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Metal complexes of C_2-symmetric chiral bipyridine ligands. X-ray structure of [bis(nitrato)(4S,5S)-2,2-dimethyl-4,5-bis(2-pyridyl)-1,3-dioxolane cobalt(II)]

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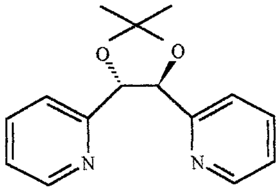
Abstract

Chelating properties of C_2-symmetric chiral bipyridine ligands are discussed. In particular we report the syntheses of the cobalt(II), nickel(II), zinc(II) and copper(II) complexes of (4S,5S)-2,2-dimethyl-4,5-bis(2-pyridyl)-1,3-dioxolane. All compounds have been characterized by IR spectroscopy, and an X-ray diffraction analysis has been carried out on one of them: $Co(L)(NO_3)_2$. The ligand coordinates the cobalt atom by the two nitrogen donors N(1) and N(2). A seven-membered chelation ring is formed, presenting a remarkable non-crystallographic twofold pseudosymmetry around the axis connecting Co and the midpoint of the C(6)—C(7) bond. The metal also binds two monodentate nitrates, thus completing a distorted coordination tetrahedron.

Introduction

Chiral bidentate ligands have been found to be very useful in asymmetric synthesis, primarily in asymmetric catalysis. In particular, chiral ligands with a C_2 symmetry axis have elicted a wide range of interest [1]. In this area, where there has been remarkable work in the use of oxygen and phosphorus-based auxiliares, relatively little is known about the application of bidentate nitrogen chiral systems [1], although they are expected to be stable, easily recoverable and profitably employed in asymmetric catalysis [2]. In this context, chiral C_2-symmetric 2,2′-bipyridines and bis(oxazolinyl)pyridines have been found to be highly effective controllers for enantioselective syntheses [3, 4, 5]. In the course of our studies on chiral pyridine ligands, we have synthesized (4S,5S)-2,2-dimethyl-4,5-bis(2-pyridyl)-1,3-dioxolane(L), the first pyridine ligand with a C_2 symmetry axis, from L-(+)-diethyltartrate [6] and, more recently, we have prepared chiral bis(oxazolinylpyridyl)dioxolane derivatives [7]. These compounds are of interest as ligands in enantioselective palladium-catalysed allylic substitution [7]. Therefore, the study of their coordinating properties to metal ions it is also of interest because of the possible application of these ligands in other metal-catalysed asymmetric reactions. The present paper deals with the synthesis and spectroscopic characterization of seven metal complexes of L and with the X-ray structure of $Co(L)(NO_3)_2$, in order to clarify the mechanism of the catalytic reaction and to use the metal complexes as new catalysts. The study of the coordinating properties of the oxazolinyl derivatives is now in progress.



Experimental

All chemicals were purchased from Aldrich Chimica and used without purification. IR spectra were recorded

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using KBr disks on a Perkin Elmer model 781 i.r. spectrophotometer. N.m.r. experiments were performed on a Varian 200 XL spectrometer. ^{1}H n.m.r. spectra were recorded at 300 K as 20% (wt./vol.) solutions in DMSO-d_6; all chemical shifts are relative to internal tetramethylsilane. Elemental analyses for C, H and N were performed on a Carlo Erba Instruments CHNS-O EA 1108 elemental analyzer.

(4S,5S)-2,2-dimethyl-4,5-bis(2-pyridyl)-1,3-dioxolane (L)

This compound was obtained by reacting (4S,5S)-2, 2-dimethyl-4,5-dicyano-1,3-dioxolane with C_2H_2 in the presence of (η^5-Cp)cobalt-1,5-cyclooctadiene, in a stainless-steel autoclave up to 14 bar and heated at 140 °C, following the procedure previously described [6] (yield: 72%.).

Metal complexes

A MeOH solution of the metal nitrate (or chloride) hydrate (1:1 molar ratio) was added to a MeOH/$CHCl_3$ (l/l v/v) solution of L. After complete dissolution of the starting material, the solution was heated at 50 °C for 4 h. Microcrystalline products were obtained after slow evaporation of the solution at room temperature. For the cobalt nitrate derivative red-purple crystals, suitable for an X-ray analysis were obtained by recrystallization from (1:3 v/v) EtOH/PhMe.

