Short Communication

NON-COVALENT INTERACTIONS IN THE CRYSTAL OF A NEW MACROCYCLIC Ag(I)-Ni(II) BINUCLEAR COMPLEX

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Abstract

A new binuclear complex, $[Ag(NiL)(C_2H_5OH)(NO_3)]\cdot C_2H_5OH$, was prepared by using [NiL] as a new "complex ligand" and was further structurally characterized. The Ag(I) and Ni(II) ions are bridged by the oxamido group from the macrocyclic ligand (L). The coordination environment of the Ag(I) ion is a distorted trigonal bipyramid, and the coordination geometry around the Ni(II) ion is slightly distorted square planar. In the crystal, unique intermolecular π···π interactions between a phenyl ring and three separate π-systems that are not aromatic were observed. The π···π interactions and C–H···O and O–H···O hydrogen bonds link the molecules to form a three-dimensional network.

Key words: π···π interaction, hydrogen bond, macrocyclic compound, silver(I)-nickel(II) complex

Introduction

Non-covalent interactions are currently attracting a lot of interest of research.[1-9] They are important for chemistry, biology and materials science.[1,4,10-20] Taking π···π interaction for an example, it contributes to self-assembly or molecular recognition processes and the packing of molecules incorporating aromatic groups in crystals,[1,4,10-13] plays a role in the binding and conformations of nucleic acids and proteins,[1,4,14] can enhance the electron transfer reactivity of copper protein pseudoazurin.[15] π···π interaction has also been used in the detection of polycyclic aromatic hydrocarbons.[10] It can also influence the conductivity of some molecular conductors,[17] the behavior of some liquid crystalline materials,[18,19] and the electronic and optical properties of some materials,[19,20] and etc. Oxamido group is a good bridge capable of linking metals to form polynuclear complexes and can mediate ferro- and antiferromagnetic coupling between metal centers.[21-26] Mono-metal complexes of macrocyclic oxamido ligands incorporating phenyl groups were first synthesized by Black et al.[27] Sites capable of being involved in metal-ligand coordination, π···π interaction and O–H···O and C–H···O hydrogen bonds are combined into a single molecule of this type of macrocyclic compounds. Therefore, they can be used as blocks to construct organic-inorganic hybrid supramolecular architectures, polynuclear complexes and etc. To continue our interest in macrocyclic complexes and non-covalent interactions,[22-25,28] herein we report a new Ag(I)-Ni(II) binuclear complex with a mononuclear complex of a macrocyclic oxamido Schiff base [NiL] (Chart 1) as a new "complex ligand". In the crystal of the binuclear complex, novel π···π interaction between a phenyl ring and three unclosed π-systems was observed. This π···π interaction and O–H···O and C–H···O hydrogen bonds are responsible for the packing of the molecules in the crystal.

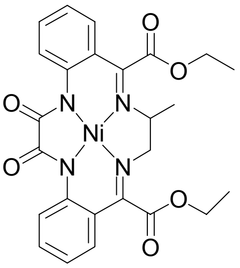

Chart 1. [NiL]

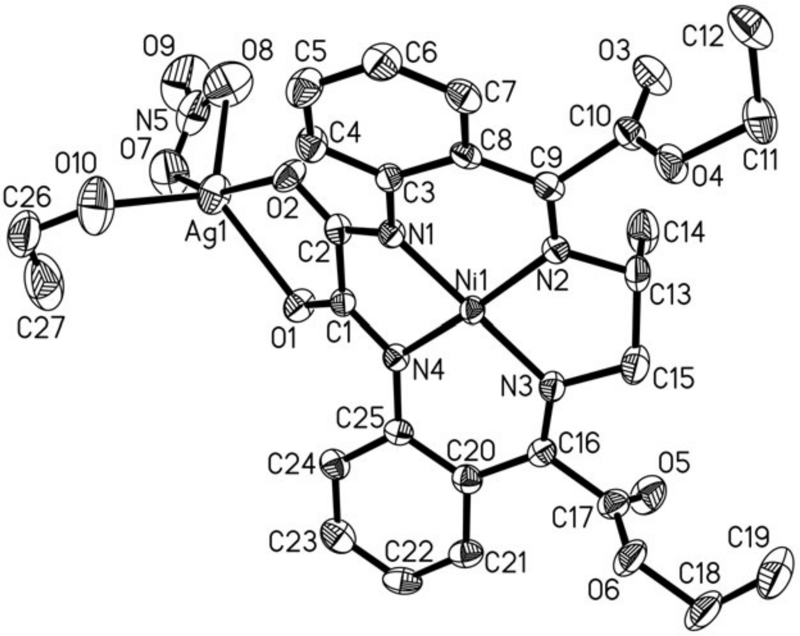

Figure 1. Molecular structure of the title complex.

