Valence Isomerization. Synthesis and Characterization of Cobalt and Nickel Complexes with Non-Innocent N_2S_2 Ligand

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The reactions of 2-phenylbenzothiazoline with $[M(CH_3COO)_2]\cdot 4H_2O$ (M = Co(II) and Ni(II)) afford the complexes $[M(phbt)_2]$ (phbt = 2-(phenylmethyleneamino)benzenethiolato) via a ring opening reaction of 2-phenylbenzothiazoline. Spectroscopic data indicate that the cobalt and nickel atoms occupy a tetrahedral and a square planar N_2S_2 environment, respectively. The single crystal X-ray structure of $[Ni(phbt)_2]$ is redetermined and this complex shows a monohelical geometry. Crystal data: $[Ni(phbt)_2]$, monoclinic, $C2/c$, $a = 23.065(4)$; $b = 6.924(2)$; $c = 13.809(2)$ Å; $\beta = 102.64(1)°$; $V = 2152.0(9)$ Å^3; $Z = 4$, $R = 0.052$ ($R_w = 0.050$). The toluene solution of $[Co(phbt)_2]$ and that of $[Ni(phbt)_2]$ lead to the complexes [Co(ddbt)] and [Ni(ddbt)] (ddbt = bis-2,2′-(1,2-diphenylethylenediimine)benzenethiolato) through the carbon–carbon bond formation, respectively. The structural features of [M(ddbt)] (M = Co and Ni) point clearly to the neutral dithiolene-like charge distribution. These complexes [M(ddbt)] have the same chemical compositions as the starting complexes $[M(phbt)_2]$, and both can be correlated in a new valence isomerism. Crystal data: [Co(ddbt)], monoclinic, $P2_1/n$, $a = 8.573(2)$; $b = 24.486(3)$; $c = 10.771(1)$ Å; $\beta = 102.08(2)°$; $V = 2211.0(9)$ Å^3; $Z = 4$, $R = 0.056$ ($R_w = 0.048$); [Ni(ddbt)], monoclinic, $P2_1/n, a = 8.631(10)$; $b = 24.365(19)$; $c = 10.798(4)$ Å; $\beta = 102.69(6)°$; $V = 2215.2(33)$ Å^3; $Z = 4$, $R = 0.078$ ($R_w = 0.075$).

The transition metal complexes with non-innocent ligands, which are represented by the dithiolene complexes, have been thoroughly investigated.[1] (The term non-innocent was introduced by Jørgensen.[2]) As might have been expected, their complexes have exhibited the interesting coordination geometry and multiple oxidation states. In recent years, the dithiolene-type metal complexes have gained more interest owing to their unusual and unprecedented physical and chemical properties, such as electrical conductivity[3] and strong near-IR absorption.[4] As a result, the electronic structures of the metal complexes with quinone, dithiolene, or diimine ligands have gradually been clarified. Pierpont et al. reported valence tautomerism in the course of the studies of the equilibrium between cobalt(III) and cobalt(II) in the complex with semiquinonate and catecholate ligands.[5] Moreover they have extended the studies to related manganese complexes.[6] Hendrickson et al. reported the results of the time-resolved optical experiments in valence-tautomeric cobalt complexes.[7] Thus the quinone ligand in a transition metal complex can clearly be characterized as fully reduced form (catecholate) or partially reduced form (semiquinone) or unreduced form (quinone).[8] On the other hand, the dithiolene or diimine metal complexes display delocalized electronic structures and there may be ambiguity even about the oxidation state assignments for the metal ion.

In this paper we report a simple synthetic method of cobalt and nickel complexes with non-innocent N_2S_2 ligands based on the carbon–carbon bond formation. The complexes with non-innocent ligands can be correlated to the starting complexes as a valence isomerism. These complexes allow us to compare directly the complexes with innocent ligands and ones with non-innocent ligands. In addition, the comparison of the cobalt and nickel complexes are undertaken to gain more insight into the electronic structures of metal complexes with non-innocent ligands. In a previous communication, we have reported the molecular structures of $[Ni(phbt)_2]$ and [Ni(ddbt)].[9]

Experimental

General Procedures. Reactions were normally carried out under argon; the solvents were thoroughly degassed by argon purge. Ethanol and methanol were dried over molecular sieve type 3A. Toluene was dried over molecular sieve type 4A. Unless otherwise stated, commercial grade chemicals were used without further purification.

Infrared spectra were obtained on a Parkin–Elmer 983G Infrared Spectrophotometer (4000—180 cm^{-1}) using the Nujol® mull technique, NMR spectra on a JEOL EX 270 instrument using tetramethylsilane as internal standard ($\delta = 0$), ESR spectra on a JEOL TM-FE1 instrument using TCNQ as standard marker. The UV-vis spectra were recorded on a Hitachi U-3400 spectrophotometer. Elemental analyses of 2-phenylbenzothiazoline, $[Co(phbt)_2]$, [Co(ddbt)], $[Ni(phbt)_2]$, and [Ni(ddbt)] were performed at Osaka University. Cyclic voltammograms were performed in a three-electrode cell with a glassy carbon disk as working electrode, platinum wire as counter electrode, and a Ag/AgCl reference electrode and were measured in CH_2Cl_2 containing 0.1 M tetra-n-butylammonium tetrafluoroborate (1 M = 1 mol dm^{-3}). The scan rates were 50 mV s^{-1}. $E_{1/2}$ (quasi-reversible) are the average of the anodic and cathodic peak potentials vs. Ag/AgCl.

