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Trans-bis(benzo(1,3)-thiazole)bis(N,N-dimethylformamide)bis(N-thiocyanato)-cobalt(II): Spectroscopy, Thermal Analysis and Crystal Structure

E. S. RAPER*, R. E. OUGHTRED, J. R. CREIGHTON

School of Chemical and Life Sciences, Newcastle upon Tyne Polytechnic, Newcastle upon Tyne, NE1 8ST, U.K.

and I. W. NOWELL

Department of Chemistry, Sheffield City Polytechnic, Sheffield, S11 WB, U.K.

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Disolution of $Co(bzt)_2(NCS)_2$ *(bzt = benzo 1,3-thiazole) in dimethyl formamide (dmf) produces* $Co(bzt)_2(NCS)_2(dmf)_2$. *The stoichiometry of the complex has been established by a combination of chemical (C, H, N) and thermal analysis. The complex has an octahedral structure with pairs of ligands in* trans *configurations as well as a* CoN_4O_2 *coordination sphere with Co–N distances of 2.185(2) Å (bzt); 2.082(2) Å (NCS) and Co–O(dmf) of 2.118(2) Å. The infrared and electronic absorption spectra are consistent with this arrangement.*

Introduction

Interactions of benzo-1,3-thiazole (*bzt*) with cobalt(II) salts have invariably produced four coordinate complexes of type $Co(bzt)_2(X)_2$ (X = Cl, Br, I and NCS) [1, 2]. Attempts to prepare six coordinate complexes with cobalt(II) have produced products such as $[Co(bzt)_4(H_2O)_2](ClO_4)_2$ and $[Co(bzt)_4ClO_4)_2]$ whose unsatisfactory chemical analyses confirm their hygroscopic nature [1]. In order to complement a previous study [3] of $Co(bzt)_2Cl_2$, in which *bzt* is monodentate (N-donating) and cobalt occupies a pseudo-tetrahedral environment, a six-coordinate complex has been prepared by dissolving $Co(bzt)_2(NCS)_2$ in dimethylformamide (*dmf*).

Herein we report the crystal structure, spectroscopy and thermal analysis of $Co(bzt)_2(NCS)_2(dmf)_2$.

Experimental

Starting Materials

Benzothiazole was obtained from the Aldrich Chemical Company. The remaining chemicals were of reagent quality and were supplied by Phase Separations Ltd.

Analyses

C, H and N were analysed by Butterworths Microanalytical Services Ltd, Teddington, Middlesex.

Preparation

The complex $Co(bzt)_2(NCS)_2$ was prepared by a previously described method [1] and characterised by infrared spectroscopy, visible (electronic spectroscopy) and thermal analysis. These procedures established the stoichiometry of the compound and confirmed the presence of a tetrahedral CoN_4 chromophore in the complex. A small quantity (*ca.* 0.1000 g) of this complex was dissolved in *dmf*.

The resultant solution was filtered and set aside. After eighteen days small, well formed red crystals separated. These were removed by filtration, washed with a small quantity of cold *dmf*, then vacuum dried. Chemical analysis gave (Calc. (obs) %): C, 44.7(44.14); H, 4.1(4.01) and N, 14.2(14.30) for $Co(bzt)_2(NCS)_2(dmf)_2$.

Physical Measurement

Infrared spectra of *bzt*, *dmf* and the two complexes involved in this study were obtained as CsI discs in the range 4000–200 cm^{-1} from a PERKIN-ELMER 577 grating spectrophotometer. Solid state diffuse electronic spectra were obtained in the range 350 to 2600 nm from a CARY 17D spectrophotometer fitted with a reflectance attachment. Magnetic measurements were performed at room temperature on a Gouy balance using $Hg[Co(NCS)_4]_2$ as standard. Molecular susceptibilities were corrected for the diamagnetism of the component atoms by means of Pascal's constants. Thermal analysis curves (TG, DTG and DTA) were obtained from Stanton-Redcroft TG 750 and DTA 673/4 instruments. Sample masses were in the range 2–7 mg and heating rates were 10 or 20 °C min^{-1}. Platinum crucibles were used for the TG data and 3 cm quartz crucibles for the DTA results. Gas flow rates were 5 cm^3 min^{-1} for the TG (air) and 200 cm^3 min^{-1} (nitrogen) for the DTA. Calibration details for the quantitative DTA data are

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*Author to whom correspondence should be addressed.

