Inorganica Chimica Acta, *176* (1990) 57–60

The synthesis, crystal and molecular structure of *mer*-tris(2-pyridinethiolato)cobalt(III)

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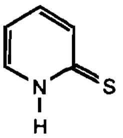
(Received March 20, 1990)

Abstract

The complex $[CoL_3]$ (HL = pyridine-2(1*H*)-thione) may be prepared by the reaction of $[Zn_4OL_6]$ with cobalt(II) chloride in aerobic conditions. The compound closely resembles the rhodium analogue. Crystallographic data: space group *C*2/*c*, $a=26.568(7)$, $b=9.322(3)$, $c=13.414(4)$ Å, $\beta=100.77(2)$, $V=3264$ Å^3, $Z=8$.

Introduction

Pyridine-2(1*H*)-thione (HL) is a versatile ligand which may adopt a variety of bonding modes in its coordination compounds [1]. Typical bonding modes include monodentate N or S bonded HL, monodentate N or S bonded L and bidentate N,S bonded chelating or bridging L. Although complexes with a wide range of transition metals have been described, coordination compounds of HL with cobalt have been little investigated. The cobalt(II) compounds $[Co(HL)_2X_2]$ (X = Cl, Br or I) [2, 3] and $[Co(HL)_4]Y_2$ ($Y = NO_3$ or ClO_4) [2] are typical tetrahedral species, and the structure of $[Co(HL)_2Cl_2]$ has been confirmed by an X-ray structural determination [4]. The mixed-ligand cobalt(III) ions $[CoL_n(en)_{3-n}]^{(3-n)+}$ ($n=1$ or 2) have been prepared, and their chiroptical properties investigated [5–7]. The homoleptic complex $[CoL_3]$ has been prepared by the reaction of $[Co(acac)_3]$ [8] or CoO(OH) [6] with HL, and has been tentatively assigned a *meridional* geometry.



HL

Experimental

Infrared spectra were recorded in compressed KBr pellet on a Perkin-Elmer FT 910 spectrometer; ^1H NMR spectra were recorded on a Brüker WM 250 spectrometer. Fast atom bombardment (FAB) mass spectra were recorded on a Kratos MS50 mass spectrometer. Pyridine-2(1*H*)-thione was used as supplied by Aldrich; $[Zn_4OL_6]$ was prepared by the literature method [9].

Synthesis of [Co(pyS)$_3$]

A suspension of $[Zn_4OL_6]$ (0.311 g, 0.33 mmol) and $[Co(H_2O)_6]Cl_2$ (0.315 g, 1.3 mmol) in methanol (15 ml) was placed in a laboratory ultrasonic cleaning tank for 1 h. The brown reaction mixture was then evaporated to dryness *in vacuo*, extracted with CH_2Cl_2 and the extract concentrated. Chromatography over silica using CH_2Cl_2 as eluent yielded a single brown product, and left a green immobile band on the top of the column. *Anal.* Found: C, 45.6; H, 3.0; N, 10.6. Calc. for $CoC_{15}H_{12}N_3S_3$: C, 46.3; H, 3.1; N, 10.8%. FAB-MS (*m*/*z*): 389 (CoL_3), 279 (CoL_2), 169 (CoL).

X-ray crystallography

An intensely dark single crystal was mounted on a glass fibre. All geometric and intensity data were taken from this crystal using an automated four-circle diffractometer (Nicolet R3mV) following procedures described previously [10]. Pertinent crystallographic data are given in Table 1. Lattice dimensions were verified by axial photography. Intensity

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0020-1693/90/$3.50

TABLE 1. Crystal data for [Co(pyS)$_3$]