Synthesis of 2-Phenylbenzothiazoline. 2-Phenylbenzothiazoline was prepared according to the general procedure of P. J. Palmer et al.[10] 2-Aminobenzenethiol (1.07 g, 10.1 mmol) was added to a solution of benzaldehyde (1.25 g, 9.99 mmol) in ethanol (20 mL) and stirred at ca. 70 °C for 20 min. Yield: 66%. Infrared spectrum: ν(N–H) at 3384 cm^{-1}, ν(aromatic C=C) at 1577 cm^{-1}. Found: C, 73.33; H, 5.26; N, 6.60%. Calcd for $C_{13}H_{11}NS$: C, 73.20; H, 5.20; N, 6.57%. ^{1}H NMR (CDCl$_3$, 23 °C) (270 MHz) δ = 7.54—7.50 (m, 2H), 7.38—7.30 (m, 3H), 7.03 (dd, 1H), 6.94 (dt, 1H), 6.75 (dt, 1H), 6.64 (dd, 1H), 6.35 (s, 1H), and 4.33 (s, 1H); ^{13}C NMR (67.8 MHz) δ = 146.28, 141.70, 128.79, 128.75, 126.56, 125.50, 121.65, 120.69, 109.75, and 70.02.

Synthesis of Bis[2-(phenylmethyleneamino)benzenethiolato]cobalt(II) ([Co(phbt)$_2$]). Cobalt(II) acetate tetrahydrate (0.75 g, 3.0 mmol) was added to a solution of 2-phenylbenzothiazoline (1.29 g, 6.1 mmol) in methanol (30 mL) and stirred at 50 °C for 20 min. The resulting red brown solution was cooled overnight. Precipitated brown powder [Co(phbt)$_2$] was collected by filtration and dried in vacuo. The purified product was obtained by recrystallization from CH_2Cl_2 and methanol mixed solution. Yield: 3.4%. This low yield is due to the careful recrystallization. Infrared spectrum: ν(C=N) at 1593 cm^{-1}, ν(aromatic C=C) at 1567 cm^{-1}. Found: C, 64.16; H, 4.34; N, 5.78%. Calcd for $C_{26}H_{20}CoN_2S_2$: C, 64.58; H, 4.17; N, 5.80%. This complex has already been prepared by Kogan et al.[11]

Synthesis of [Bis-2,2′-(1,2-diphenylethylenediimine)benzenethiolato]cobalt(II) ([Co(ddbt)]). A suspension of crude [Co(phbt)$_2$] (0.215 g, 0.45 mmol) in toluene (30 mL) was refluxed for 10 min; the solution became dark greenish blue. The solution was filtered and the solvent was removed by evaporation. The dark blue solid was dissolved in CH_2Cl_2 (ca. 20 mL) and filtered. Then the product was chromatographed on a silica gel (230—400 mesh) column with CH_2Cl_2. The complex was eluted as a first blue band. Removal of CH_2Cl_2 under reduced pressure yielded the metallic red-purple powdery product (18% yield based on crude [Co(phbt)$_2$]). X-Ray quality crystals were grown by the slow evaporation of CH_2Cl_2 and methanol mixed solution. Infrared spectrum: ν(aromatic C=C) at 1597 and 1565 cm^{-1}. Found: C, 63.89; H, 4.35; N, 5.46%. Calcd for $C_{26}H_{20}CoN_2S_2$: C, 64.58; H, 4.17; N, 5.80%.

Synthesis of Bis[2-(phenylmethyleneamino)benzenethiolato]nickel(II) ([Ni(phbt)$_2$]). To a solution of 2-phenylbenzothiazoline (0.65 g, 3.1 mmol) in ethanol (20 mL) was added nickel(II) acetate tetrahydrate (0.37 g, 1.5 mmol). The reaction mixture was refluxed for 20 min and cooled to room temperature. The resulting dark red brown precipitate was filtered off and dried in vacuo. Yield: 65%. X-Ray quality crystals were obtained from CHCl$_3$ and methanol mixed solution. Infrared spectrum: ν(C=N) at 1598 cm^{-1}, ν(aromatic C=C) at 1570 and 1558 cm^{-1}. Found: C, 64.98; H, 4.34; N, 5.89%. Calcd for $C_{26}H_{20}N_2NiS_2$: C, 64.61; H, 4.17; N, 5.80%. ^{1}H NMR (CDCl$_3$, 23 °C) (270 MHz) δ = 8.78 (d, 4H), 7.76 (s, 2H), 7.39 (t,2H), 7.38 (d, 2H), 7.22 (t, 4H), 7.01 (t, 2H), 6.66 (t, 2H), and 6.21 (d, 2H); ^{13}C NMR (67.8 MHz) δ = 166.40, 150.02, 146.58, 134.57, 131.34, 129.58, 128.79, 128.75, 121.20, and 116.73. This complex has already been prepared by Kogan et al.[11]

Synthesis of [Bis-2,2′-(1,2-diphenylethylenediimine)benzenethiolato]nickel(II) ([Ni(ddbt)]). A suspension of [Ni(phbt)$_2$] (0.105 g, 0.22 mmol) in toluene (30 mL) was refluxed for 10 min and then cooled to room temperature. After filtering, the solvent was removed on the rotary evaporator. The black crystalline product was dissolved in CH_2Cl_2 (ca. 15 mL) and filtered. The filtrate was purified by chromatography on a silica gel (230—400 mesh) column, eluting with CH_2Cl_2. A dark violet [Ni(ddbt)] was obtained by evaporation of the solvent. Yield: 56%. Single crystals suitable for X-ray crystal structure analysis were grown by the slow evaporation of CHCl$_3$ and methanol mixed solution. Infrared spectrum: ν(aromatic C=C) at 1597 and 1570 cm^{-1}. Found: C, 64.60; H, 4.21; N, 5.52%. Calcd for $C_{26}H_{20}N_2NiS_2$: C, 64.61; H, 4.17; N, 5.80%. ^{1}H NMR (CDCl$_3$, 23 °C) (270 MHz) δ = 7.71 (d, 2H), 7.21—7.35 (m, 12H), 7.14 (dt, 2H), 7.01 (dt, 2H), and 6.34 (s, 2H); ^{13}C NMR (67.8 MHz) δ = 162.07, 160.39, 143.42, 131.56, 129.02, 128.00, 127.82, 126.74, 122.86, 119.84, and 83.28.

Synthesis of [Ni(ddbt)] at Room Tempereture in the Dark. A suspension of [Ni(phbt)$_2$] (0.031 g, 0.06 mmol) in toluene (15 mL) was stirred for 1d at room temperature in the dark. The solvent was removed in vacuo and the residue was dissolved in CH_2Cl_2 (ca. 10 mL). The resulting dark brown violet solution was purified by chromatography on a silica gel (230—400 mesh) column using CH_2Cl_2 as eluent. Yield: 30%.

