# Metal complexes of chiral pyridine ligands. X-ray structure of nitratobis{2-[(2S)-2-pyrrolidinyl]pyridine}copper(II) nitrate

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Cobalt(II), nickel(II), and copper(II) complexes of 2-[(2S)-2-pyrrolidinyl]pyridine (L) have been synthesized and characterized. The crystal structure of the complex  $[Cu(L)_2(NO_3)]NO_3$  has been determined by X-ray diffraction. Crystals are monoclinic, space group P2+, with a = 10.766(3), b = 7.525(2), c = 13.447(4)Å,  $\beta = 104.64(2)^\circ$ , and Z = 2. The structure consists of  $[Cu(L)_2(NO_3)]^+$  cations and NO<sub>3</sub><sup>-</sup> anions. The copper atom has a distorted trigonal bipyramidal coordination geometry with the two pyrrolidine nitrogens and one nitrate oxygen occupying the equatorial positions and the two pyridine nitrogens at the apices. The crystalline cohesion is ensured by a network of hydrogen bonds involving the pyrrolidine groups as donors and both coordinate and uncoordinate nitrates as acceptors.

KEY WORDS: Metal complexes, chiral, pyridine, ligands, pyridine derivatives.

## Introduction

Optically active pyridine derivatives containing a chiral center  $\alpha$  to the heteroatom have been recently used in asymmetric organic syntheses.<sup>1-4</sup> The interest of these compounds is mainly due to their ability to coordinate a large variety of metals and to be efficient controllers in asymmetric reactions.<sup>5</sup>

With the purpose of examining the coordinating properties of chiral pyridines and in order to clarify their role in enantioselective reactions, at first we have turned our attention to 2-[(2S)-2-pyrrolidinyl]pyridine (L), which has been shown to be a very efficient enantioselective catalyst in the addition of diethylzinc to prochiral aldehydes.<sup>6</sup>



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The present paper deals with the synthesis and the spectroscopic characterization of six metal complexes of L and with the X-ray structure of  $[Cu(L)_2(NO_3)]NO_3$ .

#### Experimental section

Elemental analyses (C, H, and N) were made on Carlo Erba Instruments CHNS-O EA 1108 automatic equipment. The metal was determined by atomic absorption spectroscopy on a Perkin-Elmer model 303-H6A 70 instrument. Infrared spectra for KBr discs were recorded on a Nicolet 5PC FT-IR spectrophotometer.

#### 2-[(2S)-2-pyrrolidinyl]pyridine (L)

The compound was obtained in high yield (92%) from 2-[(2S)-1-benzyloxycarbonyl-2-pyrrolidinyl]pyridine by heating under reflux in 6N hydrochloric acid solution, following the procedure previously described.<sup>7</sup>

## Metal complexes

To a methanol/chloroform (1/1 v/v) solution of L a methanol solution of the hydrate metal chloride (or nitrate) (2:1 molar ratio) was added. When the starting material had dissolved completely, the solution was heated at 55°C for 1 h. After slow evaporation of the solvent at room temperature a microcrystalline product was formed and collected by vacuum filtration. Crystals suitable for X-ray diffraction were obtained only in the case of the copper nitrate derivative by recrystallization from ethanol/toluene (1/1 v/v) mixture. For all the compounds the analytical data agree with the general formula  $M(L)_2X_2 \cdot nH_2O$  (M=Co, Ni, Cu; X=Cl, NO<sub>3</sub>; n = 0-4).

