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Synthesis and characterization of Co(II), Ni(II), and Cu(II) complexes containing an eight-membered disulfanenitrile chelating ring

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Abstract

New types of λ^6 -sulfanenitrile-transition metal complexes, [MCl₂(ndsdsd)] (1) and [M(ndsdsd)₂]Cl₂ (2) (M = Co(II), Ni(II), Cu(II)), were obtained by reacting MCl₂ with bis[(nitrilo(diphenyl)- λ^6 -sulfanyl)](diphenyl)- λ^6 -sulfanediimide Ph₂S(=N-(Ph₂)S \equiv N)₂ (ndsdsd). The crystal structures of these complexes have been elucidated by X-ray crystallographic analysis. The results revealed that, in complexes 1 and 2, the two terminal nitrogen atoms chelate to the metal center to form an eight-membered sulfur-nitrogen ring. © 2008 Elsevier B.V. All rights reserved.

 $Keywords: \lambda^6$ -Sulfanenitrile; Sulfur-nitrogen ligand; Sulfur-nitrogen multiple bonds; Transition-metal complexes; X-ray structures

1. Introduction

The coordination chemistry of sulfur–nitrogen ligands has been extensively studied and has shown a unique variety of structures with a range of bonding modes [1,2]. The most commonly used starting material for the preparation of metal sulfur–nitrogen complexes is S_4N_4 , which reacts with a wide range of transition metal species. (Me₃SiNSN)₂S has also been used to generate palladium complexes of the [S_2N_3]⁻ anion [1c].

Glemser and Mews have reported that $F_3S \equiv N$ and $F_2RS \equiv N$ (R = e.g. Me₂N-, $F_2(O \equiv)S = N$ -) can easily be introduced into transition metal complexes by SO₂ displacement reactions [2]. Among these ligands, $F_2(O \equiv)S \equiv N - (F_2)S \equiv N$ has attracted special attention because of the structural properties of the complexes prepared with metal cations [2d,2f]. The X-ray structures of cobalt(II) and copper(II) complexes which were obtained from the reaction with [M(SO₂)_n][AsF₆]₂ (M = Co, Cu) show that

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the multifunctional ligand coordinates exclusively through the nitrogen atom of the SN triple bond and the alternating double-single-triple bond in the SNSN backbone of the ligand is maintained in the complexes. Very recently, we have succeeded in synthesizing a new type of λ^6 -sulfanenitrile with an SN triple bond at both ends, bis[(nitrilo(diphenyl)- λ^6 -sulfanyl)](diphenyl)- λ^6 -sulfanediimide Ph₂S(=N-(Ph₂)S=N)₂ (ndsdsd) [3]. This compound was prepared in an excellent yield from the one-pot synthesis of diphenylsulfimide (Ph₂SNH) with fluoro(diphenyl)- λ^6 -sulfanenitrile ($Ph_2FS \equiv N$) [4] in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and its molecular structure has been elucidated by X-ray crystallographic analysis. Moreover, the nucleophilic character of both end terminal nitrogen atoms in ndsdsd can be recognized in alkylation and sulfonation to vield the corresponding bis-iminosulfonium salts [3]. The aryl substituted λ^6 -sulfanenitriles such as $Ph_2RS \equiv N$ [R = e.g. Ph, Me, $Ph_2(X)S = N-(X = LP)$, HN=, O=), $Ph_2(HN=)S=C-]$ are much more stable even under acidic or alkaline conditions and have a much higher basicity of thiazyl nitrogen ($S^{VI} \equiv N$) than the above fluoro derivatives [5]. In particular, Ph₃S=N reacted with several electrophiles and CuCl₂ to give the corresponding

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iminosulfonium salts ([Ph₃S=N-R][X]: R = alkyl, tosyl, acyl, NO₂) and complexes ([CuCl₂(μ -NSPh₃)]₂ and [CuCl₂(Ph₃SN)₂]) [6]. The ndsdsd ligand has very interesting properties in metal complexes because of the electron-donating nature of the terminal thiazyl nitrogens, therefore reactions of ndsdsd with transition metal salts such as CoCl₂, NiCl₂, and CuCl₂ were performed to prepare their metal complexes. Here, we report the synthesis and the structural and spectroscopic characterizations of ndsdsd–Co(II), –Ni(II), and –Cu(II) complexes with eight-membered sulfur–nitrogen chelate rings.

2. Experimental

2.1. Material and general methods

All reagents and solvents were obtained commercially and were further purified by general methods when necessary. All NMR spectra were obtained with a Bruker Avance-400S with TMS as the internal standard. IR spectra were recorded on a Shimadzu FTIR-8400S spectrometer. UV–vis spectra were recorded on a Jasco V-550 spectrometer. Melting points were measured on a Yanaco Mp-J3 melting point apparatus. Elemental analyses were carried out at the Chemical Analysis Center of the College of Science and Technology, Nihon University.