X-Ray Crystallography. All crystals were mounted on the glass fibers with epoxy. For [Co(ddbt)], X-ray diffraction data were collected on an Enraf–Nonius CAD4 diffractometer using graphite-monochromated Mo $K\alpha$ radiation and X-ray diffraction data for [Ni(phbt)$_2$] and [Ni(ddbt)] were collected on a Rigaku AFC5 diffractometer using graphite-monochromated Mo $K\alpha$ radiation. Unit cell parameters and an orientation matrix were typically obtained from 25 machine-centered reflections with $8° \leq 2\theta \leq 30°$. Three standard reflections measured after every 150 scans showed no appreciable loss in intensity during the data collection process. The structures were solved by direct methods using MULTAN 80,[12] followed by successive cycles of least-squares refinement and difference-Fourier synthesis. All non-hydrogen atoms were refined anisotropically by block-diagonal least-squares. Hydrogen atoms were calculated with a C–H distance of 1.06 Å and were refined isotropically. Atomic scattering factors and anomalous scattering coefficients were taken from Ref. 13. The calculations were carried out using the program system UNICSIII[14] on a HITAC M680 Hitachi computer at the Computer Center of the Institute for Molecular Science. Figures 1, 2, and 3 were drawn by the use of ORTEP.[15] X-Ray crystallographic data for all the complexes are shown in Table 1.

Tables of the atom coordinates, the thermal parameters, the complete $F_o - F_c$ data, and all bond distances and angels are deposited as Document No. 70021 at the Office of the Editor of Bull. Chem.

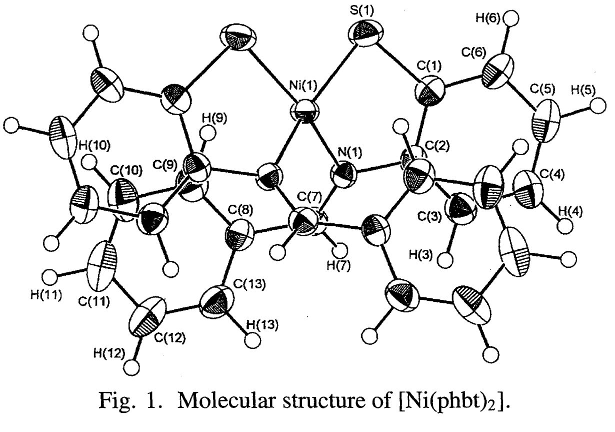

Fig. 1. Molecular structure of [Ni(phbt)$_2$].

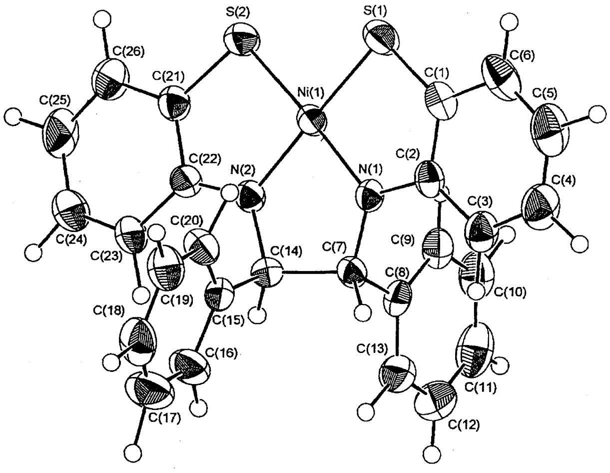

Fig. 2. Molecular structure of [Ni(ddbt)].

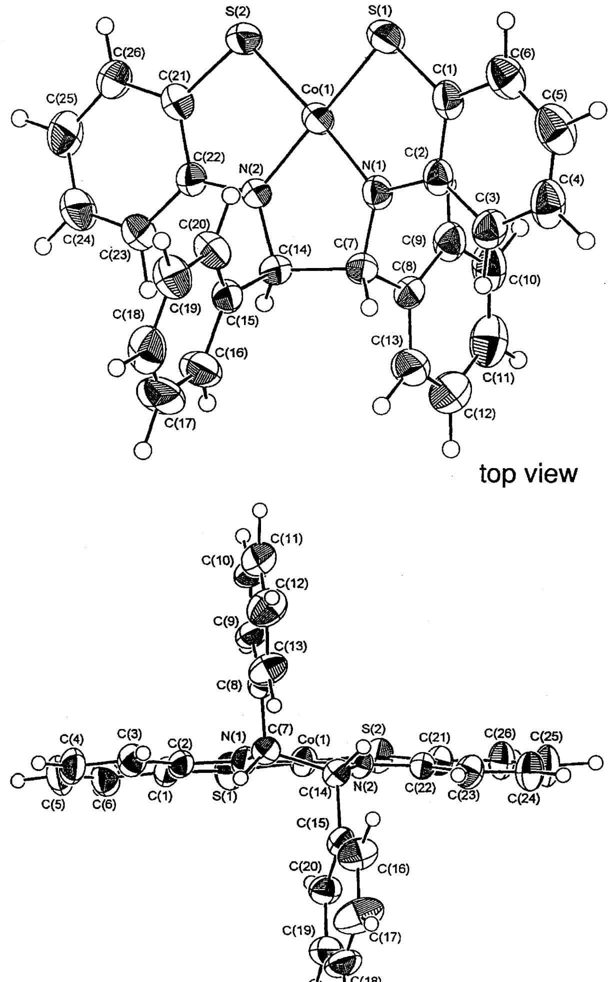

Fig. 3. Molecular structure of [Co(ddbt)].

