Inorganica Chimica Acta, 39 (1980) 211–216

X-Ray Studies on Metal Macrocyclic Complexes: the Crystal and Molecular Structure of Di-isothiocyanato(2,3:11,12)-dibenzo-1,13-dioxa-5,9-diaza-2,11-cyclopentadecadieneNi(II)

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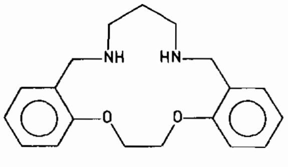
Received August 4, 1979

Crystals of $NiL(NCS)_2$ (L = 2,3:11,12-dibenzo-1,13-dioxa-5,9-diaza-2,11-cyclopentadecadiene), obtained by adding the ligand in buthanol to a methanolic solution of KSCN and $Ni(ClO_4)_2\cdot H_2O$, are triclinic ($P\bar{1}$), with cell dimensions: a = *9.836(2),* b = *18.825(7),* c = *8.003(4) Å,* α = *81.57(5),* β = *64.99(3),* γ = *55.89(1)°, Z = 2. The structure has been determined from diffractometer data by Patterson and Fourier methods and refined by full-matrix least-squares to an R value of 3.78%. The complex has distorted octahedral coordination with the thiocyanate groups in the apical positions and the equatorial plane occupied by the nitrogen and oxygen atoms of the macrocycle.*

Introduction

Macrocyclic ligands represent a class of compounds of relevant interest in coordination chemistry from different points of view ranging from synthetic to structural and analytical aspects. In particular the macrocycles with mixed oxygen–nitrogen donor atoms can be of interest for the capability to complex transition metals.

The macrocyclic ligand



was considered in a program of study on its structural and potential analytical properties in transition metal chemistry. Recently [1, 2] (Ni, Co, Cu) L complexes with different anions were synthesized and characterized on the basis of their spectral properties.

In the synthesis of the Ni-thiocyanate complex with the L ligand two kinds of crystals were obtained, both giving analytical data in agreement with the formula $NiL(NCS)_2$, but showing different colours (light blue and dark blue) and different morphology (tablets and prisms respectively). The only observed difference is related to the infrared behaviour of the thiocyanate group, which shows a different splitting of the band corresponding to the ν(CN) mode [2].

To elucidate the situation of the anion in the coordination, the X-ray analysis was undertaken. In the present paper only the crystal and molecular structure of the light blue phase is described, as the dark blue crystals were not suitable for single crystal X-ray analysis.

Experimental

The complex was prepared by adding KSCN (2×10^{-3} mol) to a methanol solution of $Ni(ClO_4)_2\cdot H_2O$ (10^{-3} mol). A white powder precipitated and was filtered off. The solution of the ligand in butanol (molar ratio 1:1) was added and heated under reflux for few minutes. Upon slow cooling, two kinds of crystals, dark blue prisms and light blue tablets, were obtained.

The electronic spectrum of the complex was run on a Shimadsu MPS 50L using the mull transmission technique.

A tablet of the light blue phase of $NiL(NCS)_2$ with dimensions 0.048, 0.119, 0.807 mm was chosen for collection of all X-ray data. Cell parameters, obtained by rotation and Weissenberg photographs, were successively refined by least squares using θ values of 15 high-angle reflections accurately measured on a Siemens AED single crystal computer controlled diffractometer, using Cu-Kα radiation. Crystal data are: $C_{21}H_{24}N_4NiO_2S_2$, M = 487.3, triclinic, a = 9.836(2), b = 18.825(7), c = 8.003(4) Å,

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TABLE I. Fractional Atomic Coordinates × 10^4 with e.s.d.'s in Parentheses.