2.2. Syntheses

The ligand, $Ph_2S(=N-(Ph_2)S\equiv N)_2$ (ndsdsd) was synthesized as previously described [3].

2.2.1. Preparation of $[MCl_2(ndsdsd)]$ (M = Co(II) (a), Ni(II) (b), Cu(II) (c)) (1)

A solution of ndsdsd $\cdot 2H_2O$ (65 mg, 0.1 mmol) in methanol (1.0 ml) was slowly added to a solution of MCl₂ (0.5 mmol) in the same solvent (0.5 ml) at ambient temperature, which started to precipitate a solid within 1 min (the solution of **2a** was precipitated with ether). The precipitate was then filtered, washed with methanol and dried under vacuum at 100 °C for 24 h, but appeared to be hygroscopic. Crystals suitable for X-ray analysis were obtained from saturated methanol (**1a**), methanol–ether (**1b**), and dichloromethane–methanol–ether (**1c**).

2.2.1.1. Data for 1a. Dark blue; Yield 94%, relative to ndsdsd · 2H₂O; mp 232–233 °C (decomp., monohydrate); IR (KBr) 3443, 1285, 1076, 1032, 984 cm⁻¹; UV–Vis (MeOH, λ_{max} , nm (ε , M⁻¹ cm⁻¹)) 207 (5.37 × 10⁴), 670 (3.90 × 10²); Anal. Calc. for C₃₆H₃₂Cl₂CoN₄OS₃: C, 56.69; H, 4.23; N, 7.35; Found: C, 56.53; H, 3.88; N, 7.36%.

2.2.1.2. Data for **1b**. Dark blue; Yield 98%, relative to ndsdsd \cdot 2H₂O; 237–239 °C (decomp., monohydrate); IR (KBr) 3383, 1277, 1076, 1031, 984 cm⁻¹; UV–Vis (MeOH, λ_{max} , nm (ε , M⁻¹ cm⁻¹)) 206 (6.19 × 10⁴), 694 (0.92 × 10²);

Anal. Calc. for C₃₆H₃₂Cl₂N₄NiOS₃: C, 56.71; H, 4.23; N, 7.35; Found: C, 56.66; H, 3.88; N, 7.37%.

2.2.1.3. Data for 1c. Dark yellow; Yield 95%, relative to ndsdsd · 2H₂O; 208–210 °C (decomp., monohydrate); IR (KBr) 3443, 1271, 1246, 1076, 1030, 984 cm⁻¹; UV–Vis (MeOH, λ_{max} , nm (ϵ , M⁻¹ cm⁻¹)) 208 (5.18 × 10⁴), 396 (sh) (7.70 × 10²); Anal. Calc. for C₃₆H₃₂Cl₂CuN₄OS₃: C, 56.35; H, 4.20; N, 7.30; Found: C, 56.36; H, 3.88, N, 7.21%.

2.2.2. Preparation of $[M(ndsdsd)_2]Cl_2$ (M = Co(II) (a), Ni(II) (b), Cu(II) (c)) (2)

A solution of MCl_2 (0.1 mmol) in methanol (1.0 ml) was slowly added to a solution of ndsdsd $\cdot 2H_2O$ (325 mg, 0.5 mmol) in the same solvent (1.0 ml) at ambient temperature. After stirring for 3 h, the solution was precipitated with ether. The precipitate was then filtered, washed with methanol and dried under vacuum at 100 °C for 24 h, but appeared to be hygroscopic. X-ray quality crystals were obtained by the slow diffusion of ether into methanol solutions of **2a–c**.

2.2.2.1. Data for **2a**. Dark blue; Yield 97%, relative to CoCl₂; 165–166 °C (decomp., dihydrate); IR (KBr) 3404, 1261, 1074, 1034, 984 cm⁻¹; UV–Vis (MeOH, λ_{max} , nm (ε , M⁻¹ cm⁻¹)) 208 (1.37 × 10⁵), 670 (9.00 × 10²); Anal. Calc. for C₇₂H₆₄Cl₂CoN₈O₂S₆: C, 61.97; H, 4.62; N, 8.03; Found: C, 61.89, H, 4.44, N, 8.00%.

2.2.2.2. Data for **2b**. Dark blue; Yield 98%, relative to NiCl₂·6H₂O; 165–167 °C (decomp., dihydrate); IR (KBr) 3382, 1261, 1074, 1031, 984 cm⁻¹; UV–Vis (MeOH, λ_{max} , nm (ε , M⁻¹ cm⁻¹)) 207 (1.09 × 10⁵), 694 (2.10 × 10²); *Anal*. Calc. for C₇₂H₆₄Cl₂N₈NiO₂S₆: C, 61.98; H, 4.62; N, 8.03; Found: C, 62.18, H, 4.43, N, 8.04%.

