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Synthesis and characterization of Co(II) and Ni(II) complexes of 2,5-diphenyl-3,4-bis(2-pyridyl)-cyclopentadienone (L). X-ray crystal structures of $CoLCl_2{\cdot}0.5CH_3CN$ and $NiLBr_2{\cdot}CHCl_3$

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ABSTRACT

The preparation and properties of [M(chelate)X_2] complexes are reported, where M = Co(II) or Ni(II), chelate = 2,5-diphenyl-3,4-bis(2-pyridyl)cyclopentadienone and X = Cl or Br. These complexes have been characterized by elemental analyses and spectroscopic methods. The crystal and molecular structures of $CoLCl_2{\cdot}0.5CH_3CN$ (**1**) and $NiLBr_2{\cdot}CHCl_3$ (**4**) have been determined by X-ray crystallography. Compound (**1**) crystallizes in the triclinic space group $P\bar{1}$, different from that of $CoLCl_2$ (monoclinic space group $P2_1/c$) that we have reported previously. Compound (**4**) crystallizes in the monoclinic space group $P2_1/n$. Both $CoLCl_2$ and $NiLBr_2$ complexes are pseudo-tetrahedral, and utilization is made of the electronic and vibrational spectra in the structural diagnosis of $CoLBr_2$ and $NiLCl_2$.

1. Introduction

The formation and characterization of complexes of the type MLX_2, where M = Co(II), Ni(II), L = ligands formed by the linkage of two pyridine residues, in the ortho position, by various groups such as $-CH_2CH_2-$, –SS–, –N=N–, –NH–, etc., and X = Cl, Br, I, NCS, have been the subject of considerable interest [1–8]. The ligands show unusual adaptability to different environments and result in the formation of structurally different complexes depending on their modes of coordination and the conformations of the coordinated L ligands. Steric effects and internal strain are expected to be different in these complexes and, depending on the structures of 1,2-di(2′-pyridyl) ligands and the stability of their compounds, synthetic conditions may vary from one group of complexes to another. In this paper we report the synthesis and characterization of a series of new MLX_2 complexes with internal strain imparted by the structurally rigid L ligand, Scheme 1. We also report the X-ray structural analysis of $CoLCl_2{\cdot}0.5CH_3CN$ and $NiLBr_2{\cdot}CHCl_3$ complexes.

2. Experimental

2.1. Materials

Solvents and starting materials were obtained from Fluka and Aldrich and used as received. The red ligand L was prepared by thermal dehydration of its white diol precursor, $LH_2(OH)_2$, over silica gel as reported elsewhere [9]. Electronic spectra in solution were recorded on a JASCO V-570 spectrophotometer. IR spectra were recorded as KBr pellets on a FT-IR JASCO 680 PLUS instrument. Elemental analyses were performed by using a Perkin–Elmer 2400II CHNS/O analyzer.

2.2. Synthesis of complexes

2.2.1. $CoLCl_2{\cdot}0.5CH_3CN$ (*1*)

A solution of the ligand L (0.193 g, 0.5 mmol) in chloroform (40 mL) was added to a suspension of $CoCl_2$ (0.091 g, 0.7 mmol) in chloroform (10 mL). The reaction mixture was stirred at room temperature for 3 h to give a cherry red solution. The unreacted $CoCl_2$ was removed by filtration and the filtrate was left in the hood for two days to give dark red crystals of $CoLCl_2$ in 95% yield (based on the ligand L). The product was recrystallized from a mixture of chloroform–acetonitrile (20:1 v/v) to give dark crystals of X-ray quality which were washed and dried in air. *Anal.* Calc. for $C_{27}H_{18}Cl_2CoN_2O{\cdot}0.5CH_3CN$: C, 62.65; H, 3.66; N, 6.52. Found: C, 62.4; H, 3.60; N, 6.60%. IR (KBr pellets, ν/cm^{-1}): ν(C=O) 1715(s); ν(C=N py) and ν(C=C aromatic) 1599, 1566, 1493, 1473, 1440(m); ν(C≡N acetonitrile) 2250(w).