Atomx	x	y	z	Atom	x	y	z
Ni	892(1)	2561(0)	2505(1)	C(19)	−588(5)	1565(2)	4584(5)
S(1)	−3196(2)	4781(1)	7593(2)	C(20)	−1799(5)	3948(2)	6034(5)
S(2)	6146(1)	705(1)	−2219(2)	C(21)	3987(5)	1358(2)	−980(5)
O(1)	−1407(3)	2825(2)	2155(4)	H(N3)	4008(61)	2040(30)	1416(66)
O(2)	140(3)	3743(2)	1298(4)	H(N4)	2038(61)	1088(29)	2947(67)
N(1)	−819(5)	3343(2)	4942(5)	H(C2)	−992(61)	377(30)	3829(64)
N(2)	2488(4)	1841(2)	−82(4)	H(C3)	−1943(59)	243(28)	1392(64)
N(3)	3098(4)	2470(2)	2441(4)	H(C4)	−2446(61)	1356(30)	−601(65)
N(4)	1152(4)	1497(2)	3792(4)	H(C5)	−2181(62)	2560(29)	−326(66)
C(1)	−1106(4)	1516(2)	3094(5)	H(1C7)	−3050(62)	3736(31)	949(66)
C(2)	−1263(5)	843(3)	2935(7)	H(2C7)	−630(61)	3219(30)	−533(65)
C(3)	−1747(6)	774(3)	1603(8)	H(1C8)	−2741(64)	4465(31)	2770(67)
C(4)	−2047(6)	1378(4)	376(7)	H(2C8)	−1860(61)	4550(30)	522(64)
C(5)	−1907(5)	2061(3)	510(7)	H(C10)	376(61)	4166(30)	−2056(67)
C(6)	−1480(4)	2138(3)	1873(6)	H(C11)	2909(61)	4116(29)	−4688(64)
C(7)	−1767(5)	3458(3)	824(7)	H(C12)	5457(62)	3644(30)	−3977(65)
C(8)	−1633(5)	4121(3)	1332(7)	H(C13)	5526(65)	3320(30)	−1191(66)
C(9)	1518(5)	3749(2)	−220(5)	H(1C15)	3842(64)	3301(30)	2178(68)
C(10)	1461(6)	3971(3)	−1911(6)	H(2C15)	1956(62)	3734(29)	3003(69)
C(11)	2928(7)	3948(3)	−3346(6)	H(1C16)	4385(63)	2145(30)	4092(67)
C(12)	4410(6)	3707(3)	−3046(6)	H(2C16)	2441(62)	2601(30)	5187(66)
C(13)	4429(5)	3497(3)	−1321(7)	H(1C17)	4506(62)	899(30)	3457(67)
C(14)	2998(5)	3512(2)	132(5)	H(2C17)	4042(62)	1105(30)	5268(64)
C(15)	2986(5)	3293(2)	2019(6)	H(1C18)	948(63)	1798(31)	6164(67)
C(16)	3395(5)	2165(3)	4158(6)	H(2C18)	2008(64)	828(31)	5757(65)
C(17)	3578(6)	1305(3)	4502(6)	H(1C19)	−1420(60)	2125(29)	5311(67)
C(18)	1845(6)	1338(3)	5220(6)	H(2C19)	−429(61)	1051(29)	5374(67)

α = 81.57(5), β = 64.99(3), γ = 55.89(1)°, V = 1104(1) Å^3, d_{meas} = 1.46 g cm^{-3}, Z = 2, d_{calcd} = 1.47 g cm^{-3}, λ(Cu-Kα) = 1.54178 Å, μ(Cu-Kα) = 32.0 cm^{-1}. Space group $P\bar{1}$ (from structural analysis)*.

A total of 3295 reflections with $\theta \leqslant 60°$ were measured on the same Siemens diffractometer using CuKα radiation and the ω–2θ scan technique. 2427 of these, having $I \geqslant 2\sigma(I)$ were considered as observed and used in the structural analysis. The intensity data were corrected for Lorentz and polarization effects but no absorption correction was applied because of the low μR value. The absolute scale factor was determined first by Wilson's method and successively as a variable parameter in the least-squares refinement.

The structure was solved by Patterson and Fourier methods and the refinement was carried out by least-squares full-matrix cycles using the SHELX system [3] of computer programs with initially isotropic and then anisotropic thermal parameters.

The hydrogen atoms were located in a ΔF map and refined isotropically. The final R index was 0.0378. The atomic scattering factors used were taken from International Tables [4]. Unit weights were used in the first stage of the refinement, then a weighting factor $w = k/((F_o)^2 + gF_o^2)$ (k = 0.4825, g = 0.0034) was introduced.

The atomic fractional coordinates and thermal parameters are listed in Tables I and II. A list of observed and calculated structure factors is available from the authors on request.