2.2.2.3. Data for 2c. Dark green; Yield 98%, relative to CuCl₂; 162–164 °C (decomp., dihydrate); IR (KBr) 3406, 1283, 1236, 1078, 1037, 986 cm⁻¹; UV–Vis (MeOH, λ_{max} , nm (ε , M⁻¹ cm⁻¹)) 208 (1.13 × 10⁵), 383 (6.75 × 10³); Anal. Calc. for C₇₂H₆₄Cl₂N₈CuO₂S₆: C, 61.76; H, 4.61; N, 8.00; Found: C, 61.83; H, 4.45; N, 7.96%.

2.3. X-ray crystallography

Diffraction data were collected with a Rigaku RAXIS RAPID imaging plate using graphite-monochromated Mo K α radiation ($\lambda = 0.71075$ Å). The data were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied which resulted in transmission factors (see Tables 1 and 2). Structures **1a–c** and **2a–c** were solved by the direct method using SHELXS-97 and were refined using SHELXL-97 [7]. Crystal data for [CoCl₂(ndsdsd)](**1a**), [NiCl₂(ndsdsd)](**1b**), [CuCl₂(ndsdsd)] (**1c**), [Co(ndsdsd)₂]Cl₂ (**2a**), [Ni(ndsdsd)₂]Cl₂ (**2b**), and [Cu(ndsdsd)₂]Cl₂ (**2c**) are given in Tables 1 and 2.

Table 1	
Crystallographic data for c	ompounds 1a-c

	1a	1b	1c
Formula	C ₃₆ H ₃₀ Cl ₂ CoN ₄ S ₃	C ₃₆ H ₃₀ Cl ₂ N ₄ NiS ₃	C36H30Cl2CuN4S3
Fw	744.65	744.43	749.26
Crystal size (mm)	0.40 imes 0.09 imes 0.06	0.48 imes 0.38 imes 0.36	0.51 imes 0.43 imes 0.14
Temperature (K)	123(2)	123(2)	123(2)
λ (Å)	0.71075	0.71075	0.71075
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	Pbca	Pbca	Pbca
a (Å)	16.696(3)	16.5832(18)	16.315(2)
$b(\mathbf{A})$	17.612(3)	17.568(3)	17.785(3)
<i>c</i> (Å)	22.944(3)	22.977(4)	22.955(3)
α (°)	90.00	90.00	90.00
β (°)	90.00	90.00	90.00
γ (°)	90.00	90.00	90.00
$V(Å^3)$	6746.9(17)	6694.1(17)	6660.6(18)
Z	8	8	8
$\rho_{\rm c} ({\rm Mg/m^3})$	1.466	1.477	1.494
$\mu (\mathrm{mm}^{-1})$	0.886	0.960	1.038
<i>F</i> (000)	3064	3072	3080
T_{\min}/T_{\max}	0.7182/0.9488	0.6558/0.7238	0.6196/0.8683
θ Range (°)	3.02-27.48	3.03-27.48	3.06-27.48
Reflections collected	61 237	60 522	60478
Independent reflections	7714	7640	7625
R _{int}	0.095	0.026	0.042
Data/restrains/parameters	7714/0/415	7640/0/415	7625/0/536
$R_1, wR_2 (I \ge 2\sigma[I])$	0.0396, 0.0752	0.0309, 0.0796	0.0269, 0.0665
R_1 , wR_2 (all data)	0.0643, 0.0827	0.0345, 0.0816	0.0320, 0.0691
Goodness-of-fit on F^2	1.026	1.073	1.043

Table 2

Crystallographic data for compounds $\mathbf{2a-}\mathbf{c}$

	$2a \cdot 2MeOH \cdot 10.5H_2O$	2b	$2c \cdot 4H_2O$
Formula	C ₇₄ H ₈₉ Cl ₂ CoN ₈	$C_{72}H_{60}Cl_2N_8$	C72H68Cl2Cu
	$O_{12.5}S_6$	NiS ₆	$N_8O_4S_6$
Fw	1612.72	1359.25	1436.14
Crystal size (mm)	0.61 imes 0.60 imes 0.33	0.34 imes 0.19 imes 0.15	0.23 imes 0.20 imes 0.17
Temperature (K)	90(2)	90(2)	123(2)
λ (Å)	0.71075	0.71075	0.71075
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/a$	$P2_1/c$	$P2_1/c$
a (Å)	17.544(3)	10.146(2)	10.470(3)
b (Å)	23.162(4)	17.284(4)	18.848(4)
c (Å)	21.496(4)	17.518(4)	17.112(6)
α (°)	90.00	90.00	90.00
β (°)	111.023(6)	93.260(9)	91.751(12)
γ (°)	90.00	90.00	90.00
$V(A^3)$	8154(3)	3067.1(12)	3375.1(16)
Z	4	2	2
$\rho_{\rm c} ({\rm Mg/m^3})$	1.314	1.472	1.405
$\mu (\mathrm{mm}^{-1})$	0.492	0.661	0.645
θ Range (°)	2.98-23.26	2.99-27.48	3.03-27.49
F(000)	3384	1412	1478
T_{\min}/T_{\max}	0.7535/0.8545	0.8064/0.9073	0.8659/0.8983
Reflections collected	46760	29012	13082
Independent reflections	11655	7004	7692
R _{int}	0.0456	0.0270	0.0359
Data/restrains/parameters	11655/0/1000	7004/0/524	7692/0/551
$R_1, wR_2 (I > 2\sigma[I])$	0.0649, 0.1671	0.0313, 0.0897	0.0571, 0.1286
R_1 , wR_2 (all data)	0.0763, 0.1746	0.0362, 0.0918	0.0890, 0.1449
Goodness-of-fit on F ²	1.042	1.141	1.041



