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Crystal Structures and Characterization of Cobalt(II), Manganese(II), and Zinc(II) Complexes of 2-[Bis-(2-benzimidazolylmethyl)amino]ethanol

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Cobalt(II), manganese(II), and zinc(II) complexes with the tripodal ligand, 2-[Bis(2-benzimidazolylmethyl)-amino]ethanol, bbt, were prepared and characterized by infrared and electronic spectra, magnetism, and conductivities. Their crystal structures were determined by X-ray diffraction method. Crystal data: [Co(bbt)(NCS)$_2$] (**1**), space group $P2_12_12_1$(orthorhombic), a=12.881(1), b=17.970(2), c=9.076(1) Å; [Mn(bbt)(NCS)$_2$](**2**), space group $P2_12_12_1$(orthorhombic), a=18.179(2), b=13.073(2), c=9.097(2) Å; [Zn(bbt)(NCS)$_2$](**3**), space group $P2_1/a$(monoclinic), a=15.421(4), b=14.803(4), c=10.589(3) Å, β=115.81(2)°. The final R values are 0.044 (**1**), 0.054 (**2**), and 0.079 (**3**), for non-hydrogen atoms. The coordination geometries of **1** and **2** can be described as a distorted octahedron. In **3**, the alcoholic oxygen of bbt is not in coordination, hence the zinc ion is five-coordinated forming a highly distorted trigonal bipyramid. In all the complexes, thiocyanate ions coordinate in *cis* form with the nitrogen atoms. The magnetic measurements revealed that **1** and **2** are high spin complexes.

In some metalloenzymes, imidazole nitrogen of histidine moiety coordinates to a metal ion in the active sites.[1] The X-ray crystallographic study of the zinc enzyme, carboxypeptidase A,[2] have revealed the active site structure where two imidazoles are bound to the zinc(II) ion. The metal-substituted carboxypeptidase A showed remarkable changes from the native enzyme in the peptidase and esterase activities.[3] One of the origins of the changes was ascribed to the structural rearrangement of the active site due to the change in coordination occured on the metal ion. Thus, it is interesting to examine for a series of metal complexes how the coordination structure changes depending on metal ions.

In a preceding paper,[4] we reported the crystal structures of [Cu(bbt)X]ClO$_4$·CH$_3$OH(X is Cl or Br), whose coordination geometry is a square pyramid. The ligand, bbt, is a benzimidazole-containing ligand with a 3N1O mixed donor set,[5] as shown in Fig. 1, and has a substantial flexibility in coordination structure.

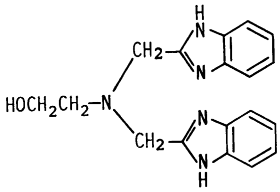

Fig. 1. Chemical structure of bbt.

In this study, we prepared the Co(II), Mn(II), and Zn(II) complexes with the general formula, [M$^{\mathrm{II}}$(bbt)(NCS)$_2$], and determined their crystal structures by X-ray diffraction method in order to investigate the metal-dependent feature of coordination structure. Furher characterizations were carried out by infrared and electronic spectra, magnetism, and conductivities. A part of this work was reported as preliminary form.[6]

Experimental

Preparations. The ligand, bbt, was prepared as described previously.[5] [Co(bbt)(NCS)$_2$](**1**), [Mn(bbt)(NCS)$_2$](**2**), and [Zn(bbt)(NCS)$_2$](**3**) were prepared by the following method. A methanol solution (10 ml) of respective metal(II) nitrate hexahydrate (2 mmol) and a hot methanol solution (30 ml) of bbt·H$_2$O (2 mmol) were mixed. To this solution was added a methanol solution(10 ml) of NH$_4$NCS (5 mmol). The resulting solution was allowed to stand for several days, the crystals of **1**, **2**, and **3** were obtained as violet irregular prisms, pale pink prisms, and colorless columnar crystals, respectively. They were filtered and dried *in vacuo* on P$_2$O$_5$ for 2 d. **1** Found: C, 48.31; H, 3.86; N, 19.32%. Calcd for C$_{20}$H$_{19}$N$_7$OS$_2$Co: C, 48.39; H, 3.86; N, 19.75%. **2** Found: C, 48.83; H, 3.93; N, 19.87%. Calcd for C$_{20}$H$_{19}$N$_7$OS$_2$Mn: C, 48.78; H, 3.89; N, 19.91%. **3** Found: C, 47.81; H, 3.78; N, 19.19%. Calcd for C$_{20}$H$_{19}$N$_7$OS$_2$Zn: C, 47.77; H, 3.81; N, 19.50%.