Results and discussion

The binuclear complex (Figure 1) contains a less reported five-coordinated Ag(I), the new precursor complex [NiL], a chelating ligand NO_3^- and an ethanol molecule ligand. Another ethanol molecule is captured in the crystal lattice. The oxamido group from the macrocyclic ligand L bridges the Ag(I) and Ni(II). The Ni(II) center assumes a very slightly distorted square-planar environment, with two deprotonated oxamido N-atoms (N(1) and N(4)) and two imino N-atoms (N(2) and N(3)) from the macrocyclic ligand as donors. The Ni-N bond lengths (Table 1) are in the range of 1.856~1.875 Å. The deviations of the four donor atoms (N(1), N(2), N(3) and N(4)) from their mean plane are –0.078 Å, +0.077 Å, –0.076 Å and +0.076 Å, respectively. The distance between Ni(1) and the above plane is 0.062 Å. The two phenyl rings tilt slightly towards the same side of the above plane to give [NiL] a saddle-shaped conformation. The methyl connected to the chiral carbon atom (C(13)), the two ester carbonyls and the

Table 1. Selected bond lengths (Å) and angles (°) for the title complex.

Ag(1)-O(1)	2.465(4)	N(2)-C(9)	1.290(6)
Ag(1)-O(2)	2.352(3)	N(2)-C(13	1.502(6)
Ag(1)-O(7)	2.462(5)	N(3)-C(16)	1.279(6)
Ag(1)-O(8)	2.524(6)	N(3)-C(15)	1.486(6)
Ag(1)-O(10)	2.351(5)	N(4)-C(1)	1.352(6)
Ni(1)-N(1)	1.856(4)	N(4)-C(25)	1.384(6)
Ni(1)-N(2)	1.868(4)	C(1)-C(2)	1.536(7)
Ni(1)-N(3)	1.871(4)	C(8)-C(9)	1.459(7)
Ni(1)-N(4)	1.875(4)	C(9)-C(10)	1.521(7)
N(1)-C(2)	1.345(6)	C(16)-C(20)	1.451(7)
N(1)-C(3)	1.407(5)	C(16)-C(17)	1.521(7)
O(2)-Ag(1)-O(1)	69.53(11)	N(1)-Ni(1)-N(3)	178.97(17)
O(7)-Ag(1)-O(1)	117.89(17)	N(2)-Ni(1)-N(3)	86.88(18)
O(1)-Ag(1)-O(8)	130.34(17)	N(1)-Ni(1)-N(4)	86.51(17)
O(10)-Ag(1)-O(1)	11.58(17)	N(2)-Ni(1)-N(4)	171.43(16)
O(2)-Ag(1)-O(7)	159.28(18)	N(3)-Ni(1)-N(4)	94.06(17)
O(2)-Ag(1)-O(8)	110.73(18)	C(2)-N(1)-C(3)	122.6(4)
O(10)-Ag(1)-O(2)	92.12(17)	C(2)-N(1)-Ni(1)	111.1(3)
O(7)-Ag(1)-O(8)	49.07(19)	C(3)-N(1)-Ni(1)	126.1(3)
O(10)-Ag(1)-O(7)	101.81(19)	C(1)-N(4)-C(25)	122.5(4)
O(10)-Ag(1)-O(8)	118.0(2)	C(1)-N(4)-Ni(1)	109.9(3)
N(1)-Ni(1)-N(2)	92.69(17)	C(25)-N(4)-Ni(1)	127.1(3)