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reported elsewhere [4]. X-ray powder photographs were recorded with a Philips XDC-700 camera incorporating Guinier-Hagg parafocussing geometry, monochromatised CuKα, (λ = 1.5405 Å) radiation and Kodirex single coated X-ray film.

Crystal Structure Analysis

Relevant crystal data are listed in Table I; intensity data were corrected for Lorentz, polarisation and absorption effects. With two formula units in the unit cell the cobalt atoms are crystallographically constrained to occupy centres of symmetry. A Fourier synthesis with the cobalt atom at, 0, 1/2, 1/2), generated the remaining non-H atomic coordinates which were refined by full-matrix least-squares analysis with anisotropic temperature factors. All the H-atoms were given idealised geometry (C–H = 1.08 Å). The aldehydic and the methyl H-atoms of the *dmf* molecule refined to final U (Å^2) values of 0.069(4) and 0.285(2) respectively. The corresponding value for the H-atoms of the *bzt* molecule is 0.067(2).

Scattering factors for all atoms were calculated from an analytical approximation [5]. Final atomic parameters are in Table II. All calculations were performed on the NUMAC, IBM 370/168 computer at the University of Newcastle upon Tyne. SHELX [6] and related programs were used in the analysis.

[Anisotropic temperature factors, observed and calculated structure factors, H-atom coordinates have been deposited with the Editor].

TABLE I. Crystallographic Data.

Compound	$CoC_{22}H_{24}N_6O_2S_4$
M_r	591.5
a, Å	9.138(2)
b, Å	10.301(3)
c, Å	14.426(3)
$\alpha = \gamma$, deg.	90
β, deg.	91.40(2)
U, Å^3	1356.5
Z	2
D_c, Mg.m^{-3}	1.45
D_m, Mg.m^{-3}	1.42
Space group	$P2_1/c$
Radiation; Å	monochromated MoKα; 0.71073
F(000)	1536
μ, cm^{-1}	19.68
Diffractometer	Enraf-Nonius CAD-4
Scan mode	$\theta - 2\theta$
2θ range, deg.	5.6 to 52.0
Total data	2655
$F_o > 2.0\sigma(F_o)$	2051
R	0.0369
R_w	0.0425
w	$2.2125/[\sigma^2(F_o) + 0.000590\ F_o{}^2]$

TABLE II. Final Fractional Coordinates (×10^4) and Equivalent Isotropic Temperature Factors, B_{eq} [22], with e.s.d.'s in Parentheses.

	x	y	z	B_{eq} (Å)^2
Co	0	5000	5000	2.40(2)
S(1)	1090(1)	8830(1)	6599(1)	4.31(4)
N(3)	631(3)	6955(2)	5439(2)	2.74(9)
C(2)	480(3)	7310(3)	6296(2)	3.4(1)
C(4)	1303(3)	7957(3)	4944(2)	2.8(1)
C(5)	1636(4)	9058(3)	5468(2)	3.4(1)
C(6)	2330(5)	10134(3)	5076(3)	5.2(2)
C(7)	2645(6)	10076(4)	4157(3)	6.0(2)
C(8)	2299(5)	8980(3)	3621(2)	4.8(2)
C(9)	1638(4)	7911(3)	4003(2)	3.4(1)
O(1)	1954(2)	4849(2)	4247(1)	3.22(9)
C(10)	2953(3)	4055(3)	4390(2)	3.1(1)
N(1)	4242(3)	4117(3)	4007(2)	3.7(1)
C(11)	5353(4)	3133(4)	4186(3)	6.4(2)
C(12)	4564(5)	5157(4)	3345(3)	5.9(2)
N(2)	1076(3)	4236(2)	6167(2)	3.36(2)
C(13)	1713(3)	3468(3)	6587(2)	2.8(1)
S(2)	2626(1)	2366(1)	7175(1)	4.41(4)

