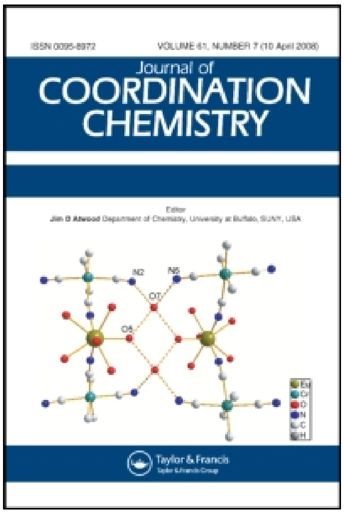

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Synthesis, Spectroscopic and X-ray Structural Study of *cis*-diazidobis-(ethylenediamine)Cobalt(III) Thiocyanate

Raj Pal Sharma[a]; Rajni Sharma[a]; Ritu Bala[a]; Miguel Quiros[b]; Juan M. Salas[b]
[a] Department of Chemistry & Centre of Advanced Studies, Panjab University, Chandigarh - 160 014, India [b] Departamento de Quimica Inorganica, Facultad de Ciencias, Universidad de Granada, 18071 Granada, Spain

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SYNTHESIS, SPECTROSCOPIC AND X-RAY STRUCTURAL STUDY OF *cis*-DIAZIDOBIS-(ETHYLENEDIAMINE)COBALT(III) THIOCYANATE

RAJ PAL SHARMA[a,*], RAJNI SHARMA[a], RITU BALA[a],
MIGUEL QUIROS[b] and JUAN M. SALAS[b]

[a]*Department of Chemistry & Centre of Advanced Studies, Panjab University, Chandigarh – 160 014, India;* [b]*Departamento de Quimica Inorganica, Facultad de Ciencias, Universidad de Granada, 18071 Granada, Spain*

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Reaction of *cis*-diazidobis(ethylenediamine)cobalt(III)nitrate with ammonium thiocyanate in a 1 : 2 molar ratio in aqueous medium gave the title cobalt(III) compound, *cis*-$[Co(en)_2(N_3)_2]SCN$, as reddish brown crystals in almost quantitative yield. The complex salt was characterized by elemental analysis, IR, electronic, ^1H and ^{13}C NMR spectroscopic studies. An X-ray structure determination revealed an ionic structure with the monoclinic space group $P2_1/c$, having cell dimensions $a = 12.1950(6)$, $b = 9.0317(5)$, $c = 12.6017(7)$ Å; $\beta = 113.419(1)^\circ$, $V = 1273.63(12)$ Å^3 and $Z = 4$. The structure was refined by a full-matrix least-square procedures to $R_1 = 0.0297$ and $wR_2 = 0.0697$.

Keywords: Cobalt III; X-ray crystallography; Spectroscopy; Ethylenediamine; Azide; Thiocyanate

INTRODUCTION

Cobalt(III) complexes continue to receive attention [1–3] owing to their important role in the development of inorganic chemistry. Cobalt is one of those trace metals that is present in the human body as a metal cofactor in the form of biologically important molecules such as the B_{12} coenzyme and vitamin B_{12} [4–7]. Cobalt is also known for its potent influence on human pathophysiological conditions, resulting either from its absence in the body, leading to anaemic symptoms [8], or its excessive presence, leading to toxic effects that result in heart disease [9]. While numerous azido divalent metal complexes are known, their corresponding cobalt(III) complexes are very rare [10–12]. Moreover, there are only a few reports of X-ray diffraction studies of azido cobalt(III) salts [13–15]. Therefore it was thought to be of interest to synthesize and study the title complex salt. Two isomers of the starting material, *cis* and *trans*, have

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[*] Corresponding author. E-mail: rpsharmapu@yahoo.com

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been reported [16]. In continuation of our interest [17–22] in cobalt(III) salts, this article reports the synthesis and characterization of *cis*-$[Co(en)_2(N_3)_2]SCN$.

EXPERIMENTAL

Caution: Azide salts as well as their complexes should be handled with care due to their explosive nature.

Materials

Technical grade reagents were used throughout this work without any further purification.