Measurements. Infrared spectra were recorded by a Hitachi-Perkin Elmer Grating Infrared Spectrophotometer Model 225. Magnetic susceptibilities were measured by the Faraday method. Conductivities of solutions were measured at 25±1 °C, using a Yanaco Conductivity Outfit MY-8. Absorption spectra were recorded by the use of a Shimadzu UV-240 spectrophotometer for 200—850 nm and a Shimadzu MPS-5000 spectrophotometer for 650—1400 nm. Absorption spectra on nujol mull were obtained by the latter instrument for 250-1400 nm.

X-Ray Crystallographic Analyses. Reflection data of the complexes were measured on a Rigaku-Denki Automatic Four-circle Diffractometer AFC-5, using graphite monochromated Mo $K\alpha$ radiation (λ=0.71069 Å) at 294±1 K. Lattice constants were determined from least-squares fit of 25 strong reflections for **1**($18<2\theta<31°$), 20 reflections for **2**($21<2\theta<39°$), and **3**($18<2\theta<33°$). Intensity data were collected by the $\omega-2\theta$ scan technique in the range of $2.5<2\theta<50°$ with a scan rate of 6°/min for **1**, and 8°/min for **2** and **3**. For weak reflections, the intensity measurement was repeated up to three times depending on their intensities. Three standard reflections were monitored after every 97 reflections, and their intensities of each complex showed good stability during the data collection. The intensity data were corrected for Lorentz and polarization effects, but not for absorption. Independent reflections with $|F_o|>3\sigma(|F_o|)$ were considered as "observed" and used in the structure analyses.

The structure of each complex was solved by the heavy atom and successive Fourier and difference-Fourier methods, and refined by the block-diagonal least-squares procedures. The final refinements were performed using anisotropic ther-

Table 1. Crystallographic and experimental data for the complexes **1**, **2**, and **3**

Complex	**1**	**2**	**3**
Space group	$P2_12_12_1$ (orthorhombic)	$P2_12_12_1$ (orthorhombic)	$P2_1/a$ (monoclinic)
a/Å	12.881(1)	18.179(2)	15.421(4)
b/Å	17.970(2)	13.073(2)	14.803(4)
c/Å	9.076(1)	9.097(2)	10.589(3)
β/°			115.81(2)
V/Å^3	2100.8(4)	2161.9(7)	2176(1)
Z	4	4	4
D_c/g cm^{-3}	1.57	1.43	1.54
D_m/g cm^{-3} a)	1.57	1.49	1.56
μ(Mo $K\alpha$)/cm^{-1}	10.7	8.1	13.7
Crystal size/mm^3	0.3×0.4×0.5	0.3×0.3×0.6	0.4×0.4×0.5
No. of unique reflections ($\lvert F_o\rvert>3\sigma(\lvert F_o\rvert)$)	2007	2583	2462
R_1 c)	0.044	0.054	0.079
R_2 d)	0.051	0.060	0.087
Largest peak/eÅ^{-3} b)	0.50	0.42	0.74

a) Measured by n-C_6H_{14}/$BrCH_2CH_2Br$ floatation. b) Largest peak in the final difference-Fourier map. c) $R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$. d) $R_2=[\Sigma(|F_o|-|F_c|)^2/\Sigma|F_o|^2]^{1/2}$.

Table 2. Atomic positional(×10^4) and thermal parameters with their estimated standard deviations in parentheses

[Co(bbt)(NCS)$_2$] (**1**)