plane of the oxamido group all tilt towards the other side of the N_4 coordination plane. The dihedral angles between plane (N(1)~N(4)) and the two phenyl rings and the oxamido group are 23.5° (for C(3)~C(8)), 13.1° (for C(20)~C(25)) and 27.1° (for C(1), C(2), N(1), N(4), O(1) and O(2)), respectively. The Ag(I) ion resides in a coordination environment between square-pyramid and trigonal bipyramid. O(1), O(8) and O(10) are at the equatorial sites. The Ag(I) ion is only 0.050 Å out of the equatorial plane. O(2) and O(7) are at the axle positions with $\angle O2AgO7 = 159.3°$. The distortion of the coordination polyhedron from a normal trigonal bipyramid or a square-pyramid is mainly due to the constraint of the structures of the chelating oxamido group and the NO_3^- anion. The distances between the Ag(I) ion and the five ligand O-atoms are in the range of 2.351~2.524 Å. The Ag(I) and Ni(II) ions are 5.562 Å apart in the binuclear molecule.

The N(1)-C(2) and N(4)-C(1) bonds in the oxamido group have lengths of 1.345 and 1.352 Å, respectively, which are not only longer than the double bonds N(2)-C(9) (1.290 Å) and N(3)-C(16) (1.279 Å), but also significantly shorter than the single bonds N(2)-C(13) (1.502 Å) and N(3)-C(15) (1.486 Å). The sums of the three bond angles around N(1) and N(4) are very close to 360° (359.8 and 358.5°, respectively). The above values suggest that N(1) and N(4) are sp^2-hybridized and that the π-electrons on these two nitrogen atoms and the carbonyls are delocalized to form conjugated systems. The length of C(1)-C(2) (1.536 Å) reveals that the C-C bond in the oxamido group is a single bond. The above analyses imply that the oxamido group is divided into two separate π-systems, each of which includes a carbonyl and an amidate nitrogen atom. The two Schiff base groups have not been involved in conjugated systems, which are evidenced by the normal lengths of C-C and C-N single bonds around the C=N groups.

In the crystal, the complex ligand [NiL] of each binuclear molecule is close to the [NiL] ligand of a neighboring binuclear molecule (Figure 2). In such an arrangements, one phenyl ring of each molecule overlaps with the area including the four nitrogen donor atoms and the Ni(II) center of the other molecule. Some atom-to-atom distances between the overlapping segments are Ni(1)···C(21) 3.349, Ni(1)···C(22) 3.427, N(1)···C(21) 3.730, N(2)···C(22) 3.429, N(3)···C(23) 3.770, N(3)···C(24) 3.800 and N(4)···C(21) 3.876 Å (Symmetry transformation: -x,-y,-z). These data reveal that $\pi\cdots\pi$ interactions exist between the phenyl ring and the nickel atom and the three π-systems including N(1), N(2) and N(3) separately if 3.8 Å is taken as the maximum atom-to-atom contact for which π···π interactions are accepted.[1,7,11] In the case of the π···π interaction occurring between two zinc-porphyrin molecules, where the nonhydrogen atoms in the porphyrin ligand belong to a single conjugated π-system, a pyrrole ring of one molecule is directly above the cavity surrounded by the four nitrogen atoms of the other.[11] The geometry of the π···π stacking between the two [NiL] ligands is quite like that between two zinc-porphyrin molecules, but the former has a novel feature that the three nitrogen atoms involved in the π···π interaction belong to three separate unclosed π-systems as indicated in the above paragraph. Evidently, the geometry of the arrangement of such two neighboring binuclear molecules is controlled by the π···π interaction.

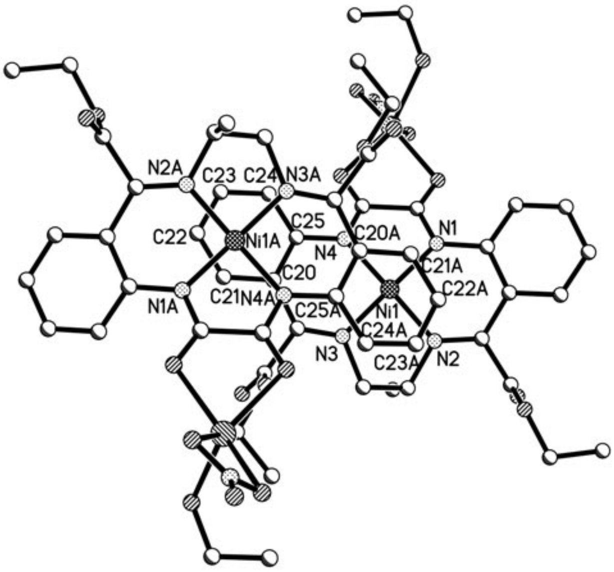

Figure 2. Plot showing the π···π interaction between two binuclear complex molecules.