2.2.2. $CoLBr_2$ (*2*)

This complex was prepared as described for compound **1** except that stoichiometric amounts of $CoBr_2$ and L (0.5 mmol) were used

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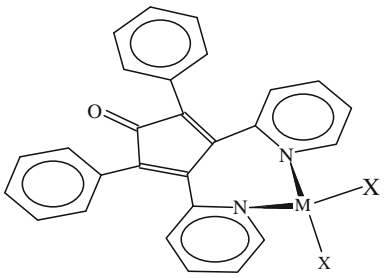

M	X	
Co	Cl	**1**
	Br	**2**
Ni	Cl	**3**
	Br	**4**

Scheme 1. Structural formulas of the complexes.

and the reaction mixture was stirred for 12 h. Red purple needle like crystals of $CoLBr_2$ were obtained in 73% yield (based on the ligand L) from the final filtrate after two days. The product was recrystallized from chloroform and dried in air. *Anal.* Calc. for $C_{27}H_{18}Br_2CoN_2O$: C, 53.59; H, 3.00; N, 4.63. Found: C, 53.90; H, 3.00; N, 4.40%. IR (KBr pellets, ν/cm^{-1}): 3050 ν(CH); ν(C=O)1718(s); ν(C=N py) and ν(C=C aromatic) 1595, 1560, 1490, 1470, 1440(m).

2.2.3. $NiLCl_2$ (**3**)

This complex was prepared as described for compound (**1**) except that $NiCl_2$ was used in excess (Ni/L≅2, 1/0.5 mmol), and the reaction mixture in chloroform was stirred for 60 h. The product was obtained as a red purple powder in 70% yield (based on the ligand L). The complex was recrystallized from dichloromethane and dried in air. *Anal.* Calc. for $C_{27}H_{18}Cl_2NiN_2O$ (516.05): C, 62.84; H, 3.52; N, 5.43. Found: C, 62.70; H, 3.40; N, 5.32%. IR (KBr pellets, ν/cm^{-1}): ν(C=O) 1717(s); ν(C=N py) and ν(C=C aromatic) 1599, 1567, 1494, 1473, 1442(m).

2.2.4. $NiLBr_2{\cdot}CHCl_3$ (**4**)

This complex was prepared as described for compound **1** except that stoichiometric amounts of $NiBr_2$ and L (0.5 mmol) were used

Table 1
Crystal and structure refinement data for $CoLCl_2{\cdot}0.5CH_3CN$ (**1**) and $NiLBr_2{\cdot}CHCl_3$ (**4**).

Compound	**1**	**4**
Empirical formula	$C_{56}H_{39}Cl_4Co_2N_5O_2$	$C_{28}H_{19}Br_2Cl_3NiN_2O$
Formula weight	1073.58	724.33
T (K)	153(2)	153(2)
Crystal system	triclinic	monoclinic
Crystal size (mm)	0.94 × 0.22 × 0.08	0.68 × 0.18 × 0.17
Space group	$P\bar{1}$	$P2_1/n$
a (Å)	8.7243(4)	7.0124(14)
b (Å)	16.6040(8)	21.595(4)
c (Å)	17.7740(9)	18.916(4)
α (°)	77.328(1)	90
β (°)	84.773(1)	96.041(4)
γ (°)	77.157(1)	90
V (Å^3)	2446.7(2)	2848.7(10)
Z, D_{calc} (g cm^{-3})	2, 1.457	4, 1.689
μ (mm^{-1})	0.945	3.793
F(0 0 0)	1096	1432
θ Range for data collection (°)	2.35–33.08	2.17–28.67
Index ranges	$-13 \leqslant h \leqslant 13$ $-25 \leqslant k \leqslant 25$ $-27 \leqslant l \leqslant 26$	$-9 \leqslant h \leqslant 9$ $-29 \leqslant k \leqslant 29$ $-25 \leqslant l \leqslant 25$
Reflections collected	44678	39897
Independent reflections	17336	7291
R_{int}	0.0226	0.0524
Completeness to θ (°)	31.00, 99.5%	28.67, 99.3%
Maximum and minimum transmission	0.9282, 0.7153	0.5648, 0.1983
Data/parameters	17336/623	7291/334
Good-of-fit on F^2	1.002	1.008
R_1/wR_2 for observed reflection [$I > 2\sigma(I)$]	0.0315/0.0822	0.0401/0.0945
R_1/wR_2 for all data	0.0419/0.0873	0.0623/0.1074
Largest resolution peak/hole(e Å^{-3})	0.566/−0.272	1.037/−0.692