All the calculations were performed on the CYBER 76 computer of Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, with financial support of the University of Parma.

Results and Discussion

Table III provides bond distances and angles in the complex, Fig. 1 shows the diagram of the molecule and Fig. 2 the molecular arrangement. The structure consists of monomeric units in which Ni(II) is coordinated by the two nitrogen and two oxygen atoms of the macrocycle and by the nitrogen atoms of thiocyanate ions. Coordination about the nickel

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*The reduced cell can be obtained by applying the transformation matrix: $\bar{1}$ 0 0 / $\bar{1}$ 1 0 / 0 0 1 (a = 9.836, b = 15.603, c = 8.003 A, α = 95.14, β = 115.01, γ = 92.65°).

TABLE II. Thermal Parameters, Anisotropic* ($\times 10^3$) for Ni, S, O, N, C, Isotropic ($\times 10^2$) for H Atoms.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}		U
Ni	38.4(3)	36.2(4)	39.1(4)	1.7(3)	−13.3(3)	−13.4(3)	H(N3)	5(1)
S(1)	71.8(7)	48.2(6)	52.6(7)	−8.9(5)	−19.4(5)	−10.5(5)	H(N4)	5(1)
S(2)	46.0(6)	77.9(8)	103.8(1.0)	−32.4(8)	−5.7(6)	−20.4(6)	H(C2)	8(1)
O(1)	43(1)	42(1)	61(2)	16(1)	−23(1)	−19(1)	H(C3)	9(1)
O(2)	45(1)	43(1)	68(2)	13(1)	−29(1)	−21(1)	H(C4)	7(1)
N(1)	60(2)	52(2)	50(2)	−7(2)	−12(2)	−18(2)	H(C5)	9(1)
N(2)	47(2)	46(2)	45(2)	−1(2)	−14(1)	−19(1)	H(1C7)	6(1)
N(3)	48(2)	42(2)	44(2)	2(1)	−22(1)	−18(1)	H(2C7)	9(1)
N(4)	46(2)	42(2)	40(2)	5(1)	−17(1)	−17(1)	H(1C8)	11(1)
C(1)	38(2)	44(2)	53(2)	3(2)	−9(2)	−18(2)	H(2C8)	6(1)
C(2)	50(2)	48(2)	73(3)	2(2)	−14(2)	−23(2)	H(C10)	6(1)
C(3)	52(3)	69(3)	86(4)	−10(3)	−15(2)	−30(2)	H(C11)	10(1)
C(4)	55(3)	92(4)	75(3)	−13(3)	−17(2)	−42(3)	H(C12)	9(1)
C(5)	44(2)	71(3)	60(3)	5(2)	−18(2)	−25(2)	H(C13)	8(1)
C(6)	37(2)	54(2)	51(2)	7(2)	−15(2)	−23(2)	H(1C15)	4(1)
C(7)	51(2)	58(3)	86(3)	31(2)	−34(2)	−27(2)	H(2C15)	6(1)
C(8)	57(3)	45(2)	102(4)	26(3)	−50(3)	−23(2)	H(1C16)	4(1)
C(9)	55(2)	39(2)	54(2)	4(2)	−24(2)	−25(2)	H(2C16)	5(1)
C(10)	71(3)	50(2)	60(3)	10(2)	−33(2)	−32(2)	H(1C17)	7(1)
C(11)	99(3)	55(2)	68(3)	13(2)	−34(2)	−43(2)	H(2C17)	7(1)
C(12)	68(3)	62(3)	68(3)	13(2)	−20(2)	−35(2)	H(1C18)	6(1)
C(13)	57(2)	52(2)	74(3)	10(2)	−28(2)	−29(2)	H(2C18)	5(1)
C(14)	53(2)	39(2)	54(2)	5(2)	−24(2)	−24(2)	H(1C19)	6(1)
C(15)	57(2)	47(2)	61(2)	3(2)	−31(2)	−28(2)	H(2C19)	7(1)
C(16)	62(2)	61(3)	57(3)	6(2)	−37(2)	−28(2)		
C(17)	63(3)	60(3)	61(3)	18(2)	−39(2)	−24(2)		
C(18)	71(3)	58(2)	50(2)	16(2)	−30(2)	−31(2)		
C(19)	55(2)	48(2)	47(2)	11(2)	−18(2)	−26(2)		
C(20)	44(2)	46(2)	34(2)	7(2)	−15(2)	−18(2)		
C(21)	52(2)	49(2)	39(2)	0(2)	−17(2)	−28(2)		

*The anisotropic temperature factors are in the form: $\exp[-2\pi^2(h^2a^*U_{11} + \ldots 2hka^*b^*U_{12})]$. The isotropic ones are in the form: $\exp[-8\pi^2 U(\sin\theta/\lambda)^2]$.

