Pergamon

0277-5387(94)00200-2

Polyhedron Vol. 14, No. 3, pp. 441–444, 1995
Copyright © 1995 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0277-5387/95 $9.50+0.00

A BINUCLEAR NICKEL(II) COMPLEX CONTAINING AN OXAMIDO-BRIDGE: SYNTHESIS, PROPERTIES AND X-RAY CRYSTAL STRUCTURE OF $[Ni(oxae)Ni(phen)_2](ClO_4)_2 \cdot 3H_2O$

PING-RONG WEI,* LU JIA, CHANG-RANG LIU and QIANG HAN

Department of Chemistry, Zhengzhou University, Zhengzhou 450052, P. R. C.

and

GE-CHEN WEI

Changchun Institute of Applied Chemistry, Academic Sinica, Changchun 130022, P. R. C.

and

SONG GAO

Research Centre of Rare Earth Chemistry, Peking University, Beijing 100871, P. R. C.

(*Received* 16 *February* 1994; *accepted* 11 *May* 1994)

Abstract—The binuclear complex $[Ni(oxae)Ni(phen)_2](ClO_4)_2 \cdot H_2O$ (oxae = N,N′-bis(2-aminoethyl)oxamido dianion, phen = 1, 10-phenanthroline) was prepared from the planar monomeric complex Ni(oxae) and characterized through analytical and spectroscopic measurements. The structure of $[Ni(oxae)Ni(phen)_2](ClO_4)_2 \cdot 3H_2O$ was investigated by single-crystal X-ray analysis. The complex has an extended oxamido-bridged structure and consists of two nickel(II) ions, one of them in a square planar environment and another in a distorted octahedral environment. The Ni—Ni distance is 5.267 Å.

Synthetic model studies involving binuclear transition metal systems have attracted much current interest.[1–3] This is in large measure due to the expectation that such studies will provide deeper insights into complex biological processes. Many metalloenzymes catalyse important reactions at binuclear metal centres.[4,5] In recent years, therefore, binuclear coordination chemistry has become one of the most active research fields. It is known that the mononuclear complex, N,N′-bis(3-aminopropyl)oxamidocopper(II) [abbreviated as Cu(oxpn)] acts as a bidentate chelating agent toward a second metal ion to form binuclear, trinuclear and tetranuclear metal complexes.[1,6–9] However, N,N′-bis(aminoalkyl)oxamidonickel(II) acts as a bidentate ligand with its two carbonyl oxygens, and the structural investigation of binuclear metal complexes bridged by the oxamide group has not been reported yet. In this paper we report the preparation of the monomeric fragment Ni(oxae) (oxae = N,N′-bis(2-aminoethyl)oxamido dianion) as a ligand, and the synthesis of a binuclear complex $[Ni(oxae)Ni(phen)_2](ClO_4)_2 \cdot H_2O$ (phen = 1,10-phenanthroline), which has been characterized by analytical and spectroscopic measurements. The crystal structure of $[Ni(oxae)Ni(phen)_2](ClO_4)_2 \cdot 3H_2O$ has been determined by X-ray diffraction techniques.

EXPERIMENTAL

Ni(oxae) was prepared according to the method described previously.[10] All other solvents and chemicals were reagent grade.

---

*Author to whom correspondence should be addressed.

Synthesis of [Ni(oxae)Ni(phen)$_2$](ClO$_4$)$_2$·H$_2$O

To Ni(oxae) (57.7 mg, 0.25 mmol) stirred in methanol were successively added a solution of Ni(ClO$_4$)$_2$·6H$_2$O (91.4 mg, 0.25 mmol) in methanol (20 cm^3) and another solution of phen (99.1 mg, 0.5 mmol) in methanol (20 cm^3). The mixture was stirred for 7 h and the solution was then filtered. Yellow microcrystals were obtained while the volume of solution was appropriately reduced, washed with absolute methanol several times and finally with ether and dried *in vacuo*. Found: C, 41.2; H, 3.4; N, 12.7; Ni, 13.2. Calc. for $C_{30}H_{30}N_8O_{11}Cl_2Ni_2$: C, 41.6; H, 3.5; N, 12.9; Ni, 13.5%. IR, ν_{max} (KBr, cm^{-1}): 3175(w, —NH$_2$), 1647(vs, C=O)), 1515(vs, —N=C—), 1100(vs, ClO$_4^-$). Λ(DMF, $\Omega^{-1}\cdot cm^2\ mol^{-1}$): 164. Crystals of [Ni(oxae)Ni(phen)$_2$](ClO$_4$)$_2$·3H$_2$O suitable for X-ray analysis were obtained from methanol solution by slow evaporation at room temperature.