Co(L)<sub>2</sub>Cl<sub>2</sub>·4H<sub>2</sub>O (found: C, 43, 57; H, 5.78; N, 11.01; Co, 12.12. C<sub>18</sub>H<sub>32</sub>Cl<sub>2</sub>CoN<sub>4</sub>O<sub>4</sub> requires C, 43.38; H, 6.47; N, 11.24; Co, 11.83%). Ni(L)<sub>2</sub>Cl<sub>2</sub>·H<sub>2</sub>O (found: C, 48.45; H, 6.01; N, 12.44; Ni, 12.98. C<sub>18</sub>H<sub>26</sub>Cl<sub>2</sub>N<sub>4</sub>NiO requires C, 48.68; H, 5.90; N, 12.62; Ni, 13.22%). Cu(L)<sub>2</sub>Cl<sub>2</sub>·2H<sub>2</sub>O (found: C, 46.18; H, 5.71; N, 11.82; Cu, 14.05. C<sub>18</sub>H<sub>28</sub>Cl<sub>2</sub>CuN<sub>4</sub>O<sub>2</sub> requires C, 46.30; H, 6.05; N, 12.00; Cu, 13.61%). Co(L)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O (found: C, 43.78; N, 5.18; N, 17.01; Co, 12.02. C<sub>18</sub>H<sub>26</sub>CoN<sub>6</sub>O<sub>7</sub> requires C, 43.46; H, 5.27; N, 16.90; Co, 11.85%). Ni(L)<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub>·0.5H<sub>2</sub>O (found: C, 44.35; H, 5.05; N, 17.19; Ni, 12.35. C<sub>18</sub>H<sub>25</sub>N<sub>6</sub>NiO<sub>6.5</sub> requires C, 44.29; H, 5.16; N, 17.22; Ni, 12.03%). Cu(L)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> (found: C, 44.23; H, 4.92; N, 17.50; Cu, 12.88. C<sub>18</sub>H<sub>24</sub>CuN<sub>6</sub>O requires C, 44.67; H, 5.00; N, 17.37; Cu, 13.13%).

## X-Ray crystallography

The crystals of the title compound belong to the monoclinic system and from the systematic absences the space group could be either  $P2_1$  or  $P2_1/m$ . The choice of the former was based on the chirality of the compound and confirmed by intensity statistics and successful refinement. Crystal data and details of intensity data collection and structure refinement are given in Table 1. The integrated intensities were measured using a modified version of the Lehmann and Larsen peak-profile analysis procedure.<sup>8</sup> During the refinement a correction for absorption effects was also applied by the method of Walker and Stuart.<sup>9</sup>

The structure was solved by using conventional Patterson and Fourier techniques and refined by full-matrix least-squares procedures based on  $F^2$ . The y coordinate of the copper atom was fixed to specify the origin in the space group. One of the two pyrrolidine rings was found disordered over two positions with a 0.5/0.5 occupancy factor ratio, the disorder involving the out-of-plane atom only. Anisotropic thermal parameters were used for all nonhydrogen atoms, except the disordered carbon atom, C17, which was refined isotropically as were the hydrogen atoms, nineteen of which were lo-

 Table 1. Crystal data and summary of intensity data collection and structure refinement

the second se	
For. wt.	483.97
Space group	P2 1
Temp., °C	22
Cell Constants (30 reflections	
with $\vartheta > 30^\circ$ used)	
a, Å	10.766(3)
b, Å	7.525(2)
c, Å	13.447(4)
$\beta$ , deg	104.64(2)
Cell vol, Å'	1054.0(5)
Formula units/unit cell	2
D <sub>cale</sub> , g cm	1.525
$\mu_{\rm ender},  {\rm cm}^{-1}$	18.9
Diffractometer	Siemens AED
Scan mode	$\vartheta$ -2 $\vartheta$
Radiation; λ, Å	Ni-filtered Cu Ka; 1.54178
Standard reflections	820
Decay of standards	none
Reflections measured	2239
$2\vartheta$ range, deg	6-140
Reflections unique	2154
Reflections observed	2026
$[F_{\alpha} \geq 4\sigma(F_{\alpha})]$	
Corrections applied	Lorentz, polarization,
	absorption, anomalous
	dispersion
Transm. factors range	0.915-1.135
Computer programs	SHELXS86, <sup>10</sup> SHELXL92, <sup>11</sup>
	PARST, <sup>12</sup> ORTEP, <sup>13</sup> PLUTO <sup>14</sup>
Source of Structure factors used	International Tables <sup>15</sup>
Structure solution	Patterson and Fourier techniques
No. of parameters varied	356
Flack × parameter	-0.02(6)
GOF	0.919
$\mathbf{B} = \Sigma   F_0  -  F   / \Sigma  F_0  \text{ for}$	0.0530
observed data	0.0000
$wR_{2}$ for all data	0 1467
Weights	$1/(\sigma^2(E_0)^2 + (0.15P)^2)$ , where P
······································	$t_{i}^{c} = 1/3 (\max(-0, \pm))$
	$2F^2$ )]
Lorgest feature final diff. man	0.45
e Å <sup>-3</sup>	0.45