Formula	$C_{15}H_{12}N_3S_3Co$
Formula weight	389.41
Space group	$C2/c$
a (Å)	26.568(7)
b (Å)	9.322(3)
c (Å)	13.414(4)
α (°)	90.0
β (°)	100.77(2)
γ (°)	90.0
V (Å^3)	3264
Z	8
F(000)	1584
D_{calc} (g/cm^3)	1.58
Crystal size (mm)	0.4×0.6×0.75
μ(Mo Kα) (cm^{-1})	14.2
Data collection instrument	Nicolet R3m/V
Radiation	Mo Kα (λ=0.71073 Å)
Orientation reflections: no. range (2θ)	30, $17° \leq 2\theta \leq 30°$
Temperature (°C)	19
No. unique data, total with $I \geq 3\sigma(I)$	2793, 2427
No. parameters	199
R^a	0.0381
R'^b	0.0504
Weighting scheme	$w^{-1} = \sigma^2F + 0.003626F^2$
Largest shift/e.s.d., final cycle	0.12
Largest peak (e/Å^3)	0.48

$^aR = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$. $^bR' = \Sigma w^{1/2}[|F_o| - |F_c|]/\Sigma w^{1/2}F_o$.

data, gathered by the 2θ–ω method, were reduced by routine procedures. Calculations were carried out using a Micro-Vax II with the program SHELXTL+ [11]. Empirical absorption corrections were applied.

All the non-hydrogen atoms were located by direct methods and refined anisotropically. Hydrogen atoms were placed in idealised positions with a fixed isotropic thermal parameter, U=0.08 Å. The final difference Fourier map had no peaks larger than 0.5 e/Å^3. Positional parameters are presented in Table 2 and bond distances and bond angles are given in Table 3.

Results and discussion

We have recently become interested in the synthesis of polynuclear complexes containing NS donor ligands based upon HL, and investigated the possibility of using transmetallation reactions for the preparation of such compounds. The tetranuclear zinc complex [Zn_4OL_6] is readily prepared from HL, and we considered that it might prove to be a suitable intermediate for the preparation of other tetranuclear clusters [9]. The advantage of the transmetallation route is that it might allow the development of a synthetic methodology for the preparation of heteronuclear clusters or clusters with nuclearities dif-

TABLE 2. Positional parameters and their e.s.d.s. for [Co(pyS)$_3$]

	x	y	z
Co(1)	3845(1)	1828(1)	1258(1)
S(1)	4412(1)	3706(1)	1309(1)
S(2)	3377(1)	−243(1)	844(1)
S(3)	3837(1)	1610(1)	2952(1)
N(1)	3816(1)	2482(3)	−123(2)
N(2)	4316(1)	321(3)	1153(2)
N(3)	3313(1)	3046(3)	1549(3)
C(1)	4139(1)	3607(3)	17(2)
C(2)	4215(2)	4439(3)	−789(3)
C(3)	3961(2)	4059(4)	−1740(3)
C(4)	3635(2)	2891(4)	−1874(3)
C(5)	3571(1)	2116(4)	−1037(3)
C(6)	4001(1)	−821(3)	940(2)
C(7)	4197(2)	−2187(4)	872(3)
C(8)	4718(2)	−2333(4)	1007(3)
C(9)	5037(2)	−1164(4)	1177(3)
C(10)	4822(1)	174(4)	1262(2)
C(11)	3340(1)	2783(4)	2551(3)
C(12)	2996(2)	3443(5)	3071(4)
C(13)	2657(2)	4404(5)	2563(4)
C(14)	2645(2)	4676(5)	1551(5)
C(15)	2978(1)	3955(4)	1065(3)