TABLE III. Bond Distances (A) and Angles (°) with e.s.d. s in Parentheses.

Ni–O(1)	2.162(4)	C(1)–C(2)	1.389(8)
Ni–O(2)	2.136(3)	C(1)–C(6)	1.395(6)
Ni–N(1)	2.023(4)	C(1)–C(19)	1.513(7)
Ni–N(2)	2.068(3)	C(2)–C(3)	1.385(10)
Ni–N(3)	2.057(5)	C(3)–C(4)	1.373(8)
Ni–N(4)	2.045(4)	C(4)–C(5)	1.391(11)
S(1)–C(20)	1.616(4)	C(5)–C(6)	1.375(9)
S(2)–C(21)	1.629(3)	C(7)–C(8)	1.456(10)
O(1)–C(6)	1.390(8)	C(9)–C(10)	1.372(6)
O(1)–C(7)	1.467(6)	C(9)–C(14)	1.407(7)
O(2)–C(9)	1.391(5)	C(10)–C(11)	1.395(7)
O(2)–C(8)	1.457(6)	C(11)–C(12)	1.382(10)
N(1)–C(20)	1.157(5)	C(12)–C(13)	1.384(7)
N(2)–C(21)	1.144(4)	C(13)–C(14)	1.384(6)
N(3)–C(15)	1.488(6)	C(14)–C(15)	1.503(6)
N(3)–C(16)	1.491(6)	C(16)–C(17)	1.521(8)
N(4)–C(18)	1.480(7)	C(17)–C(18)	1.518(9)
N(4)–C(19)	1.486(6)		

(continued overleaf)