cated from a difference map, while the remaining ones were placed at their calculated positions and refined riding on their carrier atoms. The absolute configuration was assumed on the basis of the configuration of the compound used in the synthesis.

The final atomic fractional coordinates are given in Table 2 together with equivalent isotropic displacement parameters; selected bond distances and angles are in Table 3. The calculations were performed on the GOULD POWERNODE 6040 and ENCORE91 computers of the "Centro di Studio per la Strutturistica Diffrattometrica del CNR (Parma)."

**Table 2.** Atomic coordinates  $(\times 10^4)$  and equivalent isotropic displacement parameters  $(\mathring{A}^2 \times 10^4)$  (one third trace of the diagonalized matrix), with esd's in parentheses

Atom	X/a	Y/b	Z/c	U <sub>eq</sub>
Cu	2486.3(5)	5000.0	1924.7(5)	492(2)
01	2924(4)	7723(8)	1216(4)	737(17)
02	1985(6)	9569(9)	70(5)	1031(26)
03	887(5)	7596(10)	595(4)	964(23)
04	7073(7)	- 3418(20)	3313(6)	1615(52)
05	5759(5)	-2581(13)	4084(8)	1384(41)
06	7660(5)	-1702(15)	4596(6)	1318(38)
NI	1955(4)	6410(7)	2994(3)	546(14)
N2	689(4)	3978(7)	1664(3)	541(14)
N3	3038(4)	3848(6)	775(3)	518(13)
N4	4352(4)	4571(6)	2717(4)	553(14)
N5	1933(4)	8325(7)	631(4)	584(15)
N6	6847(4)	-2496(8)	3977(4)	635(16)
C1	2690(6)	7639(11)	3607(5)	747(23)
C2	2228(7)	8705(14)	4246(6)	849(27)
C3	955(8)	8492(13)	4279(5)	850(28)
C4	201(6)	7239(12)	3682(5)	726(22)
C5	725(5)	6208(8)	3020(4)	559(16)
C6	- 55(5)	4869(11)	2313(5)	677(19)
C7 .	-475(13)	3292(19)	2925(9)	1322(58)
C8	-562(9)	1773(15)	2228(9)	1069(41)
C9	638(7)	2040(10)	1858(8)	892(33)
C10	2308(5)	3698(9)	- 193(4)	599(17)
C11	2829(6)	3286(9)	-1003(4)	652(20)
C12	4117(7)	3012(9)	-813(5)	687(22)
C13	4885(7)	3123(11)	178(6)	709(23)
C14	4299(5)	3535(8)	957(4)	560(16)
C15	5078(5)	3643(10)	2055(5)	662(20)
C16	5392(15)	1802(18)	2551(8)	1313(52)
C17A	5458(20)	2025(29)	3625(15)	911(46)
C17B	4662(22)	1652(34)	3330(17)	1028(53)
C18	4417(7)	3439(12)	3638(6)	785(25)