Physical measurements

Analyses for C, H and N were carried out on a Perkin–Elmer model 240 analyser and the nickel content was determined using a Perkin–Elmer 703 atomic absorption spectrophotometer. The IR spectra were recorded with a Shimadzu IR-435 spectrophotometer on KBr disks. Molar conductance was measured with a DDS-11A conductometer in the solution of DMF.

X-Ray data collection and structure determination of [Ni(oxae)Ni(phen)$_2$](ClO$_4$)$_2$·3H$_2$O

The single crystal was sealed in a glass capillary and mounted on a Nicolet R3M/E single-crystal diffractometer using Mo K_α radiation; 4467 reflections were measured in the range of $3° < 2\theta < 54°$, 4366 unique reflections with $I \geqslant 3\sigma(I)$ were used in the structure determination. Correction for LP factors and for absorption based on ψ scan technique were applied. The two nickel atoms were located by the Patterson technique and the other non-hydrogen atoms by successive Fourier syntheses. Hydrogen atoms were inserted at calculated positions. All positional parameters and temperature factors for non-hydrogen atoms were refined anisotropically to a final R of 0.047. All calculations were performed on an Eclipse S/140 computer using the SHELXTL program system. The crystal data and details are summarized in Table 1. Selected bond lengths and angles are given in Tables 2 and 3. Final atomic coordinates, thermal parameters and tables of observed and calculated structure factors have been deposited with the Editor as supplementary data.

Table 1. Crystallographic data for [Ni(oxae)Ni(phen)$_2$](ClO$_4$)$_2$·3H$_2$O

Molecular formula	$C_{30}H_{34}N_8O_{13}Cl_2Ni_2$
Formula weight	903.05
Crystal system	Monoclinic
Crystal size (mm)	0.44 × 0.36 × 0.56
Space group	C_c
a (Å)	20.194(4)
b (Å)	12.319(4)
c (Å)	18.204(4)
β (°)	124.92(1)
V (Å^3)	3713.5(6)
Z	4
D_{calc} (g cm^{-3})	1.62
F(000)	1856
μ (Mo K_α) (cm^{-1})	12.3
Radiation (λ, Å)	0.71069
T (K)	293
Diffractometer	Nicolet R3M/E
2θ range (°)	3–54
No. of reflection measured	4467
No. of reflection used	4366 [$I \geqslant 3\sigma(I)$]
R	0.047
R_w	0.052

RESULTS AND DISCUSSION

Elemental analyses indicated that the reaction of Ni(oxae) with Ni(ClO$_4$)$_2$·6H$_2$O and phen yielded the binuclear complex [Ni(oxae)Ni(phen)$_2$](ClO$_4$)$_2$·

Table 2. Selected bond lengths for [Ni(oxae)Ni(phen)$_2$](ClO$_4$)$_2$·3H$_2$O (Å)

Ni(1)—N(5)	1.839(8)	Ni(1)—N(6)	1.854(7)
Ni(1)—N(7)	1.910(14)	Ni(1)—N(8)	1.935(17)
Ni(2)—N(1)	2.071(6)	Ni(2)—N(2)	2.015(8)
Ni(2)—N(3)	2.065(6)	Ni(2)—N(4)	2.099(8)
Ni(2)—O(1)	2.074(6)	Ni(2)—O(2)	2.118(6)
N(1)—C(11)	1.330(15)	N(1)—C(15)	1.356(11)
N(2)—C(21)	1.318(16)	N(2)—C(25)	1.326(8)
N(3)—C(31)	1.328(14)	N(3)—C(35)	1.351(12)
N(4)—C(41)	1.361(13)	N(4)—C(45)	1.391(9)
N(5)—C(51)	1.413(15)	N(5)—C(72)	1.311(12)
N(6)—C(61)	1.468(15)	N(6)—C(71)	1.316(12)
N(7)—C(62)	1.361(21)	N(8)—C(52)	1.567(19)
O(1)—C(71)	1.316(13)	O(2)—C(72)	1.265(11)
C(11)—C(12)	1.431(12)	C(12)—C(13)	1.416(17)

Table 3. Selected bond angles for $[Ni(oxae)Ni(phen)_2](ClO_4)_2 \cdot 3H_2O$ (°)