Every binuclear molecule in the crystal provides O(1), O(5) and O(9) as acceptors and H atoms bonding with C(6), C(26) and C(19) as donors to form intermolecular C–H···O interactions with six adjacent binuclear molecules. The corresponding distances (Å) and angles (°) are: O(1)···H(6) 2.533, O(1)···C(6) 3.310, C(6)-H(6)···O(1) 141.3 (x,1+y,z); O(5)···H(26) 2.526, O(5)···C(26) 3.468, C(26)-H(26)···O(5) 164.0 (1+x,y,z); O(9)···H(19) 2.548, O(9)···C(19) 3.477, C(19)-H(19)···O(9) 162.9 (-x,1/2+y,1/2-z).[4] The HO group of the ethanol ligand as donor forms O–H···O hydrogen bond with O(7) of the seventh neighboring binuclear molecule with parameters of H···O 2.148 Å, O···O 2.998

Å and O–H···O 151.4° (1-x,1/2+y,1/2-z). It is noteworthy that the HO group of the solvent ethanol molecule in the crystal is not involved in any hydrogen bonding though there exist the weak C–H···O hydrogen bonds and that the HO group is a better proton donor than the C–H groups. This is against the experiential rule that the best proton donors and acceptors remaining form hydrogen bonds to one another.[29]

Conclusions

In conclusion, this article described the synthesis and crystal structure of a new Ag(I)-Ni(II) binuclear complex with a mononuclear complex of a macrocyclic oxamido Schiff base [NiL] as a new "complex ligand". A new type of π···π interaction that occurs between a phenyl ring and three separate π-systems that are not aromatic were observed in the crystal. Records on π···π interactions between phenyl rings and groups which are not aromatic are rare,[1,5,30] though those between aromatic groups are numerous. Obviously, the π···π interactions and the hydrogen bonds not only stabilize the crystal, but also provide energy, directionality and selectivity to organize the binuclear molecules in space to form a three-dimensional supramolecular architecture (Figure 3).

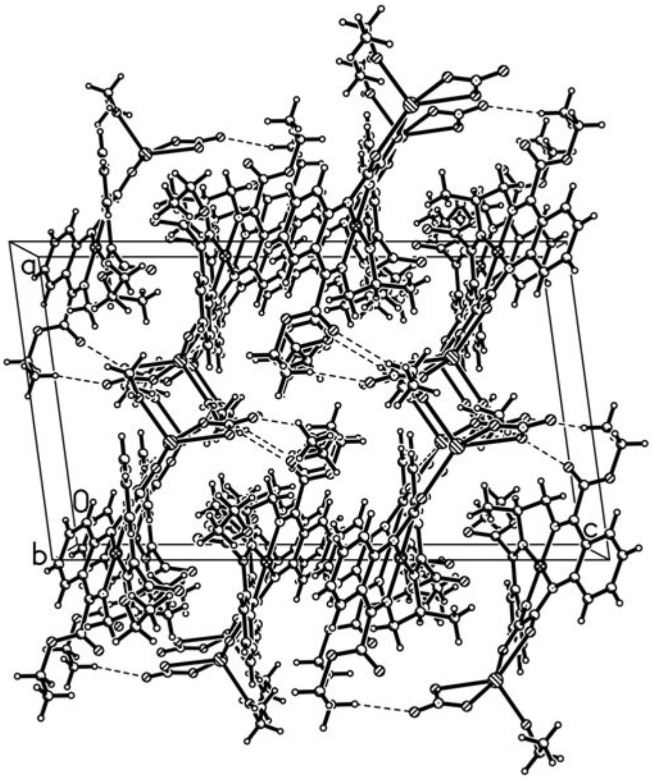

Figure 3. Packing diagram of the title complex in the crystal.

Experimental

General

All the starting materials were of analytical grade and were used as purchased without further purification. Analyses of C, H and N were determined on a Perkin-Elmer 240 elemental analyzer. The i.r. spectra were recorded on a Shimadzu IR-408 infrared spectrophotometer in the 4000-600 cm^{-1} range.