3. Results and discussion

3.1. Syntheses and general characterizations

Bis[(nitrilo(diphenyl)- λ^6 -sulfanyl)](diphenyl)- λ^6 -sulfanediimide Ph₂S(=N-(Ph₂)S=N)₂ (ndsdsd) was prepared by the reaction of Ph₂SNH with Ph₂FS=N in the presence of DBU in an excellent yield [3]. The reaction of ndsdsd with MCl₂(M = Co(II), Ni(II), Cu(II)) in the ratio 1:5 at ambient temperature gave the corresponding [MCl₂(ndsdsd)] (1), while an excess amount of ndsdsd (5 equivalents) resulted in the formation of the corresponding [M(ndsdsd)₂]Cl₂ (2) almost quantitatively (Scheme 1). The complexes obtained were crystalline and stable in air but hygroscopic.

Elemental analyses show that their compositions are mono- and di-hydrated complexes, [MCl₂(ndsdsd)] · H₂O and $[M(ndsdsd)_2]Cl_2 \cdot 2H_2O$, respectively. The electronic absorption spectra of compounds 1 and 2 in methanol solution appear to be mainly of intraligand character. These intense bands at ca. 207 nm can be attributed to the $\pi - \pi^*$ transitions on the phenyl groups of the ligand, since the uncoordinated ndsdsd reveals strong absorption at 208 nm. Other transitions in the 350-800 nm range are also observed. The d-d spectrum of Co(II) and Ni(II) complexes is observed at 670 (1a and 2a), 689 (1b), and 694 nm (2b) [8a]. The Cu(II) complexes 1c and 2c show the charge-transfer transition [8b]. In the IR spectrum of all of the complexes, the IR band is observed between 1285 and 1261 cm^{-1} which is attributed to the terminal S–N stretching vibrations. The S=N stretching band (1313 cm^{-1}) of the free ndsdsd is shifted to a slightly lower frequency upon complexation and a similar observation was previously found in the mononuclear copper(II) complex ($v_{SN} = 1225 \text{ cm}^{-1}$ in [CuCl₂(Ph₃SN)₂]) [6b] of Ph₃S \equiv N ($v_{SN} = 1267 \text{ cm}^{-1}$) [5a], suggesting that the two terminal nitrogen atoms of ndsdsd are coordinated to the metal ion.

3.2. Description of the crystal structures

In order to confirm the identity of $[MCl_2(ndsdsd)]$ (M = Co(II) (a), Ni(II) (b), Cu(II) (c)) (1) and [M(ndsdsd)_2]Cl_2 (M = Co(II) (a), Ni(II) (b), Cu(II) (c)) (2), single crystal X-ray structure determinations were carried out. ORTEP drawings of 1a and 2b are depicted in Figs. 1 and 3 (as a representative) while 2a is shown in Fig. 2. ORTEP drawings of 1b-c and 2c are depicted



Fig. 1. ORTEP drawing of **1a** (50% probability thermal ellipsoids; H and C atoms (apart from the C α atoms of the phenyl rings) have been omitted for clarity).



Fig. 2. ORTEP drawing of **2a** (50% probability thermal ellipsoids; H, C atoms (apart from the C α atoms of the phenyl rings), two chloride anions, two methanol, and uncoordinated water molecules have been omitted for clarity).



Fig. 3. ORTEP drawing of **2b** (50% probability thermal ellipsoids; H, C atoms (apart from the $C\alpha$ atoms of the phenyl rings), and two chloride anions have been omitted for clarity).