Instrumentation

Cobalt was determined [23] by a standard method and C, H, N were estimated microanalytically using a Perkin Elmer 2400 CHN instrument. IR spectra were recorded as Nujol mulls or KBr plates on a Perkin Elmer RXFT-IR system. ^1H and ^{13}C NMR spectra were recorded in DMSO-d_6 using a Bruker AC 300 F (300 MHz) spectrometer with TMS as internal reference. Electronic spectra were recorded in DMSO using a Hitachi 330 spectrometer.

Preparation

The complex salt *cis*-$[Co(en)_2(N_3)_2]NO_3$ was prepared according to a literature method [16]. A filtered, saturated solution of *cis*-$[Co(en)_2(N_3)_2]NO_3$ was treated with an excess of NH_4SCN. *cis*-$[Co(en)_2(N_3)_2]NO_3$ (1 g) was dissolved in 40 cm^3 of hot water and filtered. To this solution was added NH_4SCN (0.4591 g) dissolved in the minimum amount of water. Reddish-brown crystals appeared almost immediately and were filtered off, washed with ice-cold water and air-dried. The complex is freely soluble in water and DMSO but insoluble in acetone. The complex decomposes at 150°C. Elemental analyses are consistent with the composition $[Co(en)_2(N_3)_2]SCN$. Found: C, 19.8; H, 4.3; N, 46.5; Co, 18.0. Anal. Calcd. for the complex salt (%): C, 18.7; H, 4.9; N, 47.9; Co, 18.4.

Crystallography

Intensity data for a $0.33 \times 0.22 \times 0.05$ mm crystal were measured at room temperature on a Bruker Smart Apex CCD diffractometer with graphite-monochromatized MoKα radiation, $\lambda = 0.71073$ Å, such that θ_{max} was 25.92°. Of the total reflections measured, 2253 were unique.

This structure was solved using the SHELX-97 program [G.M. Sheldrick (1997), SHELXL97 and SHELXS97, University of Göttingen, Germany] and refined by a full-matrix least-squares procedure based on F^2. Crystallographic data are given in Table I. Fractional atomic coordinates are listed in Table II, selected interatomic parameters are given in Table III and the numbering scheme employed is shown in Fig. 1, drawn using XtalGX [S.R. Hall and D. Du Boulay (1997), Xtal-GX, University of Western Australia].

TABLE I Crystallographic data for *cis*-[Co(en)$_2$(N$_3$)$_2$]SCN

Empirical formula	$C_5H_{16}CoN_{11}S$
Formula weight	321.28
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Until cell dimensions	$a = 12.1950(6)$ Å
	$b = 9.0317(5)$ Å
	$c = 12.6017(7)$ Å
	$\beta = 113.419(1)^\circ$
Volume	1273.63(12) Å^3
Z	4
Calculated density	1.676 Mg m^{-3}
Absorption coefficient	1.515 mm^{-1}
F (000)	664
Crystal size	0.33 × 0.22 × 0.05 mm
Theta range for data collection	1.82 to 25.92°
Limiting indices	$-15 \leq h \leq 14,\ -10 \leq k \leq 10,\ -14 \leq l \leq 14$
Reflections collected/unique	12953/2253 [R(int) = 0.0292]
Completeness to theta = 25.92	91.1°
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9336 and 0.7605
Refinement method	Full-matrix least-squares on F^2
Weighting scheme	$w = 1/[\sigma^2(Fo^2) + (0.04P)^2 + 0.5P]$ where $P = (Fo^2 + 2Fc^2)/3$
Data/restraints/parameters	2253/0/163
Goodness-of-fit on F^2	1.039
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0262$, $wR2 = 0.0678$
R indices (all data)	$R1 = 0.0297$, $wR2 = 0.0697$
Largest diff. peak and hole	0.422 and − 0.209 e Å^{-3}