Atom	x	y	z	B_{eq}/Å^2
Co	1262(1)	1712.6(4)	−746(1)	1.9
N(A)	−86(5)	1843(4)	−1995(7)	3.2
C(A)	−934(5)	1912(4)	−2362(7)	2.5
S(A)	−2138(1)	2024(1)	−2930(2)	3.2
N(B)	543(5)	1887(3)	1226(6)	3.0
C(B)	404(5)	1752(4)	2460(8)	2.9
S(B)	190(2)	1571(1)	4196(2)	4.1
N(1)	1812(4)	2747(3)	−1445(6)	2.4
N(2)	2533(5)	3429(3)	−3238(6)	3.0
C(1)	2355(5)	2734(4)	−2693(8)	2.6
C(2)	1620(5)	3506(4)	−1161(7)	2.3
C(3)	1086(5)	3842(4)	9(8)	2.7
C(4)	967(6)	4605(4)	−50(9)	3.4
C(5)	1360(7)	5032(4)	−1234(9)	3.8
C(6)	1938(6)	4704(4)	−2366(9)	3.6
C(7)	2053(5)	3937(4)	−2295(8)	2.8
N(3)	1101(4)	565(3)	−1039(6)	2.4
N(4)	1480(5)	−484(3)	−2267(7)	2.9
C(8)	1634(5)	267(4)	−2115(8)	2.7
C(9)	515(5)	−14(4)	−451(8)	2.5
C(10)	−237(6)	−18(4)	685(9)	2.9
C(11)	−715(6)	−678(4)	1021(8)	2.9
C(12)	−455(6)	−1348(4)	274(9)	3.4
C(13)	301(6)	−1355(4)	−866(9)	3.1
C(14)	754(5)	−676(4)	−1188(8)	2.7
N(5)	2551(5)	1408(3)	−2396(6)	2.7
C(15)	2692(6)	2040(4)	−3440(8)	3.2
C(16)	2253(6)	721(4)	−3196(8)	2.9
C(17)	3509(6)	1249(5)	−1502(9)	3.4
C(18)	3599(5)	1777(5)	−191(8)	3.4
O	2684(3)	1634(3)	707(5)	2.6

[Mn(bbt)(NCS)$_2$] (**2**)

Atom	x	y	z	B_{eq}/Å^2
Mn	797.6(4)	1391(1)	1830(1)	2.2
N(A)	666(4)	2784(5)	623(7)	4.0
C(A)	594(3)	3605(5)	187(7)	3.1
S(A)	465(1)	4761(1)	−444(2)	3.7
N(B)	642(4)	2002(5)	3950(6)	4.1
C(B)	788(4)	2145(5)	5184(8)	3.3
S(B)	974(1)	2367(2)	6887(2)	4.6
N(1)	1978(3)	1432(4)	1452(5)	2.9
N(2)	3005(3)	1008(4)	230(6)	3.2
C(1)	2264(4)	879(5)	361(7)	3.0
C(2)	2556(3)	2000(5)	2015(7)	2.8
C(3)	2565(4)	2734(5)	3133(8)	3.2
C(4)	3233(4)	3194(5)	3474(8)	3.5
C(5)	3886(4)	2911(6)	2722(9)	3.8
C(6)	3886(4)	2169(5)	1601(8)	3.4
C(7)	3208(4)	1735(5)	1271(7)	3.0
N(3)	−224(3)	720(4)	1017(6)	2.7
N(4)	−864(3)	−70(4)	−745(6)	3.4
C(8)	−183(4)	155(5)	−204(7)	3.0
C(9)	−977(3)	880(5)	1267(6)	2.5
C(10)	−1317(3)	1419(5)	2399(7)	3.0
C(11)	−2081(4)	1495(6)	2321(8)	3.8
C(12)	−2487(4)	1045(7)	1169(9)	4.3
C(13)	−2157(4)	481(6)	71(9)	4.2
C(14)	−1378(4)	405(5)	163(7)	3.2
N(5)	1129(3)	−45(4)	110(6)	2.9
C(15)	1809(4)	247(6)	−675(7)	3.3
C(16)	510(4)	−194(6)	−897(7)	3.8
C(17)	1281(5)	−969(5)	1043(8)	3.8
C(18)	746(5)	−1039(5)	2315(7)	3.6
O	887(2)	−151(3)	3248(5)	3.0

Table 2. Continued

[Zn(bbt)(NCS)$_2$] (**3**)

