 g (0.03 mol) of solid **I** to 200 ml of a heated aqueous solution containing 7.9 g (0.03 mol) of nickel(II) sulfate hexahydrate. The resulting purple solution was stirred at 80–90 °C for 1 h, and allowed to stand overnight at room temperature. The resulting purple crystals were filtered, washed with absolute methanol and ether to give **II**: yield 12.3 g (73.6%). *Anal.* Calc. for $[Ni(C_{10}H_{24}N_{10}O_4)]SO_4 \cdot 3H_2O$: C, 21.55; H, 5.43; N, 25.14; Ni, 10.54; SO_4, 17.24; H_2O, 9.70. Found: C, 21.27; H, 5.21; N, 25.02; Ni, 10.42; SO_4, 17.08; H_2O, 9.56%.

2.3. X-ray crystallography and structure solution

Slow evaporation of a dilute aqueous solution of **II** at room temperature yielded crystals suitable for X-ray crystallographic analysis. A crystal, having dimensions of 0.195 × 0.258 × 0.316 mm and whose faces were accurately measured for later use in a calculated absorption correction, was selected and mounted in a random orientation on a Nicolet P3F diffractometer equipped with a graphite monochromated Cu Kα radiation source. Experimental conditions and crystallographic data are given in Table 1. Intensity data, gathered by the ω–2θ method were reduced by routine procedures. Calculations were carried out by the application of the direct methods program SOLV of the SHELXTL, Version 3, set of programs furnished for the P3F diffractometer [21]. See also Section 4.

Table 1
Summary of crystallographic data

Formula	$[Ni(C_{10}H_{24}N_{10}O_4)]SO_4 \cdot 3H_2O$
Formula weight	557.18
Crystal system	orthorhombic
Space group	$P2_12_12_1$ (No. 19)
Z	4
Lattice parameters	
a (Å)	11.407(2)
b (Å)	11.820(2)
c (Å)	15.937(2)
$\alpha=\beta=\gamma$ (°)	90
Cell volume (Å^3)	2148.9(5)
T (°C)	23(1)
D_{calc} (g cm^{-3})	1.722
D_{meas} (g cm^{-3})	1.710
$F(000)$	1168
Diffractometer	Nicolet P3F
Radiation: Cu Kα, graphite monochromated, λ (Å)	1.54178
Transmission factors: max.–min.	0.689–0.573
Data collection range, 2θ	3.0–129.0
Scan type	ω–2θ
Scan rate (min^{-1})	3.9–29.3
No. reflections measured	2183
No. reflection observed, $[F_o > 3\sigma(F_o)]$	2030
No. variables	389
Residuals: R, R_w	0.025, 0.034
Goodness of fit	1.335
Max. shift in final cycle	0.67
Extinction coefficient	0.00373(34)
Largest, smallest peaks in final difference map (e Å^{-3})	+0.26, −0.24

3. Results and discussion

When an aqueous solution of nickel(II) sulfate hexahydrate is treated with an equimolar amount of ethylenedinitrilotetraacetamidoxime, EDTAO, a deep purple solution results from which a purple crystalline complex precipitates. The 1:1 complex, $[Ni(CEDTAO)]SO_4 \cdot 3H_2O$, utilizes the ligand as a neutral hexadentate chelating agent and consists of discrete $[Ni(EDTAO)]^{2+}$ cations, sulfate counter-ions and crystal lattice water molecules. Bonding to the central nickel(II) atom is through four oxime and two imine nitrogen atoms resulting in a distorted octahedral configuration containing five five-membered rings. Four of these rings involve coordination with nickel(II) utilizing an oxime and a tertiary amine nitrogen, while the fifth ring involves the two tertiary amine nitrogens of the ligand. Three of the rings, Ni–N(3)–C(33)–C(3)–N(6), Ni–N(5)–C(5)–C(6)–N(6) and Ni–N(1)–C(11)–C(1)–N(5), are in a distorted plane with the other two rings being perpendicular to these (Fig. 2).