Synthesis

Diethyl 2,2'-(oxalyldiimino)bis(phenylglyoxylate) was prepared by a literature method.[27] [NiL] was synthesized in the same way used to prepare its analogues except using 1,2-propanediamine instead of other diamines.[27] The title complex $[Ag(NiL)(C_2H_5OH)(NO_3)]\cdot C_2H_5OH$ was prepared according to the following process: 0.0270g (0.05mmol) [NiL], 0.0255g (0.15mmol) $AgNO_3$ and 500 mL absolute EtOH were mixed. The mixture was stirred and heated at 70 °C for 20 minutes. The filtrate of the mixture was stored for 20 days at room temperature, and orange crystals (30% yield) suitable for X-ray single-crystal investigation were obtained. Anal. Calcd (found) for $C_{29}H_{36}AgN_5NiO_{11}$: C 43.69 (43.60), H 4.55 (4.45), N 8.79 (8.81) %. IR (KBr) ν 3400, 1730, 1630, 1610, 1550, 1440, 1380, 1210, 1040, 750 cm^{-1}.

X–Ray structure analysis

Diffraction data for the single crystals of $[Ag(NiL)(C_2H_5OH)(NO_3)]\cdot C_2H_5OH$ were collected by ω-scans technique on a Bruker Smart-1000-CCD area detector with Mo Kα radiation and graphite monochromator. Further details of crystal data, data collection and refinement can be found in Table 2.

The structure was solved by direct method and subsequent Fourier difference techniques and refined using full-matrix least-squares procedure on F^2 with anisotropic thermal parameters for all non-hydrogen atoms (SHELXS-97 and SHELXL-97).[31] Hydrogen atoms were added geometrically and refined with the riding model position parameters and fixed isotropic thermal parameters. Further details of the crystal structure investigation are available from the Cambridge Crystallographic Center with quotation number CCDC 224116.[32]

Table 2. Data collection and processing parameters for the title complex.

Empirical formula	$C_{29}H_{36}AgN_5NiO_{11}$
Formula weight	797.21
Temperature	293(2) K
Wavelength	0.71073 Å
Monochromator	Graphite
Crystal system	Monoclinic
Space group	P21/c
Unit cell dimensions	a = 13.295(4) Å, α = 90° b = 10.657(3) Å, β = 97.737(6)º c = 23.188(6) Å, γ = 90º
Volume, Z	3255.5(16) $Å^3$, 4
Calculated density	1.627 g/cm^3
Absorption coefficient	1.246 mm^{-1}
$F(000)$	1632
Crystal size	0.30 × 0.20 × 0.10 mm
θ Range for data collection	1.77° to 25.03°
Limiting indices	$-10 \le h \le 15$, $-12 \le k \le 12$, $-26 \le l \le 27$
Reflections collected / unique	13203/5752 [R_{int} = 0.0497]
Completeness to θ= 25.03°	100.0 %
Max. and min. transmission	0.8855 and 0.7062
Oberved reflections	3181 [$I > 2\sigma(I)$]
Data / restraints / parameters	5752 / 2 / 424
Goodness-of-fit on F^2	0.953
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0415, $wR2$ = 0.0941
R indices (all data)	$R1$ = 0.0979, $wR2$ = 0.1233
Largest diff. peak and hole	0.746 and -0.584 $e \cdot Å^{-3}$

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Povzetek

Pripravili smol nov dvojedrni kompleks, $[Ag(NiL)(C_2H_5OH)(NO_3)]\cdot C_2H_5OH$, v katerem je srebrov ion koordiniran s kompeksnim ligandom [NiL] in mu določili strukturo z rentgensko strukturno analizo. Srebrov(I) in nikljev(II) ion sta povezana z okamidno skupino makrocikličnega liganda (L). Koordinacijska geometrija srebrovega iona je popačena trigonalna bipiramida, nikljev ion pa je kvadratno-planarno koordiniran. V kristalu so intermolekularne $\pi\cdots\pi$ interaakcije med fenilnim obročem in tremi nearomatskimi π-sistemi. Molekule so s $\pi\cdots\pi$ interakcijami in C–H···O in O–H···O vodikovimi vezmi povezane v tridimenzionalno strukturo.