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Table 3	
Selected bond lengths (Å) and angles (°) for compounds $1a-c$	•

	1. (M C.)	2- (M NE)	2- (M C)
	$\mathbf{Ia} \ (\mathbf{M} = \mathbf{Co})$	2a (M = Ni)	3a (M = Cu)
M(1)–Cl(1)	2.2810(7)	2.2687(5)	2.2677(5)
M(1)-Cl(2)	2.2776(7)	2.2659(5)	2.2756(5)
M(1)-N(1)	2.003(2)	1.9736(14)	1.9503(13)
M(1)-N(4)	1.982(2)	1.9586(14)	1.9387(13)
S(1)–N(1)	1.468(2)	1.4702(14)	1.4716(13)
S(1)-N(2)	1.667(2)	1.6606(14)	1.6539(14)
S(1)–C(1)	1.785(2)	1.7834(16)	1.7810(16)
S(1)-C(2)	1.793(2)	1.7899(16)	1.7893(16)
S(2)–N(2)	1.554(2)	1.5570(14)	1.5604(13)
S(2)–N(3)	1.5581(19)	1.5561(13)	1.556(13)
S(2)-C(3)	1.769(2)	1.7717(15)	1.7697(15)
S(2)-C(4)	1.777(3)	1.7719(16)	1.7712(16)
S(3)–N(3)	1.675(2)	1.6758(13)	1.6758(13)
S(3)–N(4)	1.468(2)	1.4719(13)	1.4700(13)
S(3)-C(5)	1.783(2)	1.7852(16)	1.7854(16)
S(3)-C(6)	1.799(2)	1.7959(16)	1.7893(15)
Cl(1)-M-Cl(2)	111.60(3)	117.019(19)	104.954(18)
Cl(1)-M-N(1)	112.09(6)	108.50(4)	104.96(4)
Cl(1)-M-N(4)	112.27(6)	111.58(4)	125.98(4)
Cl(2)-M-N(1)	112.64(6)	113.99(4)	125.96(4)
Cl(2)-M-N(4)	108.46(6)	106.26(4)	101.06(4)
N(1)-M-N(4)	99.13(8)	97.81(6)	96.25(6)
N(1)-S(1)-N(2)	121.37(11)	121.23(7)	120.70(7)
N(1)-S(1)-C(1)	115.34(12)	116.42(8)	116.92(8)
N(1)-S(1)-C(2)	111.62(11)	111.07(8)	110.57(7)
N(2)-S(1)-C(1)	98.60(11)	98.16(7)	98.83(7)
N(2)-S(1)-C(2)	105.57(11)	105.88(7)	106.16(7)
C(1)-S(1)-C(2)	101.94(11)	101.66(7)	101.35(7)
N(2)-S(2)-N(3)	120.89(11)	120.94(7)	121.01(7)
N(2)-S(2)-C(3)	105.59(11)	105.54(7)	105.29(7)
N(2)-S(2)-C(4)	109.76(11)	109.66(8)	109.12(7)
N(3)-S(2)-C(3)	111.67(11)	111.77(7)	112.15(7)
N(3)-S(2)-C(4)	102.66(11)	102.71(8)	102.54(7)
C(3)-S(2)-C(4)	105.31(12)	105.24(8)	105.83(7)
N(3)-S(3)-N(4)	124.26(10)	124.56(7)	125.01(7)
N(3)-S(3)-C(5)	101.82(11)	101.74(7)	100.89(7)
N(3)-S(3)-C(6)	96.16(11)	96.24(7)	96.99(7)
N(4)-S(3)-C(5)	109.63(12)	109.35(8)	109.42(8)
N(4)-S(3)-C(6)	117.44(12)	117.58(8)	116.40(8)
C(5)-S(3)-C(6)	104.96(11)	104.72(7)	105.68(7)
M(1)-N(1)-S(1)	124.68(12)	125.69(8)	125.78(8)
S(1)-N(2)-S(2)	118.95(12)	118.58(8)	117.36(8)
S(2)-N(3)-S(3)	118.78(12)	118.23(8)	119.08(8)
M(1)-N(4)-S(3)	128.19(13)	128.87(8)	128.03(8)

The atom labeling scheme is shown in Fig. 1.

in Figures S1–3, Supplementary materials. Selected bond lengths and angles for complexes **1a–c** and **2a–c** are collected in Tables 3 and 4. The structures of the complexes of **2a–c** consist of well-separated $[M(ndsdsd)_2]^{2+}$ (M = Co(II), Ni(II), Cu(II)) cations and Cl⁻ anions. Crystals of **2a** and **2c** contain methanol as a lattice solvate and lattice water molecules.