A comparison of the nickel–nitrogen bond lengths in the complex (Fig. 3) shows that the Ni–N(oxime) bonds are consistently shorter than the Ni–N(imine) bonds. This is in agreement with the results reported

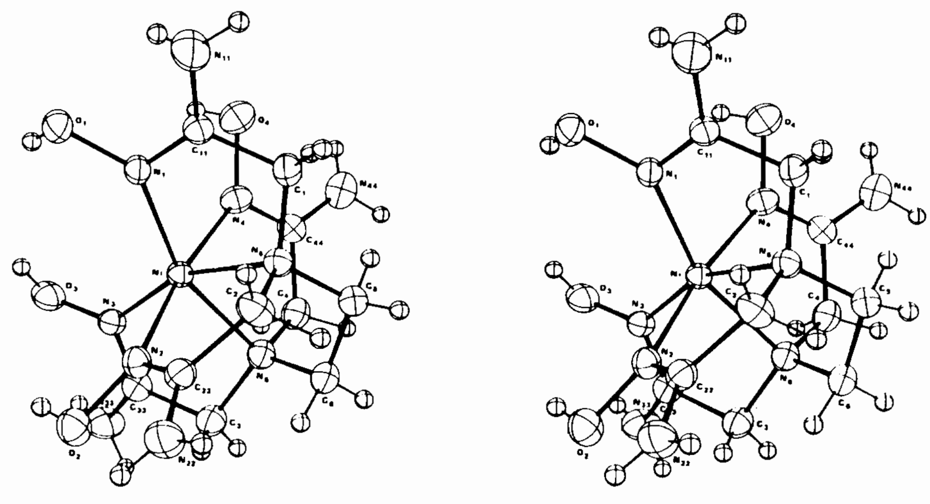

Fig. 2. Stereo drawing of isolated Ni(EDTAO)$^{2+}$. Non-hydrogen thermal ellipsoids are drawn at 50% probability.

for the structure of nickel(II) 2,2′-iminobis(acetamidoxime) chloride [17]. In fact, EDTA can be considered as two molecules of the tridentate ligand iminodiacetamidoxime, IDAO, joined by an ethylene bridge. Both ligands coordinate through the oxime and the amine nitrogens with nickel(II) to form dipositive cationic complexes with a neutral ligand.

The N(oxime)–Ni–N(amine) intrachelate angles are 77.9(1), 79.6(1), 77.6(1) and 80.0(1)° (Table 2). When compared to the same angles in the [Ni(IDAO)$_2$]$^{2+}$ cation of 78.9 and 79.2°, it can reasonably be concluded that the distortion from 90° is approximately the same for both complexes and that the α,α′-diimine chelates of iminoamidoximes with nickel(II) are geometrically similar. These values are in good agreement with bond angles reported for other octahedral nickel–oxime complexes [22]. The average Ni–N(oxime) bond length is 2.082 Å, while the average Ni–N(amine) bond length is 2.219 Å (Fig. 3). This same observation was reported for the [Ni(IDAO)$_2$]$^{2+}$ complex ion.

EDTAO can also be considered as a ligand resembling ethylenedinitrilotetraacetic acid (EDTA). Both possess

Table 2
Selected bond angles (Å)

N(1)–Ni–N(2)	94.2(1)	N(2)–Ni–N(5)	79.6(1)
N(2)–Ni–N(3)	92.7(1)	N(4)–Ni–N(5)	93.2(1)
N(2)–Ni–N(4)	171.2(1)	N(2)–Ni–N(6)	94.1(1)
N(1)–Ni–N(5)	77.9(1)	N(4)–Ni–N(6)	80.0(1)
N(3)–Ni–N(5)	159.8(1)	C(11)–C(1)–N(5)	109.3(2)
N(1)–Ni–N(6)	158.5(1)	C(1)–N(11)–N(1)	117.2(2)
N(3)–Ni–N(6)	77.6(1)	Ni–N(1)–C(11)	114.0(2)
N(5)–Ni–N(6)	84.2(1)	C(22)–C(2)–N(5)	113.0(2)
C(1)–C(11)–N(11)	116.6(2)	C(2)–C(22)–N(2)	116.5(2)
C(2)–C(22)–N(22)	117.0(2)	Ni–N(2)–C(22)	118.0(2)
C(3)–C(33)–N(33)	118.8(2)	C(33)–C(3)–N(6)	108.5(2)
C(4)–C(44)–N(44)	117.6(2)	C(3)–C(33)–N(3)	116.2(2)
Ni–N(5)–C(2)	110.2(1)	Ni–N(3)–C(33)	115.4(2)
Ni–N(5)–C(5)	105.7(1)	C(44)–C(4)–N(6)	112.5(2)
C(2)–N(5)–C(5)	111.1(2)	C(4)–C(44)–N(4)	116.0(2)
C(5)–C(6)–N(6)	109.2(2)	Ni–N(4)–C(44)	117.1(2)
Ni–N(6)–C(4)	109.1(1)	Ni–N(5)–C(1)	105.8(1)
Ni–N(6)–C(6)	105.3(1)	C(1)–N(5)–C(2)	110.1(2)
C(4)–N(6)–C(6)	111.6(2)	C(1)–N(5)–C(5)	113.7(2)
N(1)–Ni–N(3)	121.6(1)	N(5)–C(5)–C(6)	109.5(2)
N(1)–Ni–N(4)	89.2(1)	Ni–N(6)–C(3)	105.1(1)
N(3)–Ni–N(4)	92.4(1)	C(3)–N(6)–C(4)	111.1(2)
		C(3)–N(6)–C(6)	114.1(2)