Atom	x	y	z	B_{eq}/Å^2
Zn	2859(1)	4483(1)	1273(1)	4.1
N(A)	2983(6)	3339(5)	2418(9)	5.5
C(A)	3300(7)	2821(6)	3290(10)	4.2
S(A)	3781(2)	2101(2)	4542(3)	5.2
N(B)	2706(7)	4059(6)	−557(8)	5.9
C(B)	2710(7)	3808(7)	−1554(10)	4.6
S(B)	2708(3)	3391(3)	−2971(3)	7.5
N(1)	4188(5)	4953(5)	2479(7)	3.5
N(2)	5231(5)	6007(5)	3696(7)	3.6
C(1)	4329(7)	5827(6)	2730(8)	3.4
C(2)	5054(6)	4521(6)	3309(8)	3.2
C(3)	5336(7)	3617(6)	3410(9)	3.9
C(4)	6280(7)	3407(7)	4297(10)	4.4
C(5)	6961(7)	4092(7)	5087(10)	4.7
C(6)	6689(7)	4988(7)	4988(10)	4.5
C(7)	5725(6)	5185(6)	4071(8)	3.5
N(3)	1735(6)	5138(5)	1307(7)	3.9
N(4)	770(5)	6321(5)	1042(8)	4.1
C(8)	1474(6)	5972(6)	804(9)	3.8
C(9)	1103(6)	4923(6)	1894(9)	3.8
C(10)	1012(7)	4141(7)	2586(10)	4.7
C(11)	334(8)	4157(8)	3124(11)	5.4
C(12)	−262(8)	4918(8)	2986(11)	5.6
C(13)	−182(7)	5687(7)	2286(11)	5.1
C(14)	496(6)	5669(6)	1741(10)	4.2
N(5)	2967(6)	6183(5)	565(7)	4.1
C(15)	3573(7)	6519(6)	2008(8)	3.6
C(16)	1950(7)	6482(7)	51(10)	4.0
C(17)	3337(8)	6438(9)	−478(11)	5.8
C(18)	4351(10)	6209(9)	−119(12)	6.7
O	4995(6)	6890(5)	790(9)	6.5

Table 3. Selected interatomic distances and angles of the coordination spheres of **1**, **2**, and **3** with their estimated standard deviations in parentheses

Complex	**1**	**2**	**3**
Distances(l/Å)			
M-N(A)	2.086(6)	2.140(6)	2.045(9)
M-N(B)	2.040(6)	2.107(6)	1.951(10)
M-N(1)	2.089(6)	2.175(5)	2.008(7)
M-N(3)	2.089(5)	2.183(5)	2.090(9)
M-N(5)	2.302(6)	2.517(5)	2.652(8)
M-O	2.262(4)	2.400(4)	—
N(A)-C(A)	1.148(9)	1.152(9)	1.133(13)
C(A)-S(A)	1.647(7)	1.633(7)	1.607(10)
N(B)-C(B)	1.160(9)	1.168(9)	1.119(16)
C(B)-S(B)	1.633(8)	1.612(7)	1.624(12)
Angles(ϕ/°)			
N(A)-M-N(B)	94.7(2)	97.6(2)	105.1(4)
N(A)-M-N(1)	91.0(2)	90.5(2)	96.0(3)
N(A)-M-N(3)	87.6(2)	94.2(2)	104.4(4)
N(A)-M-N(5)	105.9(2)	110.1(2)	162.4(3)
N(A)-M-O	176.2(2)	177.1(2)	—
N(B)-M-N(1)	106.5(2)	105.5(2)	113.1(4)
N(B)-M-N(3)	102.6(2)	110.4(2)	116.4(3)
N(B)-M-N(5)	159.2(2)	152.1(2)	91.3(3)
N(B)-M-O	82.3(2)	80.5(2)	—
N(1)-M-N(3)	150.9(2)	142.8(2)	118.1(3)
N(1)-M-N(5)	76.7(2)	71.6(2)	71.2(3)
N(1)-M-O	87.6(2)	92.2(2)	—
N(3)-M-N(5)	75.8(2)	72.2(2)	72.9(3)
N(3)-M-O	95.3(2)	84.4(2)	—
N(5)-M-O	77.3(2)	72.0(2)	—
M-N(A)-C(A)	163.9(6)	169.3(6)	160.1(8)
N(A)-C(A)-S(A)	178.4(4)	178.2(6)	178.2(9)
M-N(B)-C(B)	152.3(6)	155.5(6)	173.4(9)
N(B)-C(B)-S(B)	178.9(7)	178.5(7)	176.6(10)

mal parameters for non-hydrogen atoms. The final shifts in the atomic parameters were less than 53(**1**), 19(**2**), and 51%(**3**) of their estimated standard deviations. Final difference-Fourier map of each complex showed no significant electron density of non-hydrogen atom(>1 e Å^{-3}). The crystallographic data, some of the experimental details, and the R values of the complexes are given in Table 1.