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Results and Discussion

Synthesis. The complexes [Co(phbt)$_2$] and [Ni(phbt)$_2$] were synthesized by reactions of an alcohol solution of 2-phenylbenzothiazoline with cobalt(II) acetate tetrahydrate or nickel(II) acetate tetrahydrate, respectively (Scheme 1). The complexes [Co(ddbt)] and [Ni(ddbt)] were simply synthesized by heating a toluene solution of [Co(phbt)$_2$] and [Ni(phbt)$_2$]. In particular, [Ni(ddbt)] could be also obtained by stirring the toluene solution of [Ni(phbt)$_2$] at room temperature in the dark, though [Co(ddbt)] was not obtained under the same condition.[16)]

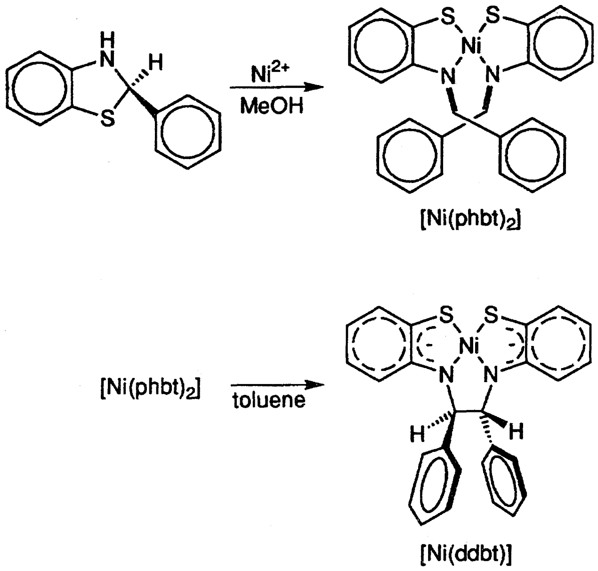
Molecular Structure of [Ni(phbt)$_2$]. A general view of [Ni(phbt)$_2$] which defines the atom numbering scheme is shown in Fig. 1. The X-ray analysis of this complex has been studies by Kogan et al.[17)] However, both the R value of 0.098 and the uncertainties in the bond lengths were rather high. In order to improve the accuracy of the structure, we have redetermined the structure of [Ni(phbt)$_2$] by single crystal X-ray diffraction using Mo $K\alpha$ radiation (Table 2). In this complex, the nickel atom is located on a crystallographic twofold axis. [Ni(phbt)$_2$] comprises a square planar nickel(II) site with *cis* nitrogen and *cis* sulfur atoms and shows a monohelical geometry. Selected bond distances are presented in Table 5. The Ni–S (2.180(1) Å) and Ni–N (1.926(2) Å) bond distances are normal as four-coordinate imino-thiolato nickel complexes.[18,19)] The C=N bond distances are shorter than those of helical complexes with ferrocenyl groups instead of phenyl ones as described in a previous paper.[19)] This result can be correlated to the strain inherent in access of two bulky ferrocenyl groups. One of the most interesting features is the short hydrogen contacts, Ni(1)···H(9)–C 2.42(4) Å, as shown in Fig. 1.

Molecular Structure of [Ni(ddbt)]. The molecular structure and atom numbering scheme for [Ni(ddbt)] is shown in Fig. 2. [Ni(ddbt)] is derived from bond formation between the two imino carbon atoms in [Ni(phbt)$_2$]. This complex has a square planar configuration, since the dihedral angle between NiNS planes is 7.2(2)°. The Ni–S (2.126(2) and 2.129(2) Å) and Ni–N (1.830(5) and 1.826(4) Å) bond distances are shorter than the normal values of Ni-thiolato and Ni-imino such as [Ni(phbt)$_2$] (Tables 3 and 5). The Ni–S distances compare with those of the neutral dithiolene complexes (2.101(2) Å in [Ni(S$_2$C$_2$Ph$_2$)$_2$],[20)] 2.122(3) Å in [Ni{S$_2$C$_2$(CF$_3$)$_2$}$_2$],[21)] 2.119(5) Å in [Ni(dddt)$_2$],[22)] 2.120—2.127(1) Å in β-[Ni(dpedt)$_2$][23)]). In addition, it seems that the Ni–N bond distances are consistent with those of the nickel complexes with semiquinonediimine ligands (1.832(11) Å in [Ni{(NH)$_2$C$_6$H$_4$}$_2$],[24)] 1.827(4) Å in [Ni{(NH)$_2$C$_2$(CN)$_2$}$_2$][25)]). Thus the Ni–S and Ni–N bond distances indicate that [Ni(ddbt)] corresponds to the neutral dithiolene complexes and/or the semiquinonediimine ones. The C–S bond distances of the neutral dithiolene ligands and the C–N bond ones of the semiquinonediimine ligands have been found in other structures to be particularly sensitive to charge distribution within the complex.[26)] The average C–S bond distance of 1.729(7) Å is typical of values found for the other neutral dithiolene structures (1.71(1) Å in [Ni(S$_2$C$_2$Ph$_2$)$_2$],[20)] 1.71(1) Å in [Ni{S$_2$C$_2$(CF$_3$)$_2$}$_2$],[21)] 1.68(2) Å in [Ni(dddt)$_2$],[22)] 1.695—1.701(4) Å in β-[Ni(dpedt)$_2$][23)]) and the average C–N bond distance of 1.352(7) Å also shows a characteristic pattern found for the other semiqui-

Table 1. Crystallographic Data for [Ni(phbt)$_2$], [Ni(ddbt)], and [Co(ddbt)]

Complex	[Ni(phbt)$_2$]	[Ni(ddbt)]	[Co(ddbt)]
Formula	$C_{26}H_{20}N_2NiS_2$	$C_{26}H_{20}N_2NiS_2$	$C_{26}H_{20}CoN_2S_2$
F.W.	483.27	483.27	483.51
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/n$	$P2_1/n$
a/Å	23.065(4)	8.631(10)	8.573(2)
b/Å	6.924(2)	24.365(19)	24.486(3)
c/Å	13.809(2)	10.798(4)	10.771(1)
β/deg	102.64(1)	102.69(6)	102.08(2)
V/Å^3	2152.0(9)	2215.2(33)	2211.0(9)
Z	4	4	4
D_{calc}/g cm^{-3}	1.49	1.45	1.45
μ(Mo Kα)/cm^{-1}	11.1	10.8	9.7
No. of measured reflections	3479	6445	4278
No. reflections used in refinement	2242[$\lvert F_o\rvert > 3\sigma(F_o)$]	3465[$\lvert F_o\rvert > 3\sigma(F_o)$]	2575[$\lvert F_o\rvert > 3\sigma(F_o)$]
No. of parameters	186	361	361
R	0.052	0.078	0.056
R_w	0.050	0.075	0.048

$R=\Sigma\lvert\lvert F_o\rvert-\lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert$, $R_w=[\Sigma w(\lvert F_o\rvert-\lvert F_c\rvert)^2/\Sigma w(F_o)^2]^{1/2}$, Weighting scheme $1/[\sigma^2(F_o)]$.