TABLE 3. Bond distances (Å) and bond angles (°) for $[Co(pyS)_3]$

Co(1)–S(1)	2.303(1)	Co(1)–S(2)	2.306(1)
Co(1)–S(3)	2.286(1)	Co(1)–N(1)	1.938(3)
Co(1)–N(2)	1.903(3)	Co(1)–N(3)	1.909(3)
S(1)–C(1)	1.753(3)	S(2)–C(6)	1.724(4)
S(3)–C(11)	1.720(4)	N(1)–C(1)	1.344(4)
N(1)–C(5)	1.321(4)	N(2)–C(6)	1.351(4)
N(2)–C(10)	1.333(4)	N(3)–C(11)	1.355(5)
N(3)–C(15)	1.310(5)	C(1)–C(2)	1.376(5)
C(2)–C(3)	1.374(5)	C(3)–C(4)	1.381(6)
C(4)–C(5)	1.372(6)	C(6)–C(7)	1.385(5)
C(7)–C(8)	1.368(6)	C(8)–C(9)	1.373(6)
C(9)–C(10)	1.385(5)	C(11)–C(12)	1.394(7)
C(12)–C(13)	1.360(6)	C(13)–C(14)	1.376(8)
C(14)–C(15)	1.369(7)		
S(1)–Co(1)–S(2)	164.5(1)	S(1)–Co(1)–S(3)	99.5(1)
S(2)–Co(1)–S(3)	93.5(1)	S(1)–Co(1)–N(1)	72.4(1)
S(2)–Co(1)–N(1)	96.4(1)	S(3)–Co(1)–N(1)	166.4(1)
S(1)–Co(1)–N(2)	97.4(1)	S(2)–Co(1)–N(2)	72.3(1)
S(3)–Co(1)–N(2)	97.8(1)	N(1)–Co(1)–N(2)	94.1(1)
S(1)–Co(1)–N(3)	92.7(1)	S(2)–Co(1)–N(3)	99.3(1)
S(3)–Co(1)–N(3)	72.8(1)	N(1)–Co(1)–N(3)	96.3(1)
N(2)–Co(1)–N(3)	167.4(1)	Co(1)–S(1)–C(1)	77.4(1)
Co(1)–S(2)–C(6)	77.1(1)	Co(1)–S(3)–C(11)	77.4(1)
Co(1)–N(1)–C(1)	101.7(2)	Co(1)–N(1)–C(5)	136.9(2)
C(1)–N(1)–C(5)	121.4(3)	Co(1)–N(2)–C(6)	102.0(2)
Co(1)–N(2)–C(10)	137.0(2)	C(6)–N(2)–C(10)	120.9(3)
Co(1)–N(3)–C(11)	101.0(2)	Co(1)–N(3)–C(15)	138.1(3)
C(11)–N(3)–C(15)	120.9(4)	S(1)–C(1)–N(1)	108.3(2)
S(1)–C(1)–C(2)	130.7(3)	N(1)–C(1)–C(2)	120.9(3)
C(1)–C(2)–C(3)	117.7(3)	C(2)–C(3)–C(4)	120.8(4)
C(3)–C(4)–C(5)	118.6(3)	N(1)–C(5)–C(4)	120.6(3)
S(2)–C(6)–N(2)	108.5(2)	S(2)–C(6)–C(7)	130.6(3)
N(2)–C(6)–C(7)	120.9(3)	C(6)–C(7)–C(8)	117.8(4)
C(7)–C(8)–C(9)	121.3(4)	C(8)–C(9)–C(10)	118.6(4)
N(2)–C(10)–C(9)	120.4(3)	S(3)–C(11)–N(3)	108.7(3)
S(3)–C(11)–C(12)	131.4(3)	N(3)–C(11)–C(12)	119.9(3)
C(11)–C(12)–C(13)	118.4(5)	C(12)–C(13)–C(14)	120.4(5)
C(13)–C(14)–C(15)	118.9(4)	N(3)–C(15)–C(14)	121.4(4)

fering from those obtained by assembly of mononuclear species.

The reaction of $[Zn_4OL_6]$ with methanolic cobalt(II) chloride in air under ultrasonic irradiation results in the formation of a dark-coloured solution, from which excellent yields of $[CoL_3]$ may be obtained after chromatography. A green product, $[Co(HL)_2Cl_2]$, is separated during this procedure, and is the sole product in the absence of air. The complex $[CoL_3]$ was characterised by elemental analysis and FAB mass spectroscopy. The FAB mass spectrum exhibited peaks for (CoL_3), (CoL_2) and (CoL). The complex appears to be identical to that previously reported [5, 8], which had been assigned the *meridional* geometry on the basis of a poorly resolved ^{13}C NMR spectrum which exhibited too many resonances for the *facial* isomer. The ^1H NMR spectrum of a CD_2Cl_2 solution of the complex is shown in Fig. 1, and closely resembles that previously