All calculations were carried out on a FACOM M-200 computer at the Computer Center of Kyushu University by the use of local version[7] of the UNICS-II[8] and ORTEP programs.[9] The atomic scattering factors were adopted from the International Tables for X-ray Crystallography.[10] Lists of their structure factors and anisotropic thermal parameters have been deposited at the office of the Chemical Society of Japan as a Document No.8441.

The final positional and isotropic thermal parameters of **1**, **2**, and **3** are given in Table 2.

Results and Discussion

Molecular Structures. The ORTEP drawings of **1**, **2**, and **3** are shown in Figs. 2, 3, and 4, respectively. The atomic numberings are labelled in the same manner for all the complexes. Selected bond distances and angles of their coordination spheres are given in Table 3.

As shown in Fig. 2, coordination geometry of **1** is described as a distorted octahedron with the principal axis through N(A), Co, and O. The equatorial plane consists of N(1), N(3), N(5), and N(B). The molecular structure of **2** is similar to that of **1** in general aspect. Each coordination bond length of **2** is slightly longer than the corresponding bond length of **1**. The deviations of the equatorial atoms from the least-squares plane (see Table 4) are smaller for **1** than those for **2**. The bond length differences between **1** and **2** are similar to those between the Co(II) and Mn(II) complexes of [M^{II}(2,2′-bipyridine)$_2$(NCS)$_2$].[11]

The ligand arrangements of **1** and **2** are similar to that of the already reported [Cu(bbt)X]ClO$_4$·CH$_3$OH (X is Cl or Br).[4] In these complexes, the three donor nitrogens(N(1), N(3), N(5)) of bbt occupy three vertexes of the basal plane of a square pyramid and the alcoholic oxygen(O) the apical position. The two benzimidazolyl planes[12] are nearly parallel (dihedral angle of the two planes: 19.5° for **1**; 16.7° for **2**; 4.7° for [Cu(bbt)X]ClO$_4$·CH$_3$OH(X is Cl or Br)).

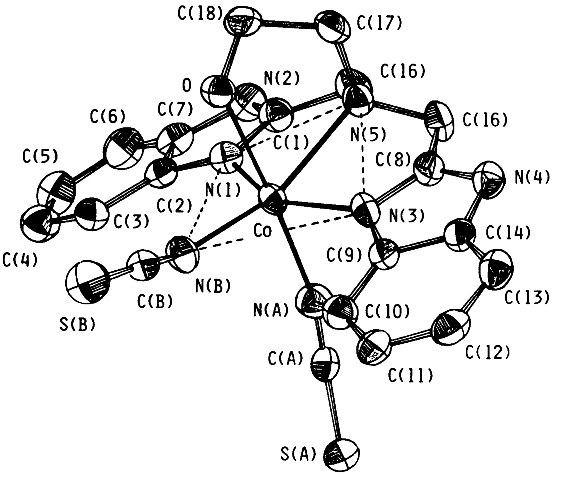

Fig. 2. ORTEP drawing of $[Co(bbt)(NCS)_2]$(**1**) (thermal ellipsoids are drawn at 50% probability level).

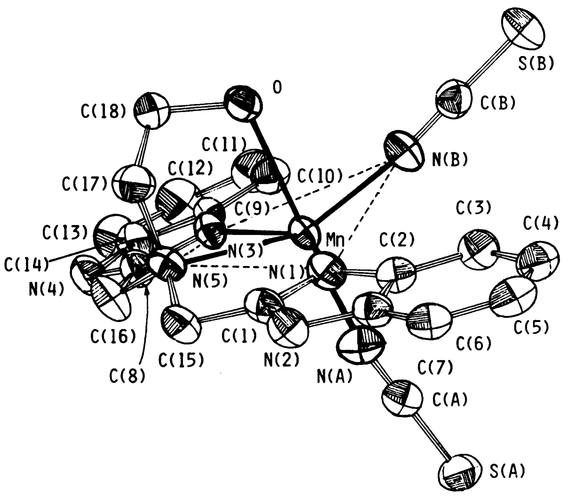

Fig. 3. ORTEP drawing of $[Mn(bbt)(NCS)_2]$(**2**) (thermal ellipsoids are drawn at 50 % probability level).