N(5)—Ni(1)—N(6)	86.0(3)	N(5)—Ni(1)—N(7)	171.5(4)
N(6)—Ni(1)—N(7)	85.9(5)	N(5)—Ni(1)—N(8)	85.9(5)
N(6)—Ni(1)—N(8)	171.8(5)	N(7)—Ni(1)—N(8)	102.2(6)
N(1)—Ni(2)—N(2)	77.9(3)	N(1)—Ni(2)—N(3)	172.5(3)
N(2)—Ni(2)—N(3)	95.3(3)	N(1)—Ni(2)—N(4)	95.5(3)
N(2)—Ni(2)—N(4)	97.1(3)	N(3)—Ni(2)—N(4)	82.2(3)
N(1)—Ni(2)—O(1)	91.3(2)	N(2)—Ni(2)—O(1)	91.3(3)
N(3)—Ni(2)—O(1)	92.0(3)	N(4)—Ni(2)—O(1)	170.1(2)
N(1)—Ni(2)—O(2)	98.4(3)	N(2)—Ni(2)—O(2)	171.8(2)
N(3)—Ni(2)—O(2)	88.8(3)	N(4)—Ni(2)—O(2)	90.5(3)
O(1)—Ni(2)—O(2)	81.3(2)	Ni(2)—N(1)—C(11)	129.8(6)
Ni(2)—N(1)—C(15)	115.6(6)	C(11)—N(1)—C(15)	114.4(7)
Ni(2)—N(2)—C(21)	136.8(5)	Ni(2)—N(2)—C(25)	115.9(7)
C(21)—N(2)—C(25)	106.8(8)	Ni(2)—N(3)—C(31)	129.3(6)
Ni(2)—N(3)—C(35)	110.7(6)	C(31)—N(3)—C(35)	119.8(7)
Ni(2)—N(4)—C(41)	120.5(5)	Ni(2)—N(4)—C(45)	110.0(6)
C(41)—N(4)—C(45)	129.5(8)	Ni(1)—N(5)—C(51)	118.8(6)
Ni(1)—N(5)—C(72)	113.7(8)	C(51)—N(5)—C(72)	127.1(9)
Ni(1)—N(6)—C(61)	115.2(5)	Ni(1)—N(6)—C(71)	113.4(9)
C(61)—N(6)—C(71)	131.4(9)	Ni(1)—N(7)—C(62)	109.8(8)
Ni(1)—N(8)—C(52)	106.7(9)	Ni(2)—O(1)—C(71)	109.4(8)
Ni(2)—O(2)—C(72)	110.7(7)	N(1)—C(11)—C(12)	122.5(10)

H_2O. The molar conductance value of the complex falls in the expected range for 1 : 2 electrolytes.[11] It is noted that the C=O (carbonyl) stretching vibration at 1604 cm^{-1} for Ni(oxae) and the —N=C— stretching vibration at 1500 cm^{-1} for the terminal ligand phen were shifted to higher frequencies in the binuclear complex. The shifts in IR suggest that a nickel(II) ion is coordinated to both the carbonyl oxygen atoms of Ni(oxae) and the nitrogen atoms of phen. In addition, the $—NH_2$ vibration at 3175 cm^{-1} for Ni(oxae) and the ClO_4^- group vibration at 1100 cm^{-1} were present in the complex.

The structure of the title compound consists of one complex cation, $[Ni(oxae)Ni(phen)_2]^{2+}$, two ClO_4^- anions and three water molecules (Fig. 1). In

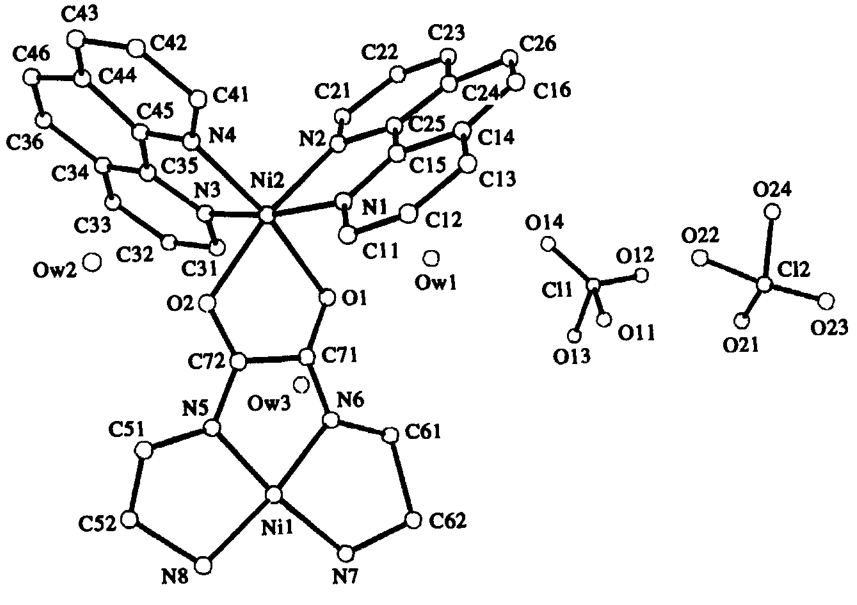

Fig. 1. The asymmetric unit in the structure of $[Ni(oxae)Ni(phen)_2](ClO_4)_2 \cdot 3H_2O$.