TABLE III. *(continued)*

N(3)–Ni–N(4)	99.4(2)	C(6)–C(1)–C(19)	122.5(4)
N(2)–Ni–N(4)	91.5(1)	C(2)–C(1)–C(19)	119.9(4)
N(2)–Ni–N(3)	89.0(2)	C(2)–C(1)–C(6)	117.7(4)
N(1)–Ni–N(4)	92.0(1)	C(1)–C(2)–C(3)	122.0(5)
N(1)–Ni–N(3)	93.9(2)	C(2)–C(3)–C(4)	119.2(6)
N(1)–Ni–N(2)	175.0(2)	C(3)–C(4)–C(5)	119.9(5)
O(2)–Ni–N(4)	169.8(2)	C(4)–C(5)–C(6)	120.3(5)
O(2)–Ni–N(3)	90.3(2)	C(1)–C(6)–C(5)	120.8(5)
O(2)–Ni–N(2)	91.7(1)	O(1)–C(6)–C(5)	123.7(4)
O(2)–Ni–N(1)	84.3(1)	O(1)–C(6)–C(1)	115.5(4)
O(1)–Ni–N(4)	91.4(2)	O(1)–C(7)–C(8)	106.4(4)
O(1)–Ni–N(3)	168.6(1)	O(2)–C(8)–C(7)	110.7(4)
O(1)–Ni–N(2)	87.3(1)	O(2)–C(9)–C(14)	113.8(3)
O(1)–Ni–N(1)	89.1(2)	O(2)–C(9)–C(10)	124.0(5)
O(1)–Ni–O(2)	79.1(1)	C(10)–C(9)–C(14)	122.2(4)
Ni–O(1)–C(7)	108.7(3)	C(9)–C(10)–C(11)	119.2(5)
Ni–O(1)–C(6)	119.1(3)	C(10)–C(11)–C(12)	119.8(4)
C(6)–O(1)–C(7)	114.2(4)	C(11)–C(12)–C(13)	120.0(5)
Ni–O(2)–C(9)	116.2(3)	C(12)–C(13)–C(14)	121.7(5)
Ni–O(2)–C(8)	108.5(3)	C(9)–C(14)–C(13)	117.1(4)
C(8)–O(2)–C(9)	122.0(4)	C(13)–C(14)–C(15)	122.5(5)
Ni–N(1)–C(20)	162.4(3)	C(9)–C(14)–C(15)	120.4(4)
Ni–N(2)–C(21)	138.2(4)	N(3)–C(15)–C(14)	112.0(3)
Ni–N(3)–C(16)	112.2(3)	N(3)–C(16)–C(17)	111.4(4)
Ni–N(3)–C(15)	111.0(3)	C(16)–C(17)–C(18)	116.1(4)
C(15)–N(3)–C(16)	112.9(4)	N(4)–C(18)–C(17)	113.3(4)
Ni–N(4)–C(19)	110.3(3)	N(4)–C(19)–C(1)	112.3(3)
Ni–N(4)–C(18)	113.0(3)	S(1)–C(20)–N(1)	178.4(4)
C(18)–N(4)–C(19)	111.2(3)	S(2)–C(21)–N(2)	176.7(5)
C(2)–H(C2)	1.03(5)	C(15)–H(1C15)	0.91(8)
C(3)–H(C3)	1.16(7)	C(15)–H(2C15)	0.95(4)
C(4)–H(C4)	1.03(7)	C(16)–H(1C16)	0.93(7)
C(5)–H(C5)	1.04(5)	C(16)–H(2C16)	0.96(4)
C(7)–H(1C7)	1.02(6)	C(17)–H(1C17)	0.94(4)
C(7)–H(2C7)	1.09(4)	C(17)–H(2C17)	0.84(6)
C(8)–H(1C8)	1.14(4)	C(18)–H(1C18)	0.93(4)
C(8)–H(2C8)	0.94(5)	C(18)–H(2C18)	0.94(5)
C(10)–H(C10)	0.97(6)	C(19)–H(1C19)	0.96(4)
C(11)–H(C11)	1.08(5)	C(19)–H(2C19)	1.05(5)
C(12)–H(C12)	0.93(5)	N(3)–H(N3)	0.94(4)
C(13)–H(C13)	0.98(7)	N(4)–H(N4)	0.84(4)

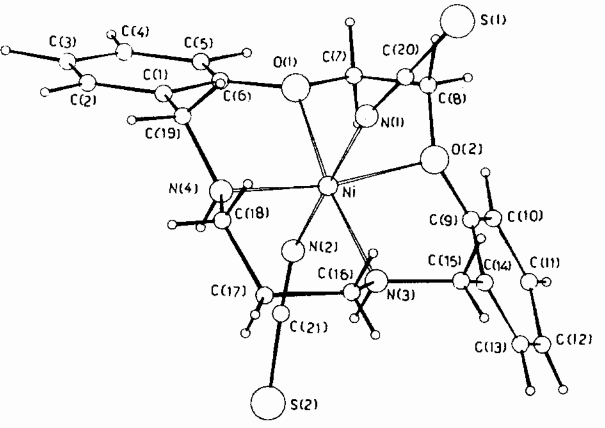

Fig. 1. Diagrammatic view of the molecule.

ion can be described as distorted octahedral. This type of coordination is in agreement with the spectral behaviour of the complex in the solid state: namely in the visible region the maxima at 980, 590, 374 nm, attributable to the $^3T_{2g}(F) \leftarrow {}^3A_{2g}$, $^3T_{1g}(F) \leftarrow {}^3A_{2g}$, $^3T_{1g}(P) \leftarrow {}^3A_{2g}$ transitions are observed.

The thiocyanate groups are in the apical positions and the equatorial plane is occupied by the nitrogen and the oxygen atoms of the macrocycle. The mean plane through N(3)N(4)O(1)O(2) is $0.01777X + 0.43478Y + 0.90036Z = 0.33936$ (X, Y and Z are orthogonal coordinates (Å) obtained from the fractional ones by applying the matrix $\| a, b\cos\gamma, c\cos\beta | 0, b\sin\gamma, -c\sin\beta\cos\alpha^* | 0,0, c\sin\beta\sin\alpha^* \|$) and the displacements of the atoms from this plane, N(4) −0.06, N(3) 0.06, O(1) 0.07, O(2) −0.07 Å show a significant tetrahedral distortion. The Ni atom, lying

TABLE IV. Puckering Parameters [5] in the Chelating Rings.