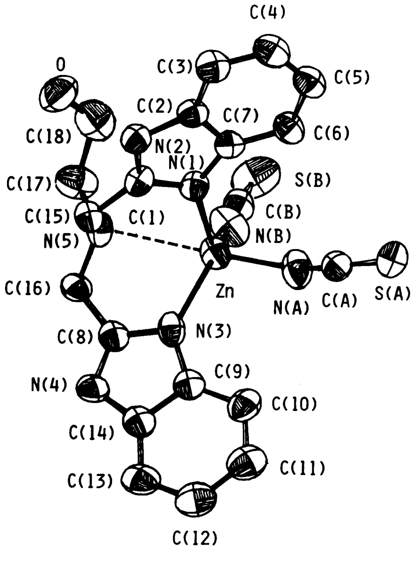

Fig. 4. ORTEP drawing of $[Zn(bbt)(NCS)_2]$(**3**) (thermal ellipsoids are drawn at 50 % probability level).

The metal-dependent nature of bbt appears in the Zn(II) complex, **3**. As shown in Fig. 4, the alcoholic oxygen does not coordinate to Zn(II) ion. The coordination number of Zn(II) is five, and the geometry can be regarded as a highly distorted trigonal bipyramid with one weak coordination bond, Zn–N(5)(2.652(7) Å). The dihedral angle of the two benzimidazolyl planes(67.1°) is larger than those of **1**, **2**, and $[Cu(bbt)X]ClO_4 \cdot CH_3OH$(X is Cl or Br).

In all the present complexes, the two thiocyanate ions coordinate in *cis* form with their nitrogen atom. Each M–NCS bond is almost linear, the deviations of the M–N–C angles from 180° being in the range 6—28°.

Intermolecular Distances. Significant intermolecular distances less than 3.51 Å are listed in Table 5. The distances, N(4)–O in **1** and **3**, and N(2)–O in **2** are less than 3 Å, implying the presence of hydrogen bonds. The distances S(A)–O in **1** and **2**, and S(B)–O and S(A)–N(2) in **3** also suggest the presence of weak hydrogen bonds since their distances are less than or nearly equal to the sum of van der Waals radii of sulfur atom (1.8 Å) and oxygen(1.5 Å) or nitrogen atom(1.55 Å).[13]

In **1** and **2**, there seems to exist a contact between

TABLE 4. EQUATIONS OF LEAST-SQUARES PLANES OF THE EQUATORIAL ATOMS OF 1 AND 2, AND DEVIATIONS OF THE ATOMS IN THEIR COORDINATION SPHERES

Complex	Equation of least-squares plane[a)] [Deviations of atoms from the plane/Å]
	Plane through N(1), N(3), N(5), and N(B)
1	$0.7771x-0.1214y+0.6176z=0.6308$ [N(1) −0.226, N(3) −0.235, N(5) 0.273, N(B) 0.188, N(A) −2.237, O 2.096, Co −0.160]
2	$0.1210x-0.7897y+0.6015z=0.0266$ [N(1) −0.275, N(3) −0.263, N(5) 0.329, N(B) 0.209, N(A) −2.414, O 2.102, Mn −0.286]

a) The equation is expressed as $Ax+By+Cz=D$, where x,y,z are in Å units referred to the crystallographic axes.

TABLE 5. SELECTED CONTACT DISTANCES(<3.51 Å) OF THE COMPLEXES

Complex	Contact (i) – (ii)	Distance(l/Å)	Symmetry code of atom (ii)
1	N(4)-O	2.968(7)	$1/2-x,\ -y,\ z-1/2$
	S(A)-O	3.154(5)	$x-1/2,\ 1/2-y,\ -z$
	C(A)-S(B)	3.497(7)	$x,\ y,\ z-1$
	N(A)-S(B)	3.509(7)	$x,\ y,\ z-1$
2	N(2)-O	2.925(7)	$1/2-x,\ -y,\ z-1/2$
	S(A)-O	3.170(5)	$-x,\ 1/2+y,\ 1/2-z$
	C(A)-S(B)	3.480(7)	$x,\ y,\ z-1$
	N(A)-S(B)	3.487(7)	$x,\ y,\ z-1$
3	N(4)-O	2.876(11)	$x-1/2,\ 3/2-y,\ z$
	S(B)-O	3.307(8)	$1-x,\ 1-y,\ -z$
	S(A)-N(2)	3.341(8)	$1-x,\ 1-y,\ 1-z$