In spite of the metal ligand molar ratio used in the reaction, metal complexes of formula $M(L)X_2$ were obtained. For all the compounds the analytical data agree with the general formula $M(L)X_2 \cdot nH_2O$ (M = Co, Ni, Cu, Zn; X = Cl, NO_3; n = 0–2). For $NiCl_2$ a not well identified product was isolated. (Found: C, 40.6; H, 3.4; N, 12.5; $C_{15}H_{18}CoN_4O_9$ calcd.: C, 41.0; H, 3.7; N, 12.8%. Found C, 44.3; H, 4.3; N, 7.1; $C_{15}H_{18}Cl_2CoN_2O_3$ calcd.: C, 44.6; H, 4.5; N, 6.9%. Found: C, 38.05; H, 4.15; N, 12.22; $C_{15}H_{20}N_4NiO_{10}$ calcd.: C, 37.9; H, 4.2; N, 11.8%. Found: C, 38.2; H, 4.55; N, 11.4; $C_{15}H_{20}CuN_4O_{10}$ calcd.: C, 37.5; H, 4.2; N, 11.7%. Found: C, 43.9; H, 4.6; N, 7.0; $C_{15}H_{18}Cl_2CuN_2O_3$ calcd.: C, 44.1; H, 4.4; N, 6.85%. Found: C, 41.9; H, 4.6; N, 6.9; $C_{15}H_{20}Cl_2N_2O_4Zn$ calcd.: C, 42.0; H, 4.7; N, 6.5%. Found: C, 39.0, H, 3.9; N, 12.3; $C_{15}H_{18}N_4O_9Zn$ calcd.: C, 38.85, H, 3.9, N, 12.1%.)

Table 1 lists ^{1}H NMR data for L and for the zinc nitrate complex, in DMSO-d_6 solution. The proton signal shifts observed in the zinc(II) complex and, in particular for the pyridine rings, are indicative that they are affected by coordination to the zinc centre.

Table 1. ^{1}H n.m.r. data (DMSO-d_6) of L and $Zn(L)(NO_3)_2 \cdot H_2O$

Compound	δ (ppm)	No. of protons
L	8.48 d	2
	7.84 m	2
	7.55 d	2
	7.34 m	2
	5.19 s	2
	1.56 s	6
$Zn(L)(NO_3)_2 \cdot H_2O$	8.50 d	2
	7.85 m	2
	7.57 d	2
	7.35 m	2
	5.20 s	2
	1.57 s	6

X-ray diffractometry

Single crystal X-ray diffraction analysis was carried out at room temperature by a computer-controlled Enraf–Nonius CAD4 diffractometer using MoKα (l = 0.71073 Å) radiation. Automatic peak search, centering, and indexing procedures, indicated a primitive monoclinic lattice; by the examination of systematic absences and intensities statistics the space group was determined as $P2_1$. Relevant details concerning the data collection and the structure determination are collected in Table 2. No crystal decay was observed. The intensity data were processed with a peak-profile analysis procedure and corrected for Lorentz and polarization effects. The phase problem was solved by direct methods, using SIR 92 [8]. A full-matrix least-squares refinement was carried out with SHELXL 93 [9] on F^2, using all unique data. The dioxolane ring is disordered over two conformations due to a pseudo twofold axis bisecting the molecule. Anisotropic thermal displacement parameters were refined for all non-hydrogen atoms, with the exception of disordered carbon atoms. An empirical absorption correction [10] was applied after the last isotropic refinement cycle. The H atoms bonded to asymmetric carbons C(6) and C(7) were located by inspection of the DF map and refined isotropically. The remaining H atoms were introduced at calculated positions, riding on their carrier atoms, according to the protocols built in the refinement program. The correctness of the absolute configuration was confirmed by the value of Flack's parameter [11], which was refined according to SHELXL 93 protocol, giving the value of 0.07(6) for the (4S,5S) enantiomer. Programs PARST 97 [12], ZORTEP [13], PLUTO [14] were used for analyzing and drawing the molecular structure and the crystal packing. Use was made of the packages of the Cambridge Structural Database [15]. All the calculations were performed on an ENCORE 91 computer of the Centro di Studio per la Strutturistica Diffrattometrica

Table 2. Crystal data and structure refinement for Co(L)$(NO_3)_2$

Identification code	Co(L)$(NO_3)_2$
Empirical formula	$C_{15}H_{16}CoN_4O_8$
Formula weight	439.25
Temperatuer (K)	293 (2)
Wavelength (Å)	0.71069
Crystal system, space group	monoclinic, $P2_1$
Unit cell dimensions (Å, °)	a = 10.612 (2)
	b = 11.986 (2) β = 111.05 (5)°
	c = 7.625 (2)
Volume (Å^3)	905.1 (3)
z, Calculated density (g/cm^3)	2, 1.612
Absorption coefficient (mm^{-1})	1.001
F (000)	450
θ range for data collection (°)	3–27
Index ranges	$-13 \leqslant h \leqslant 13$, $0 \leqslant k \leqslant 15$, $0 \leqslant l \leqslant 9$
Reflections collected/unique	2215/2078 [R (int) = 0.0480]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2077/2/263
Goodness-of-fit on F^2	1.102
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0575, w$R2$ = 0.1330
R indices (all data)	$R1$ = 0.1373, w$R2$ = 0.2002
Absolute structure parameter	0.07 (6)
Extinction coefficient	0.014 (6)
Largest ΔF peak/hole (e/Å^3)	0.557/−0.745