The cobalt atom in $[CoCl_2(ndsdsd)]$ (1a) and $[Co(ndsdsd)_2]Cl_2$ (2a) is surrounded by two nitrogen and two chlorine atoms or four nitrogen atoms originating from two coordinated ndsdsd ligands, respectively. In both, the geometries around the Co atoms are slightly distorted tetrahedra. The bite angles of N–Co(1)–N in 1a

Selected bond lengths (Å) and angles (°) for compounds 2a–c			
Compound 2a			
Co(1) - N(1)	1.995(4)	S(3)–N(3)	1.667(4)
Co(1)-N(4)	1.994(4)	S(3)–N(4)	1.474(4)
Co(1)-N(5)	1.990(4)	S(4)–N(5)	1.470(4)
Co(1)-N(8)	1.965(4)	S(4)–N(6)	1.663(4)
S(1)–N(1)	1.481(4)	S(5)-N(6)	1.567(4)
S(1)-N(2)	1.672(4)	S(5)–N(7)	1.554(4)
S(2)–N(2)	1.570(4)	S(6)–N(7)	1.676(4)
S(2)–N(3)	1.564(4)	S(6)–N(8)	1.467(4)
N(1)-Co(1)-N(4)	103.29(15)	N(5)-Co(1)-N(8)	105.84(15)
N(1)-Co(1)-N(5)	107.44(15)	Co(1)-N(1)-S(1)	131.2(2)
N(1)-Co(1)-N(8)	113.90(15)	Co(1)-N(4)-S(3)	124.8 (2)
N(4)-Co(1)-N(5)	117.55(15)	Co(1)-N(5)-S(4)	136.4(2)
N(4)-Co(1)-N(8)	109.11(16)	Co(1)-N(8)-S(6)	140.0(2)
Compound 2b			
Ni(1)-N(1)	1.9201(14)	S(2)–N(2)	1.5520(14)
Ni(1)-N(4)	1.9165(14)	S(2)–N(3)	1.5566(14)
S(1)–N(1)	1.4792(14)	S(3)–N(3)	1.6564(14)
S(1)–N(2)	1.6676(14)	S(3)–N(4)	1.4717(14)
N(1)-Ni(1)-N(4)	92.20(6)	$N(4)-Ni(1)-N(4)^{*}$	180.00(3)
$N(1)-Ni(1)-N(1)^{*}$	180.00(8)	Ni(1)-N(1)-S(1)	124.24(9)
$N(1)-Ni(1)-N(4)^{*}$	87.80(6)	Ni(1)-N(4)-S(3)	130.65(9)
Compound 2c			
Cu(1)–N(1)	1.984(3)	S(2) - N(2)	1.549(3)
Cu(1)-N(4)	1.984(3)	S(2)–N(3)	1.551(3)
S(1)–N(1)	1.471(3)	S(3)–S(3)	1.652(3)
S(1)–N(2)	1.665(3)	S(3)–N(4)	1.468(3)
N(1)-Cu(1)-N(4)	91.68(11)	$N(4)-Cu(1)-N(4)^{*}$	180.00(19)
$N(1)-Cu(1)-N(1)^{*}$	180.00(2)	Cu(1)-N(1)-S(1)	125.36(17)
$N(1)-Cu(1)-N(4)^{*}$	88.32(11)	Cu(1)-N(4)-S(3)	125.17(19)

The atom labeling scheme is shown in Figs. 2 and 3.

 $(99.13(8)^{\circ})$ and **2a** $(103.29(15)-105.84(15)^{\circ};$ mean $104.6^{\circ})$ are smaller than the ideal tetrahedral angle, while the N-Co-N angles in $[Co(F_2(O=)S=N-(F_2)S=N)_4][AsF_6]_2$ are 108.0(2)-110.5(2)° (mean 109.5°) [2d]. These smaller angles are probably attributed to the stereochemical requirement of the chelate ring, because the Cl-Co(1)-Cl and Cl-Co(1)-N bond angles (mean 111.4°) in 1a and other N-Co(1)-N bond angles (mean 112.0°) in 2a are similar to a regular tetrahedral angle. Similarly, the bite angles of N-M–N of **1b** $(97.81(6)^{\circ})$ and **1c** $(96.25(6)^{\circ})$ in the distorted tetrahedra with Ni(II) and Cu(II) centers are also considerably less. The bond angles of Co(1)-N(1)-S(1) and Co(1)-N(4)-S(3) are 124.68(12) and 128.19(13)° in 1a, which are somewhat smaller than the corresponding bond angles in 2a (124.8(2)-140.0(2)°; mean 133.1°). The Co(1)-N bond lengths in **1a** (1.982(2)-2.003(2) Å; mean 1.993 Å) are close to those of **2a** (1.965(4)-1.995(4) Å; mean 1.986 Å) and $[Co(F_2(O=)S=N-(F_2)S=N)_4][AsF_6]_2$ (mean 1.969 A) [2d,2f]. The distances between the cobalt and nitrogen atoms (N(2) and N(3)) in 1a are 3.584(2) and 3.907(2) Å, indicating that the nitrogen atoms of the chelate ring are not coordinated to the cobalt atom. These are also similar to the corresponding distances in the other complexes. Therefore, the structures in all of the present complexes

show a rare example of an eight–membered cyclometallathiazene¹ [1b].