Scheme 1.

Table 2. Atomic Parameters for [Ni(phbt)$_2$]

Atom	x/a	y/b	z/c	$B_{\mathrm{eq}}$$^{a)}$/Å^2
Ni(1)	0	0.0939(1)	1/4	2.4
S(1)	0.0465(0)	0.3077(1)	0.3547(1)	3.5
N(1)	0.0215(1)	−0.0881(4)	0.3573(2)	2.3
C(1)	0.0971(1)	0.1396(5)	0.4206(2)	2.8
C(2)	0.0798(1)	−0.0542(4)	0.4171(2)	2.5
C(3)	0.1171(1)	−0.1976(5)	0.4633(2)	3.2
C(4)	0.1737(1)	−0.1492(6)	0.5148(3)	3.8
C(5)	0.1914(1)	0.0436(6)	0.5199(2)	4.1
C(6)	0.1539(1)	0.1875(5)	0.4743(2)	3.5
C(7)	−0.0120(1)	−0.2177(4)	0.3837(2)	2.7
C(8)	−0.0740(1)	−0.2499(5)	0.3354(2)	2.7
C(9)	−0.1108(1)	−0.1015(5)	0.2920(2)	3.4
C(10)	−0.1694(1)	−0.1395(6)	0.2466(3)	4.2
C(11)	−0.1913(2)	−0.3248(7)	0.2462(3)	4.9
C(12)	−0.1557(2)	−0.4718(6)	0.2914(3)	4.8
C(13)	−0.0970(1)	−0.4370(5)	0.3372(3)	3.7

a) $B_{\mathrm{eq}}=(4/3)\Sigma_i\Sigma_j\beta_{ij}a_i\cdot a_j$.

nonediimine structures (1.38(2) Å in [Ni{(NH)$_2$C$_6$H$_4$}$_2$],[24] 1.330(4) Å in [Ni{(NH)$_2$C$_2$(CN)$_2$}$_2$][25]). These bond distances also reveal that 2-iminobenzenethiolato moieties of [Ni(ddbt)] result in a non-innocent ligand. [Ni(ddbt)] is packed with the interligand S···S contacts (3.49—3.58 Å) in the range of sulfur–sulfur van der Waals contacts (ca. 3.70 Å).

Although the hydrogen atoms on C7 and C14 of [Ni(ddbt)] are difficult to find from the difference-Fourier map only, bond distances and angels around C7 and C14 clearly indicate an sp^3 hybridization for these atoms. As a consequence, C7 and C14 come to asymmetric carbon atoms. The helical chirality P (or M) in [Ni(phbt)$_2$] is probably related to the two asymmetric centers *R*,*R* (or *S*,*S*) in [Ni(ddbt)].[27]

Molecular Structure of [Co(ddbt)]. The molecular structure and atom numbering scheme for [Co(ddbt)] is shown in Fig. 3. This complex with a dihedral angle between the CoNS planes of 8.2(1)° is isostructural with [Ni(ddbt)] and it is thought that 2-iminobenzenethiolate moieties result in a non-innocent ligand (Tables 4 and 5). Indeed, the Co–N (1.815(4) and 1.819(3) Å) bond distances correspond to those of the neutral semiquinonediimine cobalt complex.[28] On the other hand, the Co–S (2.139(2) and 2.136(2) Å) bond distances are shorter than those of the neutral dithiolene cobalt complexes (2.161(6) Å in [Co{S$_4$C$_4$(CF$_3$)$_4$}]$_2$,[29] 2.31 Å in (Perylene)-[Co{S$_2$C$_2$(CN)$_2$}$_2$](CH$_2$Cl$_2$)$_{0.5}$,[30] 2.190(2) Å in (Per)$_4$-[Co{S$_2$C$_2$(CN)$_2$}$_2$]$_3$[31]). In addition, the C–S (1.737(6) and 1.741(5) Å) bond distances, which are sensitive to charge distribution, are longer than those in the corresponding

Table 3. Atomic Parameters for [Ni(ddbt)]

Atom	x/a	y/b	z/c	B_{eq}[a)]/$Å^2$
Ni(1)	0.4916(1)	0.5928(0)	0.2992(1)	2.7
S(1)	0.7171(2)	0.5737(1)	0.4163(2)	3.9
S(2)	0.3670(2)	0.5292(1)	0.3714(2)	3.4
N(1)	0.5804(5)	0.6517(2)	0.2356(4)	2.7
N(2)	0.3120(5)	0.6092(2)	0.1804(4)	2.6
C(1)	0.8226(7)	0.6264(3)	0.3661(6)	3.3
C(2)	0.7360(7)	0.6640(2)	0.2765(5)	2.8
C(3)	0.8155(7)	0.7102(3)	0.2407(6)	3.7
C(4)	0.9756(8)	0.7163(3)	0.2880(7)	4.8
C(5)	1.0624(8)	0.6778(3)	0.3716(7)	5.1
C(6)	0.9889(8)	0.6338(3)	0.4099(7)	4.6
C(7)	0.4702(7)	0.6876(2)	0.1497(5)	2.7
C(8)	0.4172(7)	0.7365(2)	0.2160(6)	3.0
C(9)	0.4367(7)	0.7391(3)	0.3475(6)	3.5
C(10)	0.3783(3)	0.7835(3)	0.4024(7)	4.6
C(11)	0.3013(9)	0.8249(3)	0.3294(8)	5.2
C(12)	0.2834(9)	0.8234(3)	0.1990(8)	5.3
C(13)	0.3413(8)	0.7789(3)	0.1434(6)	4.2
C(14)	0.3256(7)	0.6512(2)	0.0864(5)	2.8
C(15)	0.3496(7)	0.6269(2)	−0.0377(5)	2.8
C(16)	0.2679(9)	0.6497(3)	−0.1506(6)	4.4
C(17)	0.2945(10)	0.6305(3)	−0.2646(7)	5.5
C(18)	0.3985(9)	0.5881(3)	−0.2674(6)	4.9
C(19)	0.4790(8)	0.5637(3)	−0.1553(7)	4.1
C(20)	0.4535(7)	0.5837(3)	−0.0407(6)	3.5
C(21)	0.1875(7)	0.5365(3)	0.2638(6)	3.0
C(22)	0.1794(7)	0.5785(2)	0.1706(5)	2.7
C(23)	0.0366(7)	0.5853(3)	0.0770(6)	3.6
C(24)	−0.0898(8)	0.5518(3)	0.0817(7)	4.7
C(25)	−0.0805(8)	0.5104(3)	0.1748(7)	5.0
C(26)	0.0557(8)	0.5023(3)	0.2650(7)	4.2