Table 3. Bond distances (Å) and angles (°) with s.u.'s in parentheses

Bond distances			
Co—O(3)	2.07 (1)	Co—O(8)	2.41 (1)
Co—O(5)	2.47 (1)	Co—N(1)	2.11 (1)
Co—O(6)	2.027 (9)	Co—N(2)	2.054 (9)
Bond angles			
O(3)—Co—O(5)	55.2 (4)	O(8)—Co—N(1)	152.3 (4)
O(3)—Co—O(6)	128.8 (4)	O(8)—Co—N(2)	88.0 (4)
O(3)—Co—O(8)	85.0 (4)	N(1)—Co—N(2)	110.8 (4)
O(3)—Co—N(1)	112.5 (4)	Co—O(3)—N(4)	100.6 (8)
O(3)—Co—N(2)	94.4 (4)	Co—O(5)—N(4)	84 (1)
O(5)—Co—O(6)	85.5 (4)	Co—O(6)—N(3)	100.0 (8)
O(5)—Co—O(8)	85.9 (5)	Co—O(8)—N(3)	82.2 (9)
O(5)—Co—N(1)	87.1 (4)	Co—N(1)—C(1)	111.9 (8)
O(5)—Co—N(2)	149.4 (4)	Co—N(1)—C(5)	127.9 (8)
O(6)—Co—O(8)	58.3 (4)	Co—N(2)—C(8)	128.0 (8)
O(6)—Co—N(1)	94.3 (4)	Co—N(2)—C(12)	115.8 (8)
O(6)—Co—N(2)	116.3 (4)		

del C.N.R. in Parma. Geometric parameters are given in Table 3. The coordinates for this structure have been deposited at the Cambridge Crystallographic Data Center. The deposition number is 104040.

Results and discussion

Crystal structure of Co(L)$(NO_3)_2$

A perspective view of the molecule is shown in Figure 1, along with the labelling scheme. The ligand coordinates the cobalt atom by the two nitrogen donors N(1) and N(2). A highly puckered seven-membered chelation ring is formed, with average endocyclic torsion angles Co—N—C—C = 1(2)°, N—C—C—C = 64(2)° and C(5)—C(6)—C(7)—C(8) = −120(1)°. The molecule presents a remarkable non-crystallographic two-fold pseudosymmetry around the axis containing Co, the midpoint of the C(6)—C(7) bond and C(14). The dioxolane ring is distributed over two equally populated conformations, related by the pseudo-twofold axis. Both conformations have envelope geometry, with C(13A) and C(13B) deviating 0.38 Å and 0.32 Å, respectively, from the least-squares plane defined by O(1), O(2), C(6) and C(7). The five-membered ring forms a dihedral angle of 45° with the average chelation ring, while the two pyridinic groups which provide the donor atoms make angles of 17° with the chelation plane. The metal also binds two monodentate nitrates through O(3) and O(6), thus completing a distorted coordination tetrahedron. The relative flexibility and large dimensions of the chelating system allow N(1) and N(2) to fit well the ideal tetrahedral angle [N(1)—Co—N(2) = 110.8(4)°], while steric hindrance of the nitrates induces the deformation of the coordination polyhedron [O(3)···Co···O(6) = 128.8(4)°]. Two other oxygens belonging to the anions form long contacts to the cation [Co···O(5) = 2.47(1), Co···O(8) = 2.41(1) Å], expanding the coordination sphere. The resulting geometry is still irregular due to the constraints represented by the low bite angle of nitrates (120(1)° on average). The capability of the (1,2-bis(pyridin-2-yl)ethane-N,N′) system to act as a flexible ligand in different coordination polyhedra is indicated by the presence in the crystallographic literature of six complexes in which the fragment is bound to tetracoordinated metals (Pd, Pt, Cu or Zn) presenting square planar, distorted square planar and tetrahedral geometry. The N—Co—N angle varies between 87° and 119°, due to the torsional degrees of freedom around the C(6)—C(7), C(7)—C(8) and C(5)—C(6) bonds. As a general trend, it is seen that for angles N—Co—N close to 90°, the torsion angle C(5)—C(6)—C(7)—C(8) ranges between −43 and 56°, while for N—Co—N greater than 100° the torsion angles around C(6)—C(7) have absolute values greater than 94°. In the present compound C(5)—C(6)—C(7)—C(8) = −120(1)°. The torsional freedom around C(5)—C(6) and C(7)—C(8) is constrained by the requirement of the chelating ring closure. In the present compound N(1)—C(5)—C(6)—C(7) = 65(1)° and N(2)—C(8)—C(7)—C(6) = 63(2)°. The crystal packing is based on van der Waals interactions.