TABLE II Fractional atomic coordinates for *cis*-[Co(en)$_2$(N$_3$)$_2$]SCN

	x/a	y/b	z/c	U(eq)
Co	17300(2)	46590(3)	31515(2)	211(1)
N(1A)	211(2)	5615(2)	2402(2)	286(4)
N(2A)	− 397(2)	5311(2)	1385(2)	275(4)
N(3A)	− 1013(2)	5073(2)	406(2)	425(5)
N(4A)	1237(2)	3545(2)	4231(2)	312(4)
N(5A)	289(2)	3534(2)	4227(1)	278(4)
N(6A)	− 602(2)	3438(2)	4283(2)	428(5)
N(1E)	2325(2)	5878(2)	2192(2)	278(4)
C(1E)	3046(2)	7088(3)	2943(2)	395(5)
C(2E)	2457(2)	7618(3)	3724(2)	401(5)
N(2E)	2210(2)	6288(2)	4294(1)	295(4)
N(3E)	1307(1)	3024(2)	1991(1)	269(4)
C(3E)	2326(2)	2074(3)	2187(2)	361(5)
C(4E)	3043(2)	2046(2)	3506(2)	363(5)
N(4E)	3204(1)	3604(2)	3924(1)	291(4)
S	43865(6)	45395(8)	12585(5)	490(2)
C(1T)	5128(2)	4608(3)	2697(2)	380(6)
N(1T)	5622(2)	4653(3)	3719(2)	616(7)

RESULTS AND DISCUSSION

cis-Diazidobis(ethylenediamine)cobalt(III)thiocyanate has been synthesized by the reaction of *cis*-diazidobis(ethylenediamine)cobalt(III)nitrate with ammonium thiocyanate, as reported in the literature [16]. The composition of the complex was confirmed

TABLE III Selected bond angles (°) and distances (Å) for *cis*-$[Co(en)_2(N_3)_2]SCN$

N(1A)–Co–N(4E)	176.60(7)	Co–N(1A)	1.9175(17)
N(1A)–Co–N(4A)	94.02(7)	Co–N(4E)	1.9223(16)
N(4E)–Co–N(4A)	82.98(7)	Co–N(4A)	1.9686(17)
N(1A)–Co–N(1E)	88.02(7)	Co–N(1E)	1.9739(17)
N(4E)–Co–N(1E)	95.11(7)	Co–N(2E)	1.9773(17)
N(4A)–Co–N(1E)	174.76(7)	Co–N(3E)	1.9966(17)
N(1A)–Co–N(2E)	88.41(7)	N(1A)–N(2A)	1.230(2)
N(4E)–Co–N(2E)	93.08(7)	N(2A)–N(3A)	1.181(3)
N(4A)–Co–N(2E)	87.73(7)	N(4A)–N(5A)	1.154(2)
N(1E)–Co–N(2E)	87.51(7)	N(5A)–N(6A)	1.120(2)
N(1A)–Co–N(3E)	93.11(7)	N(1E)–C(1E)	1.484(3)
N(4E)–Co–N(3E)	85.51(7)	C(1E)–C(2E)	1.508(3)
N(4A)–Co–N(3E)	93.85(7)	C(2E)–N(2E)	1.490(3)
N(1E)–Co–N(3E)	90.85(7)	N(3E)–C(3E)	1.449(3)
N(2E)–Co–N(3E)	177.73(7)	C(3E)–C(4E)	1.541(3)
N(2A)–N(1A)–Co	118.54(14)	C(4E)–N(4E)	1.488(3)
N(3A)–N(2A)–N(1A)	177.1(2)	S–C(1T)	1.675(3)
N(5A)–N(4A)–Co	125.56(15)	C(1T)–N(1T)	1.185(3)
N(6A)–N(5A)–N(4A)	174.7(2)		
C(1E)–N(1E)–Co	106.80(13)		
N(1E)–C(1E)–C(2E)	109.55(18)	Hydrogen bond:	
N(2E)–C(2E)–C(1E)	107.37(18)	N(2E)···N(1T)	2.953(3)
C(2E)–N(2E)–Co	107.86(13)		
C(3E)–N(3E)–Co	111.01(13)		
N(3E)–C(3E)–C(4E)	105.92(16)		
N(4E)–C(4E)–C(3E)	107.71(17)		
C(4E)–N(4E)–Co	108.94(12)		
N(1T)–C(1T)–S	178.1(2)		