a) $B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

Table 4. Atomic Parameters for [Co(ddbt)]

Atom	x/a	y/b	z/c	B_{eq}[a)]/$Å^2$
Co(1)	0.4956(1)	0.5924(0)	0.3025(1)	2.9
S(1)	0.7238(2)	0.5730(1)	0.4177(1)	3.9
S(2)	0.3671(2)	0.5292(1)	0.3741(1)	3.5
N(1)	0.5844(4)	0.6506(2)	0.2390(4)	2.9
N(2)	0.3169(4)	0.6080(2)	0.1839(3)	2.6
C(1)	0.8308(6)	0.6261(2)	0.3684(5)	3.4
C(2)	0.7415(6)	0.6637(2)	0.2799(4)	3.0
C(3)	0.8201(7)	0.7093(2)	0.2432(5)	3.8
C(4)	0.9830(7)	0.7152(3)	0.2914(6)	4.8
C(5)	1.0685(6)	0.6776(3)	0.3746(6)	5.3
C(6)	0.9933(6)	0.6333(3)	0.4128(5)	4.5
C(7)	0.4768(6)	0.6864(2)	0.1524(4)	2.9
C(8)	0.4230(6)	0.7360(2)	0.2175(4)	2.9
C(9)	0.4416(7)	0.7400(2)	0.3485(5)	3.6
C(10)	0.3827(7)	0.7854(2)	0.4019(5)	4.6
C(11)	0.3056(7)	0.8265(3)	0.3274(6)	5.4
C(12)	0.2896(8)	0.8236(2)	0.1972(6)	5.4
C(13)	0.3480(7)	0.7784(2)	0.1440(5)	4.4
C(14)	0.3312(6)	0.6503(2)	0.0901(4)	2.7
C(15)	0.3552(6)	0.6258(2)	−0.0354(4)	3.0
C(16)	0.2770(7)	0.6492(2)	−0.1481(5)	4.6
C(17)	0.3029(9)	0.6296(3)	−0.2628(5)	6.2
C(18)	0.4040(7)	0.5872(3)	−0.2659(5)	4.8
C(19)	0.4812(7)	0.5635(2)	−0.1542(5)	4.2
C(20)	0.4560(6)	0.5829(2)	−0.0394(5)	3.6
C(21)	0.1872(6)	0.5357(2)	0.2648(5)	3.2
C(22)	0.1819(5)	0.5778(2)	0.1722(4)	2.8
C(23)	0.0408(6)	0.5841(2)	0.0793(5)	3.7
C(24)	−0.0866(6)	0.5515(3)	0.0814(6)	4.5
C(25)	−0.0813(7)	0.5107(3)	0.1731(6)	4.9
C(26)	0.0548(6)	0.5027(2)	0.2649(5)	4.0

$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

cobalt complexes (C–S, 1.694(6) Å in $[Co\{S_4C_4(CF_3)_4\}]_2$,[29)] 1.717(7) Å in $(Per)_4[Co\{S_2C_2(CN)_2\}_2]_3$[31)]). However, in contrast to mononuclear [Co(ddbt)], these cobalt complexes have cobalt–sulfur-bonded dinuclear or polynuclear structures and this difference is anticipated to exert influence on bond orders. The observed shortest Co···Co distance is 6.20 Å and this distance excludes Co–Co contacts between adjacent molecules. From steric considerations, the bulky size of two phenyl groups, which displace above and below the coordination plane, favors a structure with the two planar units widely separated. The interligand S···S contacts (3.46—3.56 Å) are also observed in [Co(ddbt)].

Spectroscopic Characterization of the Compounds. Characterization of $[Co(phbt)_2]$ was performed by the measurement of the UV-vis spectrum. The electronic spectrum of $[Co(phbt)_2]$ reveals a broad band in the region of about 6000 to 10000 cm^{-1} ($\log \varepsilon_{max} = 1.90$), which is typical of the tetrahedral cobalt(II) complexes.[32)] Despite the dominant overlapping charge transfer band around 20000 cm^{-1}, $[Ni(phbt)_2]$ exhibits a weak band around 15000 cm^{-1}, which is a typical d–d transition for square planar nickel(II) complex.[33)] The intense blue [Co(ddbt)] and the intense violet [Ni(ddbt)] show very strong absorption bands at 15040 cm^{-1} ($\log \varepsilon = 4.43$) and 11980 cm^{-1} ($\log \varepsilon = 4.56$), respectively, in $CHCl_3$ (Table 6). These bands are features common to dithiolene-like complexes with electron-transfer properties.[34)]

Table 5. Selected Structural Data for $[Ni(phbt)_2]$, [Ni(ddbt)], and [Co(ddbt)]

	$[Ni(phbt)_2]$	[Ni(ddbt)]	[Co(ddbt)]
M(1)–S(1)	2.180(1)	2.126(2)	2.139(2)
M(1)–S(2)		2.129(2)	2.136(2)
M(1)–N(1)	1.926(2)	1.830(5)	1.815(4)
M(1)–N(2)		1.826(4)	1.819(3)
C(1)–S(1)	1.755(3)	1.728(7)	1.737(6)
C(21)–S(2)		1.729(6)	1.741(5)
C(2)–N(1)	1.436(3)	1.352(7)	1.365(6)
C(22)–N(2)		1.351(7)	1.357(6)
C(7)–N(1)	1.288(4)	1.464(7)	1.460(6)
C(14)–N(2)		1.464(8)	1.470(6)
C(7)–C(7)*	3.852(4)		
C(7)–C(14)		1.561(8)	1.561(7)

*intramolecular contact related to the twofold axis.