Results and Discussion

The red crystalline product obtained from a solution of $Co(bzt)_2(NCS)_2$ in *dmf* has a room temperature magnetic moment of 5.20 B.M. which is consistent with six coordinate cobalt(II). The diffuse reflectance spectrum of the complex consists of a charge transfer band (385 nm, 28 571 cm^{-1}) and two d–d absorptions. The ν_2 transition ($^4T_{1g}(F) \rightarrow {}^4T_1(P)$) occurs at 545 nm (18 349 cm^{-1}) and the ν_2 transition ($^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$) occurs at 1120 nm (8 929 cm^{-1}). The energy ratio ν_2/ν_1 of 2.05 agrees with the theoretical value (2.1–2.2) and confirms the assignment [7]. Calculation of D_q (942 cm^{-1}) [8] produces a value which is slightly less than that obtained for a CoN_6 chromophore [9] and appears to be consistent with a CoN_4O_2 system [7]. The value of B′ (471 cm^{-1}) was obtained from a graphical correlation of the ν_2/ν_1 and D_q/B ratios [7] and is probably unrealistically low.

The infrared spectrum of the complex clearly shows the presence of all three ligands. N-bonded thiocyanate is indicated by the presence of ν(C–N) at 2040 cm^{-1}, ν(C–S) at 820 cm^{-1} and δ(NCS) at 480 cm^{-1} [10]. Dimethylformamide has only one donor atom available and the ν(CO) band in the complex (1650 cm^{-1}) is only slightly shifted, relative to the free molecule (1670 cm^{-1}), upon coordination. Benzothiazole contributes many absorptions to the spectrum most of which are unchanged upon coordination. The major area of interest involves those bands due to the 'thioamide' portion of the molecule.

Of these the ν(C–N) and ν(N–C–S) bands occur at 1450 and 1420 cm^{-1} in the complex and are not significantly shifted upon coordination, they do however show some splitting. A complicating feature of this region of the spectrum is the presence of ν(C–H) bands of *dmf* at 1490, 1430 and 1390 cm^{-1} [11]. The ν(C–S) band of the ligand (660 cm^{-1}) is shifted to 680 cm^{-1} in the complex and suggests the possibility of an interaction between the 'thioamide' portion of *bzt* and the metal. The low frequency region of the complex (600–250 cm^{-1}) contains, in addition to δ(NCS), bands due to DMF (370 cm^{-1}) and *bzt* (430 cm^{-1}) but no ν(M–L) activity.

Thermogravimetric analysis (TG) (Fig. 1(a)) in air gives an overall mass loss of 88.0% (theor. 87.4%) to CoO in the temperature range 100 to 1000 °C. Stepped mass losses, obtained from the discontinuities on the TG curve, show a 48.0% mass loss in the temperature range 100–180 °C, which is consistent with the loss of two *bzt* molecules (theor. 45.5%), and a 22.0% mass loss in the range 180–250 °C is consistent with *dmf* loss (theor. 24.0%). Infrared spectra of the deposits obtained at 180 and 250 °C provided confirmation for these decomposition processes. The final stage (250–1000 °C) accounted for the conversion of $Co(NCS)_2$ to CoO.

A differential thermal analysis (DTA) (Fig. 1(b)) curve consists of a sharp endotherm ($T_p = 110$ °C) and a broad highly detailed endotherm whose profile was generally not reproducible. The enthalpy of the low temperature endotherm, 134.0 (±10.0) kJ·mol^{-1}, is rather large and suggests that some ligand removal also occurs at this temperature [12].