the cation two nickel atoms are bridged by a deprotonated oxamido group to form a binuclear complex. On the oxae side, the Ni(1) atom is four coordinate with a square-planar environment and lies at a distance of 0.006 Å out of the plane of the four nitrogen atoms [N(5), N(6), N(7) and N(8)]. The bond lengths of Ni(1)—N vary from 1.839 to 1.935 Å. On the terminal ligand phen side, the coordination polyhedron around the Ni(2) atom is better described as a distorted octahedron. The Ni(2) atom is surrounded by two oxygen atoms [O(1) and O(2)] from the oxae and four nitrogen atoms [N(1), N(2), N(3) and N(4)] from two phen molecules (Fig. 2). In the distorted octahedral environment, the equatorial plane is made up of four atoms [O(1), O(2), N(2) and N(4)] while N(1) and N(3) atoms occupy the two apical positions with Ni(2)—N(1) and Ni(2)—N(3) bond lengths of 2.071 and 2.065 Å, respectively. The Ni(2) atom is pulled out of this plane toward N(1) by 0.010 Å. The bond lengths of Ni(2)—O are 2.074 and 2.118 Å with the average value of 2.096 Å. The bond lengths of Ni(2)—N vary from 2.015 to 2.099 Å with the average value of 2.062 Å. The bond angles in the equatorial plane vary from 81.3 to 97.1° about the theoretical 90° value. The angles at Ni(2) atom involving the apical position N(1) are in the range of 77.9–98.4° while the angles at Ni(2) atom involving another apical position N(3) are in the range of 82.2–95.3°. The distance between two nickel atoms separated by oxamido-bridged group in the binuclear complex is 5.267 Å while Ni(1) and Ni(2) atoms are displaced 0.010 and 0.055 Å, respectively, from the plane of O(1), O(2), C(71), C(72), N(5) and N(6) (maximum deviation 0.109 Å). The Ni(1) and Ni(2) atoms are attached below and above this plane, respectively.

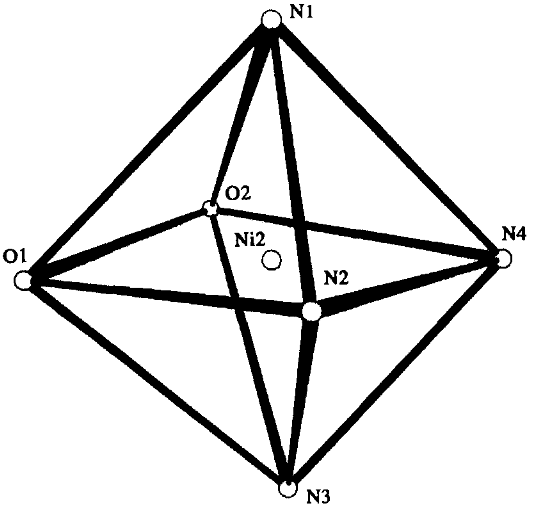

Fig. 2. The coordination polyhedron about the octahedral nickel centre.

Acknowledgement—This work is supported by the National Natural Science Foundation of China.

REFERENCES

1. Y. Journaux, J. Sletten and O. Kahn, *Inorg. Chem.* 1985, **24**, 4063
2. F. Lloret, M. Julve, R. Ruiz, Y. Journaux, K. Nakatani, O. Kahn and J. Sletten, *Inorg. Chem.* 1993, **32**, 27.
3. S. Gehring, P. Fleischhauer, H. Paulus and W. Haase, *Inorg. Chem.* 1993, **32**, 54.
4. J. R. Lancaster (ed.), *The Bioinorganic Chemistry of Nickel.* VCH, New York (1988).
5. R. M. Buchanan, M. S. Mashuta, K. J. Oberhausen, F. F. Richardson, Q. Li and D. N. Hendrickson, *J. Am. Chem. Soc.* 1989, **111**, 4497.
6. H. Ojima and K. Nonoyama, *Z. Anorg. Allg. Chem.* 1972, **389**, 75.
7. Y. Journaux, J. Sletten and O. Kahn, *Inorg. Chem.* 1986, **25**, 439.
8. Z-M. Liu, Z-H. Jiang, D-Z. Liao, G-L. Wang, X-K. Yao and H-G. Wang, *Acta Chim. Sinica* 1991, **49**, 981.
9. H. Okawa, Y. Kawahara, M. Mikuriya and S. Kida, *Bull. Chem. Soc. Jpn.* 1980, **53**, 549.
10. H. Ojima and K. Yamada, *Nippon Kagaku Zasshi* 1968, **89**, 490.
11. W. J. Geary, *Coord. Chem. Rev.* 1971, **7**, 81.