I.r. spectra

Concerning the i.r. bands, the more significant shifts involve the pyridine rings. In fact a positive shift,

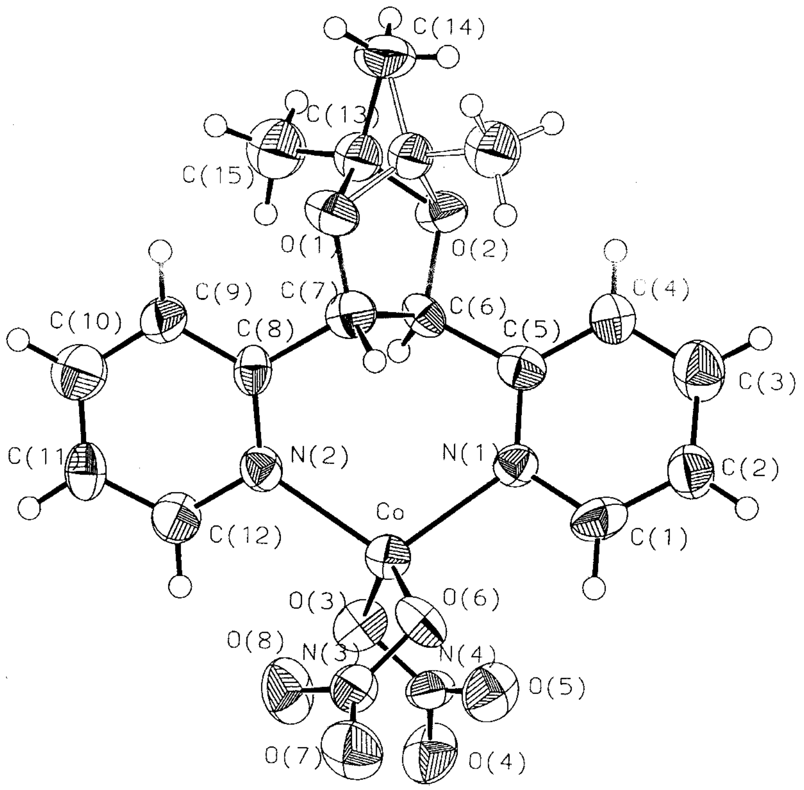

Fig. 1. ORTEP view of the $Co(L)(NO_3)_2$, complex with 40% probability ellipsoids. The dioxolane ring is represented in two conformations, equally populated, involving the displacement of C(13) and C(15). Conformer A is labeled, conformer B is shown with white bonds.

$\Delta\nu = 10\text{–}15\ cm^{-1}$, is observed for the $\nu(C{=}N)$ upon coordination. With the exception of the absorption due to the anionic group, a similar spectroscopic pattern, observed in the spectra of all complexes, is a strong evidence, together with stoichiometric and preparative similarities, that the complexes have the same structure as that $Co(NO_3)_2$. We report also, in Table 4, the i.r. absorptions attributable to the unidentate behaviour of the nitrate ligands in the $Co(L)(NO_3)_2$ complex.

Conclusions

The analogous stoichiometries, $M(L)X_2 \cdot nH_2O$, and the similar spectroscopic patterns, observed in the 4000–600 cm^{-1} region for all the complexes, suggest a similar structural situation mainly concerning the ligand behaviour of L. Thus, with the exception of the Ni complex, where an hexacoordination involving two water molecules could be present, in the other complexes a distorted tetrahedral geometry seems to be present. Moreover, the X-ray structure confirmed the N,N bidentate ligand behaviour of L, which involves deformation of a seven-membered chelation ring, this could justify the catalytic properties of the metal complex, probably depending by the lability of the M–N interaction.

Table 4. NO stretching frequencies (cm^{-1}) in $Co(L)(NO_3)_2$

1515 m	1380 s	1300 m	1008 m	810 w
1490 s		1280 ms		700 w

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