The cobalt(II) atoms are crystallographically constrained to occupy symmetry centres and are octahedrally coordinated by pairs of *trans* related *bzt*, *dmf* and thiocyanate groups (Fig. 3). The discrete molecules are held together by van der Waals forces, there are no H-bonds and no short intermolecular distances (Fig. 4).

The environment around the cobalt atom is essentially regular, the angles at the cobalt atom all being close to 90 °C (Table III, Fig. 3); however, the cobalt-nitrogen (thiocyanate) distance is significantly less than the corresponding distance to *bzt*.

Both the *bzt* and the *dmf* molecules are essentially planar (Table IV) and are twisted out of their respective equatorial planes. The dimensions of the coordinated *dmf* molecule are similar to those recently reported for $(\eta^5\text{-}C_5H_5)_2MoH_2\cdot ZnBr_2\cdot DMF$ [13]. Bond lengths and angles within the *bzt* molecule (Fig. 2) are similar to those which have been

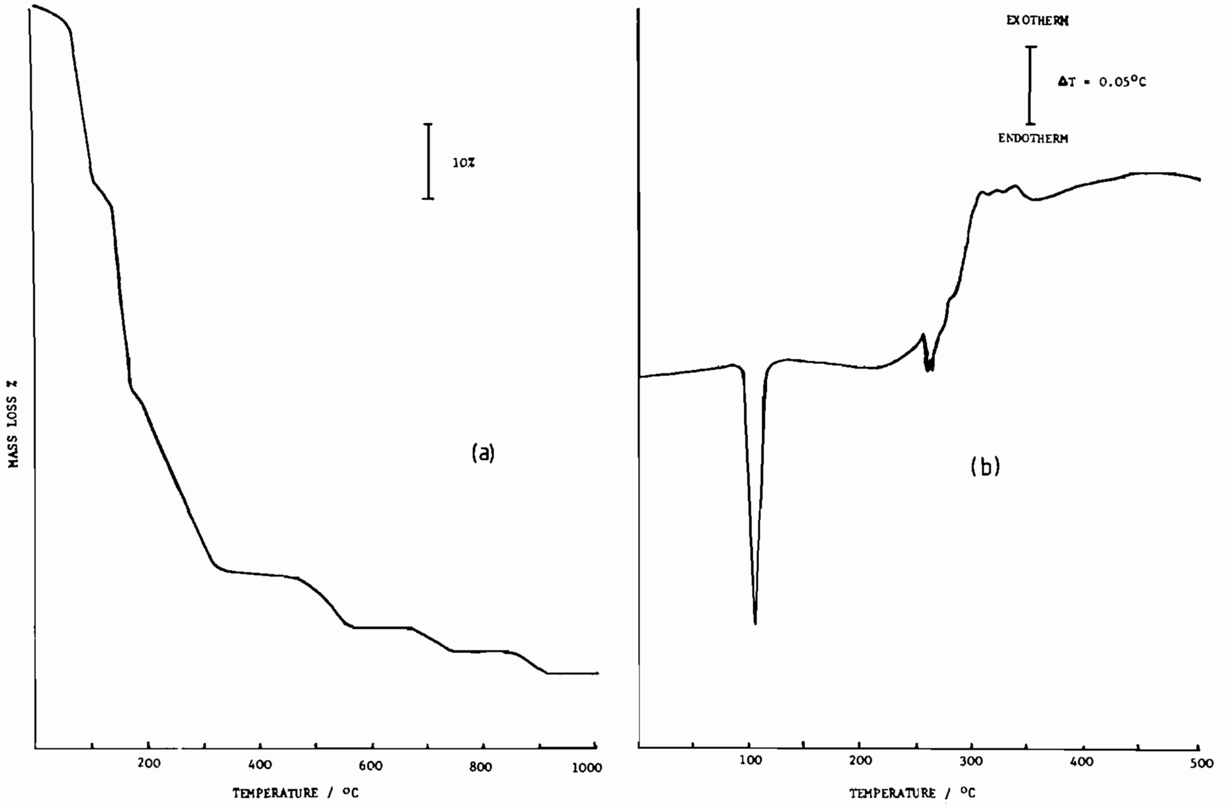

Fig. 1. Thermogravimetric analysis curves of the complex: (a) TG curve, (b) DTA curve.