## **Results and discussion**

## X-Ray structure

The structure consists of  $[Cu(L)_2(NO_3)]^+$  cations and NO<sub>3</sub><sup>-</sup> anions. As can be seen from Figure 1, which shows an ORTEP drawing of the cation, the configuration around the copper atom is a distorted trigonal bipyramid in which the pyrrolidine nitrogens of the two L molecules and one oxygen from the nitrate group occupy the equatorial positions and the two pyridine nitrogens the apical ones. The principal distortions from the ideal geometry are to be found in the trigonal girdle where, in spite of the fact that the three angles to copper total 359.9°, the N2-Cu-N4 angle is as large as 142.9(2)° and the N4-Cu-O1 angle is as narrow as 94.4(2)°, this being imposed by steric requirements of the L ligand molecules. The N1···N3 direction makes an angle of 7.8(1)° with the normal to the equatorial

 Table 3. Selected bond distances (Å) and angles (°) with esd's in parentheses

Cu-O1	2.357(6)	N4-C18	1.490(10)
Cu-N1	1.983(5)	C5-C6	1.491(9)
Cu-N2	2.029(5)	C6-C7	1.574(16)
Cu-N3	1.990(5)	C7-C8	1.465(18)
Cu - N4	2.047(4)	C8-C9	1.511(15)
01-N5	1.240(6)	C14-C15	1.504(8)
02—N5	1.213(9)	C15-C16	1.538(15)
O3-N5	1.243(8)	C16-C17A	1.438(23)
N2-C6	1.485(9)	C16-C17B	1.464(30)
N2-C9	1.485(9)	C17A-C18	1.548(24)
N4-C15	1.498(9)	C17B-C18	1.451(27)
N3-Cu-N4	83.6(2)	O2-N5-O3	120.0(6)
N2-Cu-N4	142.9(2)	O1-N5-O3	119.3(5)
N2-Cu-N3	99.2(2)	O1-N5-O2	120.6(6)
NI-Cu-N4	97.6(2)	N2-C6-C5	112.3(5)
N1-Cu-N3	173.5(2)	C5-C6-C7	111.5(7)
NI-Cu-N2	83.7(2)	N2-C6-C7	103.6(6)
01-Cu-N4	94.4(2)	C6-C7-C8	103.6(10)
01-Cu-N3	86.3(2)	C7-C8-C9	100.7(9)
01-Cu-N2	122.6(2)	N2-C9-C8	105.1(7)
Ol-Cu-Nl	87.2(2)	N4-C15-C14	111.3(5)
Cu-O1-N5	110.2(4)	C14-C15-C16	112.6(6)
Cu-N2-C9	114.7(4)	N4-C15-C16	104.6(7)
Cu-N2-C6	111.1(3)	C15-C16-C17B	106.3(12)
C6-N2-C9	106.9(6)	C15-C16-C17A	106.3(11)
Cu-N4-C18	110.9(4)	C16-C17A-C18	103.9(14)
Cu-N4-C15	110.8(4)	C16-C17B-C18	107.6(16)
C15-N4-C18	107.8(5)	N4-C18-C17B	105.5(11)
		N4-C18-C17A	105.4(9)



Fig. 1. ORTEP diagram and numbering scheme in  $[Cu(L)_2(NO_3)]^+$ . Thermal ellipsoids are drawn at the 30% probability level. The hydrogen atoms are represented by spheres of arbitrary radius. Only one of the two configurations giving rise to the disorder in the N4 · · · C17 pyrrolidine ring is shown.

plane. The two Cu—N distances within the same ligand are significantly different, but the corresponding distances from the two ligands are equivalent. The Cu—N distances to the pyridine nitrogens average 1.976 Å and to the pyrrolidine nitrogens 2.056 Å, so reflecting the difference in the nature of the nitrogen hybridization. The above values are close to the corresponding ones reported for related compounds.<sup>16-18</sup> The Cu—O distance to the nitrate oxygen is 2.357(6) Å, slightly longer than that, 2.299(7) Å, found in [Cu(NO<sub>3</sub>)(bpy)<sub>2</sub>]-NO<sub>3</sub>·H<sub>2</sub>O<sup>19</sup> in which the nitrate oxygen atom occupies one of the equatorial positions of a distorted trigonal bipyramid.