Table 2
Electronic absorption spectral data for **1**–**4** and the red L, λ/nm (ε/L mol^{-1} cm^{-1}).

$CoLCl_2$ (**1**)	$CoLBr_2$ (**2**)	$NiLCl_2$ (**3**)	$NiLBr_2$ (**4**)	Red L
254 (24324)	255 (21830)	260 (17860)	255 (18700)	258(20090)
287 (12622)	288 (12341)	292 (11800)	296 (14000)	324(5012)
360 (3250)	360 (3162)	360 (2850)	360 (2540)	492(1167)
510 (1488)	512 (1625)	521 (1504)	526 (1700)	
569 (1183)	594 (1112)	852 (10)	888 (26)	
610 (795)	626 (895)	984 (44)	1007 (51)	
650 (465)	664 (626)			
985 (19)	1020 (24)			
1340 (73)	1400 (112)			

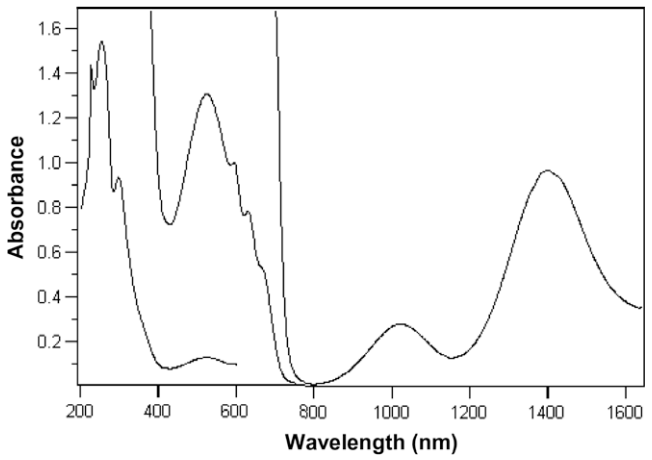

Fig. 1. UV–Vis spectrum of $CoLBr_2$ (400–200 nm, 7.1×10^{-5} M; 800–400 nm, 8.0×10^{-4} M; 1600–800 nm, 8.8×10^{-3} M) in CH_2Cl_2.

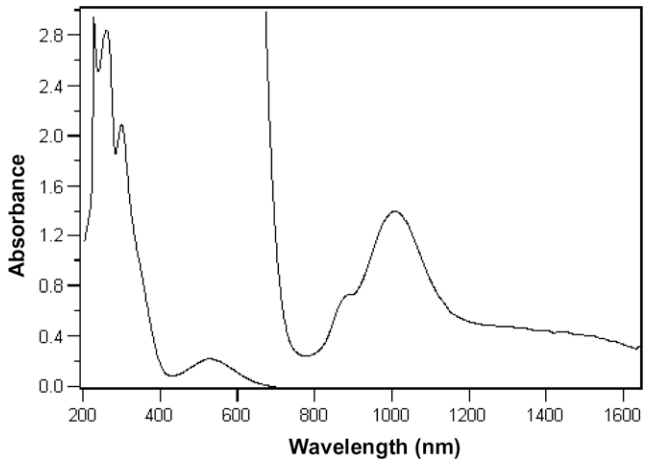

Fig. 2. UV–Vis spectrum of $NiLBr_2$ (700–200 nm, 1.5×10^{-4} M; 1600–700 nm, 2.45×10^{-2} M) in CH_2Cl_2.