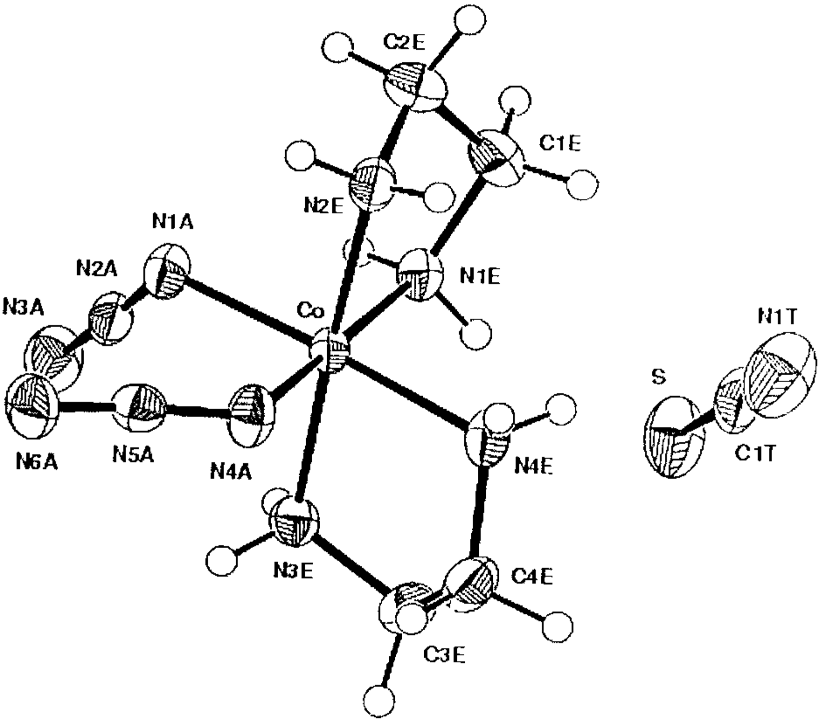

FIGURE 1 Molecular structure of *cis*-$[Co(en)_2(N_3)_2]SCN$.

by elemental analyses and electronic, IR and NMR spectroscopy. *cis*-[Co(en)$_2$(N$_3$)$_2$]-SCN formed in almost quantitative yield and its crystal structure has been established by single-crystal X-ray methods.

Tentative assignments of IR spectra have been made on the basis of earlier reports in the literature [24]. Two IR bands in the CH$_2$ rocking region at 797 and 894 cm^{-1} indicate a *cis* geometry [25]. Two strong bands at 2017 and 2045 cm^{-1} for the azide group confirm the *cis* geometry. The band at 458 cm^{-1} is assigned to δ(SCN) and a strong band at 2080 cm^{-1} to ν(SCN)$^-$ [26].

Electronic spectra of the complex salt were recorded in DMSO solution. The visible absorption spectra of the title complex is identical to that of the similar complex cation [16], and this is taken as evidence for isomeric purity. The complex absorbs strongly at 523 and 309 nm, corresponding to transitions [27] from the $^1A_{1g}$ ground state to singlet states $^1T_{1g}$ and $^1T_{2g}$, respectively.

NMR spectra of the salt were recorded in DMSO-d_6. Chemical shift values are expressed as δ (ppm) downfield from tetramethylsilane as internal standard. Three signals at 5.2, 4.8 and 4.1 ppm are attributed to nitrogen protons [28] of ethylenediamine while CH$_2$ protons of ethylenediamine group are observed at 2.5 ppm. The ^{13}C NMR spectrum shows characteristic signals at 45 ppm for carbons of ethylenediamine and at 134 ppm for the thiocyanate group [29].

The nature of the complex has been unambiguously established by single-crystal X-ray crystallography. The structure consists of [Co(en)$_2$(N$_3$)$_2$]$^+$ cations and SCN anions. In the complex cation *cis*-[Co(en)$_2$(N$_3$)$_2$]$^+$ the central metal cobalt is surrounded by six nitrogen atoms originating from two coordinated ethylenediamines and two azides, resulting in octahedral geometry, as expected. Bond lengths and angles for the title complex are comparable with those in *cis*-[Co(en)$_2$(N$_3$)$_2$]NO$_3$ given in the literature [13].

The ionic character of the SCN ion is indicated by comparison of bond lengths and angles in *cis*-[Co(en)$_2$(N$_3$)$_2$]SCN with those of NH$_4$SCN [30]. The bond lengths S–C = 1.675(3) Å, C–N = 1.185(3) Å and bond angle S–C–N = 178.1(2)° for *cis*-[Co(en)$_2$(N$_3$)$_2$]SCN while corresponding value for NH$_4$SCN are S–C = 1.645(9) Å, C–N = 1.173(5) Å, bond angle S–C–N = 179.6(4)°.

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Supplementary Data

Full lists of crystallographic data are available from the author on request.

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