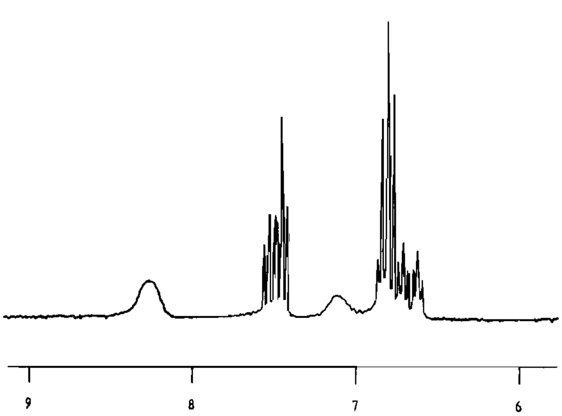

Fig. 1. ^1H NMR spectrum (250 MHz, CD_2Cl_2, 25 °C) of *mer*-$[Co(pyS)_3]$.

reported for *mer*-$[RhL_3]$ [12]. The three ligands are magnetically independent, and three sets of overlapping resonances are observed. The only significant differences observed are in the broadening of the resonances at δ8.2 (2H) and δ7.1 (1H). These resonances may be assigned to the three different H_6 protons of the ligands. The upfield shift of the δ7.1 proton is greater than that observed in the corresponding rhodium complex, and is assigned to the proton attached to C(15) which lies in the shielding region above a pyridine ring. The spectrum is unchanged in the temperature range −30 to +30 °C, and we consider that the broadening is a consequence of the temperature independent paramagnetism of the cobalt rather than a fluxional process. The complex is redox active and exhibits a single quasireversible reduction centred at −0.53 V in its cyclic voltammogram (MeCN, supporting electrolyte $[^nBu_4N][PF_6]$, versus internal ferrocene/ferrocinium, $E_a-E_p=120$ mV).

The crystal and molecular structure of $[CoL_3]$ is shown in Fig. 2, and confirms the *meridional* arrangement of the three ligands about the cobalt centre. The structure is similar in many respects to that of *mer*-$[RhL_3]$ [12]. The bite angle of each of the chelating ligands (72.4(1), 72.3(1) and 72.8(1)°) is slightly larger than in the rhodium complex (69.2, 69.2 and 69.5°), and this is a natural consequence of the shorter M–S and M–N bonds in the cobalt complex. Each of the ligands is to all intents and purposes planar. The Co–S bonds are approximately 0.08 Å shorter than corresponding Rh–S bonds, whereas the Co–N bonds are 0.11–0.13 Å longer than the Rh–N bonds. Once again, this is a consequence of the fixed ligand geometry. The pattern of bond lengths within the complex resembles that in $[RhL_3]$, with two long and one short M–S bond, and two short and one long M–N bond. As expected,

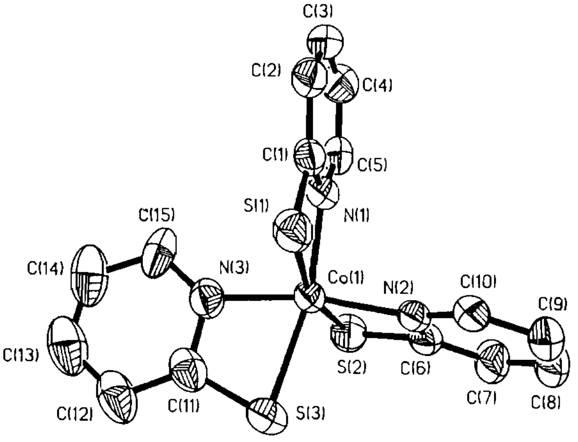

Fig. 2. Crystal and molecular structure of *mer*-[Co(pyS)$_3$] showing the numbering scheme adopted. Hydrogen atoms have been omitted for clarity.

the Co–S distances are significantly shorter than those observed in [Co(HL)$_2$Cl$_2$] [4].

In conclusion, we have confirmed that the complex [CoL$_3$] possesses a *meridional* geometry. We have also shown that the preformed cluster [Zn$_4$OL$_6$] is not a suitable precursor for the synthesis of polynuclear complexes by transmetallation reactions.

Supplementary material

Tables of anisotropic displacement parameters and structure factors (10 pages) are available from author E.C.C.

Acknowledgement

We thank the Science and Engineering Research Council for support.

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