The geometries around the metal centers in 1b and 1c are of distorted tetrahedral coordination, while 2b and 2c adopt an essentially flat structure with square planar Ni(II) and Cu(II) centers. The M-Cl bond lengths in 1b-c and the M-N bond lengths in 1b-c and 2b-c have the values of 2.2659(5)-2.756(5) Å and 1.9165(14)-1.984(14) Å, respectively, indicating the coordination character of the bonds. The M(NSN)₂S rings in 1b-c and 2b-c adopt a boat-twist conformation. Among them, complex 1c is one of the rare examples of a tetrahedral Cu(II) complex. The bond angles around the Cu(II) ion with two nitrogen and two chlorine atoms span the range $96.25(6)-125.98(4)^{\circ}$, substantially deviating from the ideal tetrahedral angle. The dihedral angle between the Cl(1)-Cu(1)-Cl(2) and N(1)-Cu(1)-N(4) planes of 72.08° shows deviation from the ideal 90° for a tetrahedral arrangement. These observed bond angles in 1c are not significantly different from the corresponding bond angles $(96.9(3)-125.8(1)^{\circ})$ of $[CuCl_2(Ph_3SN)_2]$ [6b]. The bond lengths of Cu(1)-Cl (2.2677(5)-2.2756(5) Å; mean 2.261 Å) and Cu(1)–N (1.9387(13)-1.9503(13) Å; mean 1.945 Å) in 1c are also similar to those of $[CuCl_2(Ph_3SN)_2]$ (Cu-Cl; mean 2.249(2) Å, Cu-N; mean 1.969(4) Å) [6b].

The coordinated and internal S–N bond lengths of complexes 1 and 2 are very similar. The coordinated S–N bond lengths of 1.467(4)-1.481(4) Å are close to the terminal S–N bond length of the free ligand (1.457(2) Å) [3]. The internal S–N bond lengths range from 1.5520(14) to 1.793(2) Å. Such bond lengths lie between those of single and double bonds and are close to those of the free state (1.550(2)-1.656(2) Å). The mean values of the bond angles around the sulfur atoms in the ligand are also close to those of the free state. These results indicate that the bond order in the N \equiv S–N=S \equiv N–S \equiv N backbone of ndsdsd has been maintained.

Recently, Mews et al. have reported the X-ray structures of the $F_2(O=)S=N-(F_2)S=N-A$ system (A = Co, Cu, AsF₅, BF₃, Me) [2f]. They concluded that the S–N bond length decreases with increasing A–N–S angle. The results obtained in this work may also be related to Mews finding. The coordinated S–N bond lengths (mean 1.472 Å) and M– N–S bond angles (mean 128.5°) in **1** and **2** are significantly shorter and larger, respectively, than those of *N*-methylated [Ph₃S=N-Me][ClO₄] (S-N: 1.514(3) Å, C-N-S: $118.6(3)^{\circ}$) [6a].

4. Conclusions

The reaction of ndsdsd with MCl_2 (M = Co(II) (a), Ni(II) (**b**), Cu(II) (**c**)) in the ratio 1:5 at ambient temperature gives the corresponding [MCl₂(ndsdsd)] (1), while an excess of ndsdsd (5 equivalents) results in the formation of the corresponding $[M(ndsdsd)_2]Cl_2$ (2) almost quantitatively. The products were characterized by X-ray crystallography. IR spectroscopy, and elemental analysis. The X-ray structures of 1 and 2 indicate the following characteristic properties. The two terminal nitrogen atoms of ndsdsd exhibit similar bidentate coordination mode when combined with Co(II), Ni(II), and Cu(II) centers in the corresponding complexes 1 and 2. The eight-membered M(NSN)₂S rings in 1 and 2 adopt a boat-twist conformation. The geometry around the metal centers in 1 and 2a is a distorted tetrahedral coordination with smaller N-M-N bite angles, while 2b and 2c adopt an essentially flat structure with square planar Ni(II) and Cu(II) centers. The s-character of the M-N bond increases, which leads to S-N bond shortening. The coordinated S-N bond lengths in 1 and 2 are similar to those of the free ligand, and the internal S-N bond lengths lie between those of single and double bonds. These results indicate that the bond order in the $N \equiv S - N = S = N - S \equiv N$ backbone of ndsdsd has been maintained.

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Appendix A. Supplementary material

ORTEP drawings of **1b–c** and **2c** (Figs. S1–S3) and X-ray crystallographic files in CIF format for the structure determination of **1** and **2**. CCDC 648178, 648179, 648180, 648181, 648182 and 648183 contain the supplementary crystallographic data for this **1a**, **1b**, **1c**, **2a**, **2b** and **2c**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam. ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2008.01.036.