Ring	q_2/Å	q_3/Å	ϕ_2/°	Q/Å	Conformation
NiO(1)C(6)C(1)C(19)N(4)	0.707	−0.091	70.4	0.710	boat
NiO(2)C(9)C(14)C(15)N(3)	0.784	0.014	240.2	0.780	boat
NiN(4)C(18)C(17)C(16)N(3)	0.132	−0.572	12.3	0.590	chair
NiO(2)C(8)C(7)O(1)	0.459	–	275.1	–	twist (C_2)

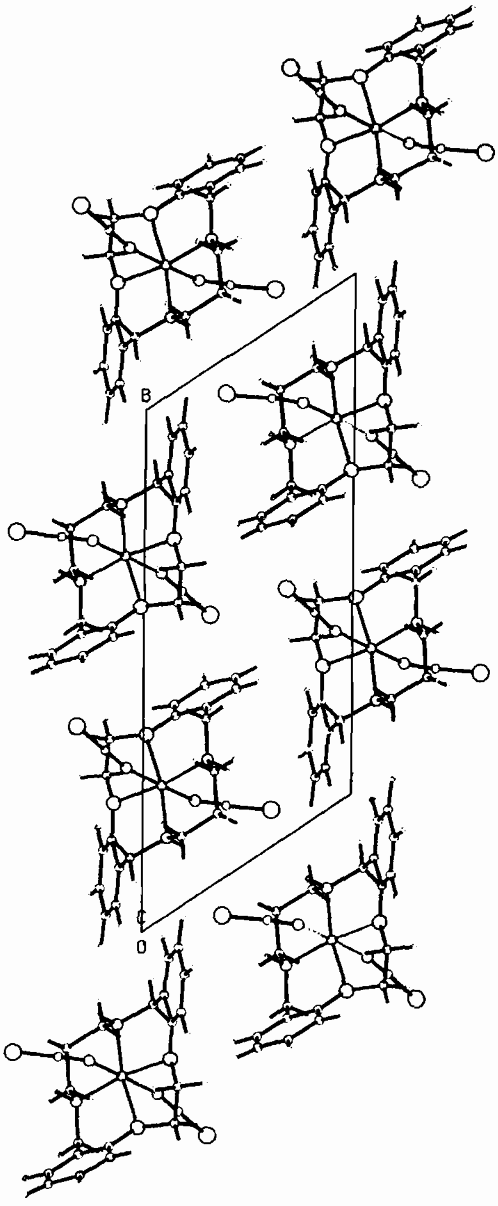

Fig. 2. Molecular Packing.

only 0.003 Å out of that plane, can be considered in the centre of the tetrahedron.

In coordinating, the macrocycle forms one five-membered NiO(2)C(8)C(7)O(1) and three six-membered, NiO(1)C(6)C(1)C(19)N(4), NiO(2)C(9)-C(14)C(15)N(3), NiN(4)C(18)C(17)C(16)N(3) chelate rings. The puckering [5] parameters quoted in Table IV indicate a boat conformation for the two six-membered rings involving nitrogen and oxygen as donor atoms and a chair conformation for NiN(4)-C(18)C(17)C(16)N(3). The puckering parameters of the five-membered chelate ring suggest for it a C_2 twist conformation. The Ni, O(1), O(2) are roughly coplanar, while C(7) and C(8) are displaced by 0.357 and −0.301 Å respectively from the mean plane through the ring.

The Ni–N distances involving the amine nitrogens (Ni–N(3) 2.057(5), Ni–N(4) 2.045(4)) Å are shorter than usual for Ni(II) octahedral amine complexes (*e.g.* 2.102 Å on $Ni(OPDA)_4Cl_2(OPDA)_2$ [6], but in good agreement with those found in 14-membered macrocycle-Ni complex, $Ni(C_{20}H_{22}N_2O_4)I_2$ [7] and in diisothiocyanato(2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene)Ni(II) [8]. On the contrary, the Ni–O distances (Ni–O(1) 2.162(4), Ni–O(2) 2.135(4) Å) are longer than the sum of Pauling's covalent radii, 2.05 Å (octahedral Ni(II): 1.36 Å, O: 0.66 Å) [9]. The differences from the expected values can be ascribed to the constraint of the macrocycle in coordinating.