ESR spectra were measured at 77 K in toluene. Although the ESR signals for $[Co(phbt)_2]$ have not been observed at 77 K, the complex [Co(ddbt)] exhibits g_1 at 2.472, g_2 at 2.046, and g_3 at 2.014[35)] (Fig. 4) and this pattern is similar to those of square planar low-spin cobalt(II) complexes.[36)]

Table 6. Electronic Spectral Data and Electrochemical Potentials for [Co(phbt)$_2$], [Co(ddbt)], [Ni(phbt)$_2$], and [Ni(ddbt)]

	$\nu_{\max}/10^3\,\mathrm{cm}^{-1}$ ($\log\varepsilon$; ε in $\mathrm{mol}^{-1}\,\mathrm{dm}^3\,\mathrm{cm}^{-1}$)	$E_{1/2}$/V vs. Ag/AgCl (ΔE_p/mV)
[Co(phbt)$_2$]	8.26 (1.90), 14.40 (2.53), 15.60 (2.63), 19.80br (3.38), 23.24br (3.54), 29.66br (4.15)	−1.26 (164)
[Co(ddbt)]	7.36 (3.29), 9.60 (2.82), 12.37 (3.65), 12.90 (3.64), 15.04 (4.43), 18.50sh (3.33), 22.44br (3.12), 29.64br (3.50)	−1.27 (136), −0.04 (134)
[Ni(phbt)$_2$]	11.80 (1.82), 15.40sh (2.28), 20.00sh (3.53), 21.90 (3.59)	−0.96 (124)
[Ni(ddbt)]	8.75 (3.43), 10.13 (3.36), 11.98 (4.56), 13.70sh (3.85), 17.07 (3.15), 18.54 (3.14), 21.16 (3.09), 28.10 (3.63), 30.96 (3.77)	−0.97 (136), −0.10 (146)

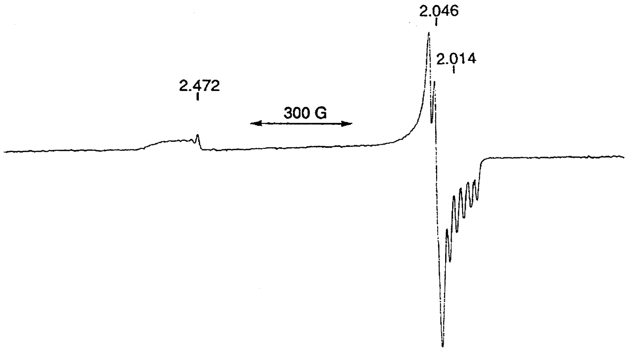


Fig. 4. ESR spectrum of [Co(ddbt)] at 77 K, 9.21 GHz, in toluene (1000 G scan range, 3000 G midrange).

In the ^{1}H NMR spectrum of [Ni(phbt)$_2$], the N=CH protons (7.76 ppm) appear as singlet and the 2-iminobenzenethiolato protons appear as two sets of doublet (7.38, 6.21 ppm) and two sets of triplet (7.01, 6.66 ppm).$^{37)}$ This result indicates the C_2 symmetrical structure in $\mathrm{CDCl_3}$. Moreover, the ^{1}H NMR spectrum of [Ni(phbt)$_2$] gives two sets of triplet (7.39, 7.22 ppm) and one set of doublet (8.78 ppm) for pendant phenyl groups. This doublet ($\delta = 8.78$) assigned to the aromatic *ortho* protons is shifted downfield relative to the normal phenyl groups. ^{1}H NMR investigations of [Ni(phbt)$_2$] using one enantiomer of Pirkle's reagent, [9-(1-hydroxy-2,2,2-trifluoroethyl)anthracene],$^{38)}$ show a doubling of several proton signals, demonstrating the presence of two diastereomeric species. This is indeed a clear demonstration that this system is chiral. In the ^{1}H NMR spectrum of [Ni(ddbt)], one sharp peak due to the protons on asymmetric carbon atoms, which are generated by the carbon–carbon bond formation, is observed at $\delta = 6.34$. This result indicates that [Ni(ddbt)] also has C_2 symmetrical structure in $\mathrm{CDCl_3}$ (Fig. 5). The 2-iminobenzenethiolato protons of [Ni(ddbt)] don't exhibit clear peak sets such as [Ni(phbt)$_2$]. This behavior may be due to the delocalized ground state of [Ni(ddbt)].

Cyclic voltammograms of [Co(phbt)$_2$] and [Co(ddbt)] show quasi-reversible oxidation reduction waves due to $\mathrm{Co^{II/I}}$ couple$^{39)}$ at $E_{1/2} = -1.26$ and -1.27 V, respectively. In cyclic voltammograms of [Ni(phbt)$_2$] and [Ni(ddbt)], the quasi-reversible waves at $E_{1/2} = -0.96$ V for [Ni(phbt)$_2$] and $E_{1/2} = -0.97$ V for [Ni(ddbt)] are assigned to the $\mathrm{Ni^{II/I}}$ couple (Fig. 6).$^{40)}$ The most interesting peculiarity in the cyclic voltammetric studies is that [Co(ddbt)] and [Ni(ddbt)] exhibit two quasi-reversible redox waves in contrast to one quasi-reversible redox wave for [Co(phbt)$_2$] and [Ni(phbt)$_2$]. Furthermore, the excess redox wave of [Co(ddbt)] and [Ni(ddbt)] occurs at low potentials ($E_{1/2} = -0.04$ V for [Co(ddbt)] and $E_{1/2} = -0.10$ V for [Ni(ddbt)]). This similarity of [Co(ddbt)] and [Ni(ddbt)] shows that these redox processes are governed by the ligands.