In each L ligand the angle between the planes of the two rings is ca.  $60^{\circ}$  and the pyrrolidine ring adopts an envelope conformation, with the out-of-plane atom, C8 and C17, being about 0.5–0.6 Å out of the plane of the other four atoms.

As far as we are aware, this is the first X-ray study of a 2-pyrrolidinopyridine metal complex, while there are three reports in the literature of 4-pyrrolidinopyridine complexes;<sup>20-22</sup> in all of these coordination to metal occurs only via the pyridine nitrogen atom.

As regards the molecular packing, hydrogenbonded chains are formed by the complex cations along the b direction: the hydrogen bonds involve the pyrrolidine N2-H group, whose H atom appears to be bifurcated, and the coordinate nitrate ion  $(N2 \cdot \cdot \cdot O2^i$ 3.245(7)Å,  $N2-H \cdot \cdot \cdot O2^i 137^\circ$ ;  $N2 \cdot \cdot \cdot O3^i$  3.253(7)Å,  $N2-H \cdot \cdot \cdot O3^i$  155° with i = -x, y - 1/2, -z). Further hydrogen bonds exist between the cationic chains and the uncoordinate nitrate ion, the donor being the pyrrolidine N4-H group  $(N4 \cdot \cdot \cdot O5^{ii} 2.977(10)$ Å,  $N4-H \cdot \cdot \cdot O5^{ii} 123^\circ$ , with ii = x, y + 1, z).

## Infrared spectra

Selected vibrational bands for the metal complexes and the uncoordinate ligand are reported in Table 4. The more significan shifts involve the pyridine ring (see for example the  $\nu$ (C=N) band which undergoes a positive shift,  $\Delta \omega = 8 \cdot 18 \text{ cm}^{-1}$ , upon coordination). The marked similarities in the spectra of all the complexes, taken together with the stoichiometric and preparative similarities, provide strong evidence that the complexes have the same structure as that of [Cu(L)<sub>2</sub>(NO<sub>3</sub>)]NO<sub>3</sub>. The presence in the spectra of all the complexes of a medium band in the range 3100-3160 cm<sup>-1</sup> agrees well with the neutral nature of L. As far as the nitrate metal complexes are concerned, a strong band at 1385 cm<sup>-1</sup> is always present due to the ionic nature of the nitrate group, while no evidence occurs for the monodentate ligand behavior of the nitrate group as found in [Cu(L)<sub>2</sub>(NO<sub>3</sub>)]NO<sub>3</sub>.

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Table 4. Selected vibrational bands (cm-1)

L	Co(L) <sub>2</sub> Cl <sub>2</sub> ·4H <sub>2</sub> O	$Ni(L)_2Cl_2$ $H_2O$	$Cu(L)_2Cl_2$ $\cdot 2H_2O$	$\frac{\text{Co}(\text{L})_2(\text{NO}_3)_2}{\cdot\text{H}_2\text{O}}$	$\frac{\text{Ni}(\text{L})_2(\text{NO}_3)_2}{\cdot 0.5\text{H}_2\text{O}}$	$[Cu(L)_2(NO_3)]NO_3$	Assignment
	3430br	3250br	3398m	3438br	3310m		ν (OH)
					3190m		
3180m	3105sh	3160m	3100m	3105sh	3106m	3100m	ν (NH)
1617sh	1635m	1625m	1635m	1635m	1625sh	1630sh	$\nu$ (C=N)
1590s	1610ms	1608ms	1604s	1611ms	1610ms	1600ms	δ (NH)
1567s	1560m	1560m	1568m	1560m	1565m	1570m	. ,
1470m	1484m	1489m	1482m	· 1485m	1485m	1480m	pyridine
1430m	1420m	1439m	1430m	1430sh	1435sh	1420m	ring
				1385vs	1385vs	1385vs	ν (NO <sub>3</sub> )

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