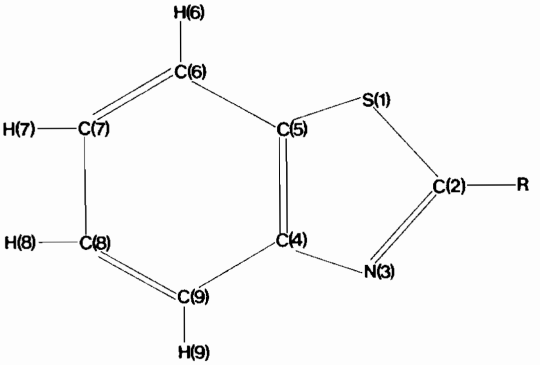

Fig. 2. Benzo-1,3-thiazole with atomic labelling (R = H).

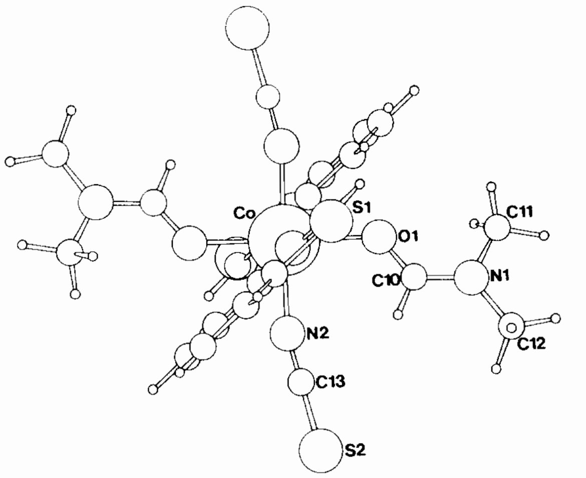

Fig. 3. Perspective view of the complex with atomic labelling.

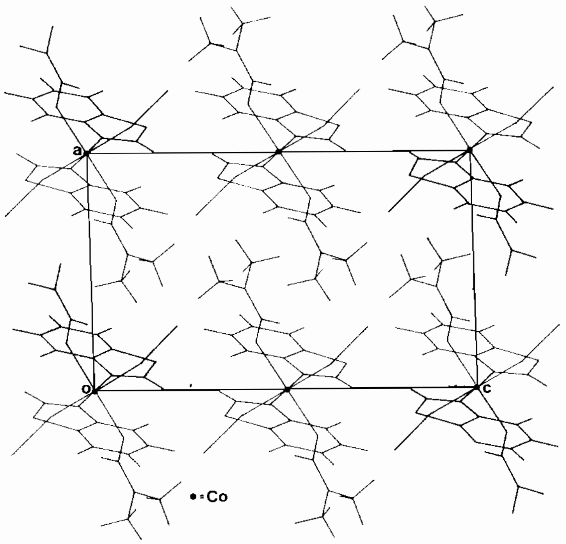

Fig. 4. Unit cell contents viewed down *b*.

reported for related coordinated molecules [14, 15]. A distinctive feature in the complexes of benzothiazole and its derivatives is the presence of localised

TABLE III. Bond Lengths (Å) and Angles (°) with e.s.d. in Parentheses.