In Table V main torsion angles in the ligand are quoted. The conformation of the O–C–C–O chain can be described as *anti–gauche–eclipsed*, although the torsion angle around O(2)–C(8) [97.6(5)°] strongly deviates from the theoretical value of 120° required for an *eclipsed* conformation. In the N–C–C–C–N chain, the conformation is *anti–gauche–gauche–anti*. In the diprotonated uncomplexed ligand [10], the conformation about the O–C–C–O chain is *anti–gauche–anti* and about the N–C–C–C–N chain is *gauche–gauche–anti–anti*. The tetrahedral distortion of the N_2O_2 donor system in the diprotonated and uncoordinated ligand is more significant than in the coordinated ligand as indicated by the displacements from the mean plane, 0.353, −0.381 Å for oxygens, −0.413, 0.441 Å for nitrogen atoms. The value of dihedral angle between the two benzene rings, 61.5°, indicates a larger folding of the ligand in the complex with respect to the diprotonated uncomplexed molecule where the same angle is 48.8°.

TABLE V. Torsion Angles (°) in the Macrocyclic Ring.

C(7)O(1)C(6)C(1)	178.7(4)	C(16)N(3)C(15)C(14)	170.5(4)
O(1)C(6)C(1)C(19)	−2.1(6)	N(3)C(15)C(14)C(9)	68.7(5)
C(6)C(1)C(19)N(4)	−63.9(5)	C(15)C(14)C(9)O(2)	−0.8(6)
C(1)C(19)N(4)C(18)	−166.5(4)	C(14)C(9)O(2)C(8)	168.2(4)
C(19)N(4)C(18)C(17)	−177.3(4)	C(9)O(2)C(8)C(7)	97.6(5)
N(4)C(18)C(17)C(16)	72.9(6)	O(2)C(8)C(7)O(1)	57.9(5)
C(18)C(17)C(16)N(3)	−74.6(6)	C(8)C(7)O(1)C(6)	180.0(4)
C(17)C(16)N(3)C(15)	−177.7(4)		

TABLE VI. Weighted Least-squares Lines through the thiocyanate Groups with Displacements of Each Atoms.[a]

N(1)C(20)S(1)Ni*

$(X - 4.43608)/0.02576 = (Y - 5.73060)/0.72326 = (Z - 4.45635)/0.69009$[b]

N(1) 0.010(7) Å	C(20) 0.002(3) Å	S(1) 0.012(7) Å	Ni 0.573(2) Å

N(2)C(20)S(2)Ni*

$(X - 5.14175)/0.6095 = (Y - 2.12396)/-0.56794 = (Z + 0.78740)/-0.55313$[b]

N(2) 0.021(6) Å	C(21) 0.004(3) Å	S(2) 0.025(6) Å	Ni 1.441(2) Å

[a] The starred atoms are not included in the lines. [b] X, Y, Z are the orthogonal coordinates.

Both thiocyanate groups deviate significantly from linearity, the deviation in N(2)C(21)S(2) being larger, as can be seen from the values quoted in Table VI, where the analysis for the linearity of the two groups is made. It appears that the deviation is more significant for the N(2)C(21)S(2) group, which also is more bent with respect to the Ni–N bond. The different situation of the two groups is related to the different environment of the sulphur atoms of the two groups: S(2) makes a contact of 3.490(4) Å with N(4) atom of an adjacent molecule $\measuredangle$ (N(4)^i–H^i–S(2)) = 140°, H^i. . .S(2) = 2.80 Å ($i = 1 - x, \bar{y}, \bar{z}$), the shortest interatomic contact formed by S(1) involves a C(7) carbon atom of a molecule at (x, y, z + 1) (S. . .C 3.481(5) Å). This different situation of the thiocyanate groups can justify the splitting observed for the ν(C–N) bond in the IR spectrum (2090, 2060 cm^{-1}) [2].

The line through N(1), N(2) is nearly perpendicular to the N_2O_2 plane, the angle being 88.0°; the Ni atom is 0.089 Å off of this line.

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