References

 (a) P.F. Kelly, J.D. Woollins, Polyhedron 5 (1986) 607;
 (b) T. Chivers, F. Edelmann, Polyhedron 5 (1986) 1661;
 (c) P.F. Kelly, A.M.Z. Slawin, A. Soriano-Rama, J. Chem. Soc., Dalton Trans. (1996) 53;

¹ The only example of the eight-membered MS_3N_4 ring system, $[Cp_2Ti(S_3N_4)]$, was prepared by the reaction of $[Cp_2Ti(CO)_2]$ with S_4N_4 . The seven-atom NSNSNSN sequence is an approximately planar in three independent molecules. The bite angle of N–Ti–N is equivalent for the three molecules with a mean of $94.6(2)^\circ$. The coordinated S–N bond lengths (1.482-1.500 Å) and the internal S–N bond lengths (1.555-1.605 Å) in $[Cp_2Ti(S_3N_4)]$ are similar to those observed in 1 and 2 (see: C.G. Marellus, R.T. Oakley, W.T. Pennington, A.W. Cordes, Organom-tallics 5 (1986) 1395). An cyclometallathiazene of MS_4N_3 , $[Pt(S_4N_3)Cl]$, has been reported, but the S_4N_3 ligand is coordinated to platinum as a tridentate *via* the terminal S atoms and central nitrogen atom (see: H. Endres, E. Galantai, Angew. Chem., Int. Ed. Engl. 19 (1980), 653).

(d) T. Chivers, A Guide to Chalcogen–Nitrogen Chemistry, World Scientific Publishing Co. Pte. Ltd., Singapore, 2005, Chapter 7, p. 122 and references therein.

- [2] (a) O. Glemser, R. Mews, Angew. Chem., Int. Ed. Engl. 19 (1980) 883;
 - (b) U. Behrens, R. Hoppenheit, W. Isenberg, E. Lork, J. Petersen, R. Mews, Z. Naturforsch. 49b (1994) 238;
 - (c) U. Behrens, E. Lork, J. Petersen, A. Waterfeld, R. Mews, Z. Anorg. Allg. Chem. 623 (1997) 1518;
 - (d) R. Hoppenheit, E. Lork, J. Petersen, R. Mews, Chem. Commun. (1997) 1659;
 - (e) U. Behrens, J. Petersen, E. Lork, P.G. Watson, R. Mews, Angew. Chem. Int. Ed. Engl. 36 (1997) 1878;
 - (f) R. Mews, T. Borrmann, R. Hoppenheit, E. Lork, S. Parsons, J. Petersen, M. Schröter, W.-D. Stohrer, A. Waterfeld, P.G. Watson, J. Fluorine Chem. 125 (2004) 1649;
 - (g) R. Mews, E. Lork, P.G. Watson, B. Görtler, Coord. Chem. Rev. 197 (2000) 277.
- [3] T. Fujii, M. Kanno, M. Hirata, T. Fujimori, T. Yoshimura, Inorg. Chem. 44 (2005) 8653.
- [4] T. Fujii, S. Asai, T. Okada, W. Hao, H. Morita, T. Yoshimura, Tetrahedron Lett. 44 (2003) 6203.

- [5] (a) T. Yoshimura, K. Hamada, M. Imado, K. Hamata, K. Tomoda, T. Fujii, H. Morita, C. Shimasaki, S. Ono, E. Tsukurimichi, N. Furukawa, T. Kimura, J. Org. Chem. 62 (1997) 3802;
 (b) T. Yoshimura, T. Fujii, S. Murotani, S. Miyoshi, T. Fujimori, M. Ohkubo, S. Ono, H. Morita, J. Organomet. Chem. 611 (2000) 272;
 (c) T. Fujii, T. Fujimori, S. Miyoshi, S. Murotani, M. Ohkubo, T. Yoshimura, Heteroat. Chem. 12 (2001) 263;
 (d) T. Fujii, T. Suzuki, T. Sato, E. Horn, T. Yoshimura, Tetrahedron Lett. 42 (2001) 6151;
 (e) T. Fujii, T. Ikeda, T. Mikami, T. Suzuki, T. Yoshimura, Angew. Chem., Int. Ed. 41 (2002) 2576.
- [6] (a) T. Yoshimura, T. Fujii, K. Hamata, M. Imado, H. Morita, S. Ono, E. Horn, Chem. Lett. (1998) 1013;
- (b) T. Yoshimura, T. Fujii, H. Dai, Chem. Lett. (2002) 1000.

Press, Oxford, England, 1987, p. 533.

- [7] G.M. Sheldrick, SHELXS97 and SHELXL97. Program for Crystal Structure Solution and Refinement, University of Gottingen, Germany, 1997.
- [8] (a) B.N. Figgis, in: G. Wilkinson, R.D. Gillard, J.A. McCleverty (Eds.), Comprehensive Coordination Chemistry, vol. 5, Pergamon Press, Oxford, England, 1987, p. 213;
 (b) B.J. Hathaway, in: G. Wilkinson, R.D. Gillard, J.A. McCleverty (Eds.), Comprehensive Coordination Chemistry, vol. 5, Pergamon