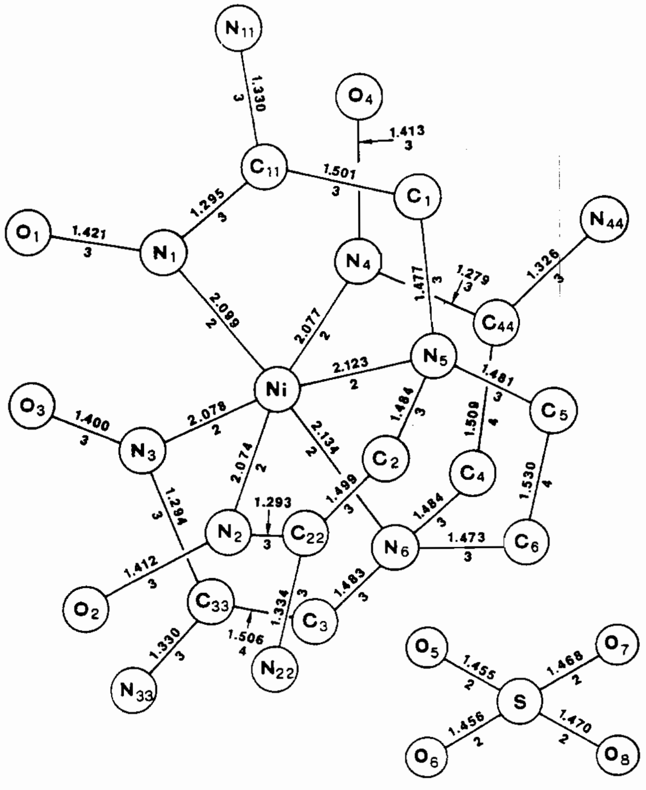

Fig. 3. Intramolecular bond distances (Å) with the e.s.d. of the least significant digit given below each value.

the capability of forming octahedral complexes involving five five-membered chelate rings if the molecule acts as a hexadentate ligand. The structure of the complex formed between nickel(II) and EDTA has been reported [23]. Although its coordination about the nickel is octahedral, the EDTA is found to coordinate as a pentadentate ligand with one uncomplexed $-CH_2COOH$ group and the sixth position is occupied by a water molecule. A comparison of the two ligands, EDTAO and EDTA, shows that both result in a hexadentate coordination with a central nickel(II) atom. The marked difference is that EDTAO reacts as a neutral ligand, whereas EDTA is anionic upon complexation. The structure of the nickel(II)–ethylenedinitrilotetraacetamide complex has been reported [24], but in this case the potentially hexadentate ligand reacts as a tetradentate species with two bonded water molecules completing the octahedral coordination sphere.

In conclusion, it has been shown that EDTAO does react with nickel(II) as a neutral ligand to form a stable octahedral complex. Coordination with the central nickel(II) ion involves both oxime and amine nitrogen atoms which is consistent with other amidoxime coordination compounds which possess the diimine moiety.

4. Supplementary material

Atomic coordinates have been deposited with the Cambridge Crystallographic Centre. Additional material is obtainable from the authors.

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