Symmetry code – None x, y, z;

The coordination sphere			
Co–O(1)	2.118(2)	N(2)–Co–N(3)	89.9(1)
Co–N(2)	2.082(2)	N(2)–Co–O(1)	90.0(1)
Co–N(3)	2.185(2)	N(3)–Co–O(1)	89.8(1)
		Co–N(2)–C(13)	155.7(2)
		Co–O(1)–C(10)	126.2(2)
		Co–N(3)–C(2)	120.1(2)
		Co–N(3)–C(4)	130.2(2)
The bzt molecules			
S(1)–C(2)	1.715(3)	C(2)–S(1)–C(5)	89.0(1)
C(2)–N(3)	1.299(4)	S(1)–C(5)–C(4)	109.7(2)
N(3)–C(4)	1.405(4)	C(5)–C(4)–N(3)	114.5(2)
C(4)–C(5)	1.392(4)	C(4)–N(3)–C(2)	109.6(2)
C(5)–S(1)	1.734(3)	N(3)–C(2)–S(1)	117.2(2)
C(5)–C(6)	1.404(5)	C(9)–C(4)–C(5)	120.3(3)
C(6)–C(7)	1.365(6)	C(4)–C(5)–C(6)	121.3(3)
C(7)–C(8)	1.399(5)	C(5)–C(6)–C(7)	117.7(3)
C(8)–C(9)	1.377(5)	C(6)–C(7)–C(8)	121.4(4)
C(9)–C(4)	1.399(4)	C(7)–C(8)–C(9)	121.3(3)
		C(8)–C(9)–C(4)	118.0(3)
		S(1)–C(5)–C(6)	129.0(3)
		C(9)–C(4)–N(3)	125.3(3)
The thiocyanate groups			
N(2)–C(13)	1.147(4)	N(2)–C(13)–S(2)	179.4(3)
C(13)–S(2)	1.633(3)		
The dmf molecules			
C(10)–O(1)	1.239(4)	O(1)–C(10)–N(1)	124.2(3)
C(10)–N(1)	1.315(4)	C(10)–N(1)–C(12)	120.3(3)
N(1)–C(11)	1.453(5)	C(10)–N(1)–C(11)	121.4(3)
N(1)–C(12)	1.470(5)	C(12)–N(1)–C(11)	118.3(3)

TABLE IV. Equations of Selected Least Squares Mean Planes with Atomic Displacements (Å) and Relevant Dihedral Angles (°).

Plane 1

bzt

$0.8968X - 0.3867Y + 0.2148Z + 0.5757 = 0$

[N3 0.0045; C2 0.0057; S1 −0.0091; C4 −0.0007; C5 −0.0057; C6 0.0094; C7 0.0043; C8 −0.0070; C9 −0.0012]

Plane 2

dmf

$0.3552X + 0.5561Y + 0.7514Z - 7.9883 = 0$

[O1 −0.0061; N1 0.0184; C10 0.0014; C11 −0.0094; C12 −0.0043]

Dihedral angles	Planes	Angle (°)
	Co N3 O1/bzt	42.3
	Co N3 N2/bzt	48.0
	Co N3 O1/dmf	56.3
	Co N3 N2/dmf	81.6
	bzt/dmf	74.6

π-density in the S(1)–C(2)–N(3) portion of the molecule. Within uncoordinated benzothiazole derivatives the C–S bonds range from 1.73 to 1.78 Å while the C–N distances in the range 1.28–1.45 Å, are frequently significantly different from one another [16]. Consequently, localisation of π-density appears to be significant in this structure as it was in $Co(btz)_2Cl_2$ [3]. Such localisation is possibly part of the process of optimising the factors which are likely to favour a π-interaction between the d-orbitals of the cobalt atom and the π-MO system of the heterocyclic molecule. Narrowing of the Co–N(3)–C(2) angle (120.1(2)°) at the expense of the Co–N(3)–C(4) (130.2(2)°) value favours this process. However the Co–N(3) distance, 2.185(5) Å is in the range for many N-donating heterocycles [17–20] and the Co···C(2) distance, 3.185(3) Å is rather long for a strong π-interaction. Consequently a change of environment with the metal in a low oxidation state, appears to be necessary in order to stabilise such an interaction [21].

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