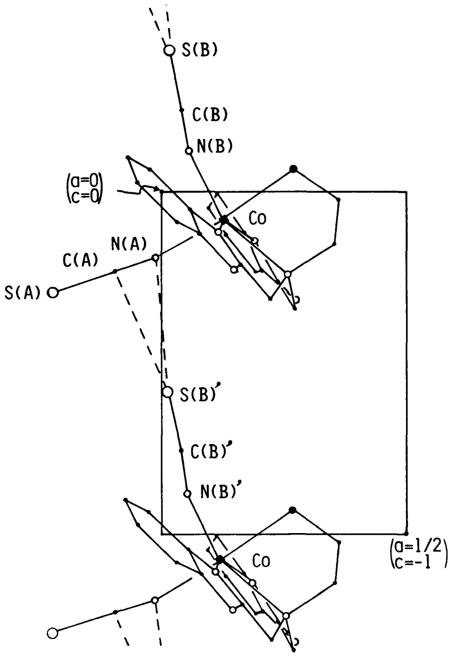

Fig. 5. Perspective view of the C≡N and S contact in the crystal **1**.

TABLE 6. ELECTRONIC SPECTRAL, CONDUCTANCE, AND MAGNETIC DATA

Complex	$\tilde{\nu}_{max}/10^3$ cm^{-1} a)		Λ_m	μ_{eff}/B.M. (295 K)
	Solution	Mull	Ω^{-1} mol^{-1} cm^2	
1	17.7[206] 13.0[≈16]	19.4 13.0^{sh}	82$^{b)}$	4.76
2			75$^{c)}$	5.99
3			80$^{b)}$	

a) Band maxima in visible region; sh indicates a shoulder; molar extinction coefficient ε(mol^{-1} cm^2) is in brackets. b) Solvent methanol at 1×10^{-3} mol dm^{-3} (25 °C). c) Solvent DMF at 1×10^{-3} mol dm^{-3}(25 °C).

thiocyanate C≡N and S of adjacent complex entities, as shown in Fig. 5. In the case of **3**, no such contact was observed.

Characterization of the Complexes. The infrared spectra of **1**, **2**, and **3** in KBr disks are similar to each other in 400—4000 cm^{-1} region. Each spectrum showed two sharp peaks due to the N-coordinated thiocyanate ions,[14] *i.e.*, at 2108 and 2070 cm^{-1} for **1**, 2097 and 2063 cm^{-1} for **2**, and 2093 and 2070 cm^{-1} for **3**. The splitting of the ν(CN) band is compatible with the *cis*-coordination of the two thiocyanate ions which was verified by X-ray analyses.

Electronic spectra, conductance, and magnetic data are listed in Table 6. The effective magnetic moments of **1** and **2** indicate that both are high spin complexes.[15] The electronic spectra of **1** in methanol and nujol mull are shown in Fig. 6. Both spectra show two broad bands in the visible region (*cf.* Table 6), which are assignable to the $^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$ and $^4T_{1g}\rightarrow{}^4A_{2g}$ transitions on the assumption of octahedral symmetry.[16] The high intensity and broadening of these bands are implying a considerable distortion from the regular octahedron. The molar conductance value of **1** in methanol indicates a 1 : 1 electrolyte,[17] suggesting that one of the thiocyanate ions is replaced by a methanol molecule. This is compatible with the observed spectral differences in band position and shape between two phases. The conductivity measurements also showed that **2** and **3** are 1 : 1 electrolytes in the solutions.[17] No bands due to d-d transitions were observed for **2** and **3** in either nujol or solution.

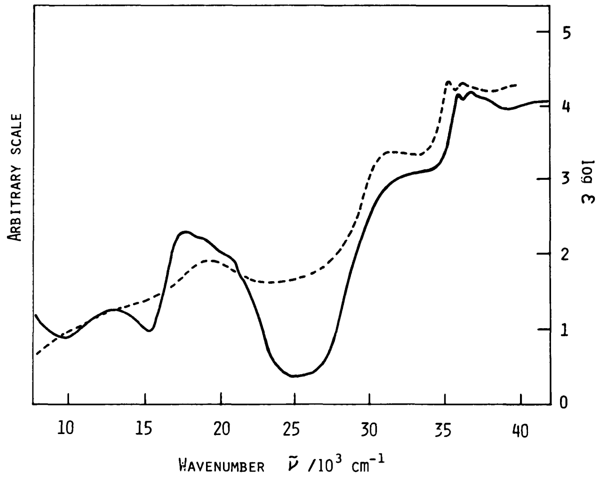

Fig. 6. Electronic spectra of **1**.
——: MeOH solution, ----: Nujol mull.

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