Conclusion

The complexes [Co(ddbt)] and [Ni(ddbt)] have been structurally characterized by X-ray crystallography and the structural features of [Co(ddbt)] and [Ni(ddbt)] point clearly to the neutral dithiolene-like charge distribution. While the nickel and cobalt atoms exhibit the much different coordination chemistry, the coordination environments around each metal center in [Co(ddbt)] and [Ni(ddbt)] are best described as square planar. The differences of both molecular structures are less pronounced. This fact strongly suggests that the molecular structures are governed by the needs of ligands. The observed structural characteristics offer some proof for mixing of resonance structures, as shown in Fig. 7. Furthermore, since [Co(phbt)$_2$] and [Ni(phbt)$_2$] and the corresponding [Co(ddbt)] and [Ni(ddbt)] have the same chemical compositions, respectively, we can consider them isomers. In general, the chemical composition is necessarily changed by the bond formation or dissociation. Nevertheless, the reaction of [Co(phbt)$_2$] or [Ni(phbt)$_2$] yielding [Co(ddbt)] or [Ni(ddbt)] forms a new carbon–carbon bond, but the chemical compositions remain unaltered. This isomerism, which should be designated valence isomerism like an isomerization of quadricyclene,$^{41)}$ is not common in metal complex systems. The total number of chemical bonds in the resonance structure of [M(ddbt)] is the same as that in [M(phbt)$_2$] and this means that the resonance structure with M(II) in Fig. 7 is adequate as a representation of [M(ddbt)] (M = Co and Ni).

ESR spectrum of [Co(ddbt)] exhibits typical characteristics in square planar low-spin cobalt(II) complex. Furthermore, the complex [Ni(ddbt)] appears diamagnetic, as evi-

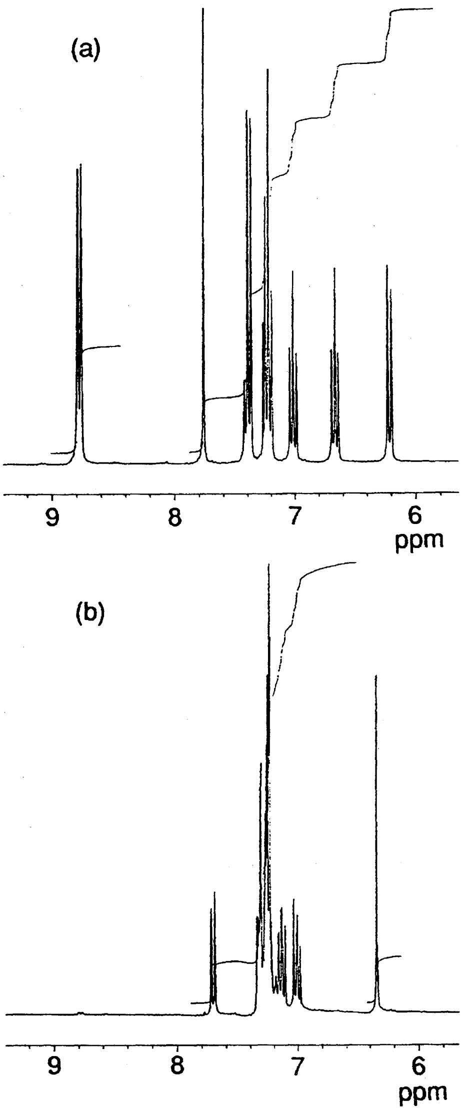


Fig. 5. The ^{1}H NMR spectra (270 MHz, $CDCl_3$) of [Ni$(phbt)_2$] (a) and [Ni$(ddbt)_2$] (b).

denced by sharp resonances in the ^{1}H NMR spectrum at room temperature. These results suggest that the metal orbital is not appreciably influenced by the delocalized electrons.[42]

The presence of Ni···H–C interaction[43] in [Ni$(phbt)_2$] can be deduced by ^{1}H NMR spectroscopy and X-ray crystal structures: ^{1}H NMR studies indicate a downfield shift of the resonance assigned to the interacting hydrogen ($\delta = 8.78$)[44] and X-ray diffraction studies indicate the presence of the short Ni···H–C contact (Ni(1)···H(9)–C 2.42(4) Å). Furthermore, the reaction of [Ni$(phbt)_2$] yielding [Ni(ddbt)] easily occurs in non-polar solvents like toluene and hardly occurs in polar solvents like EtOH. In addition, this reaction proceeds even at room temperature in the dark. These results support the conclusion that the Ni···H–C interaction, like the hydrogen bond, plays an important role as a driving force in this reaction.[45]

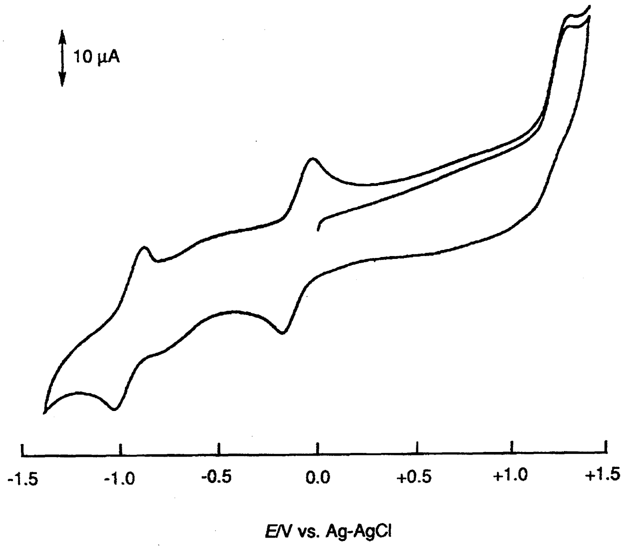


Fig. 6. Cyclic voltammogram of [Ni(ddbt)].

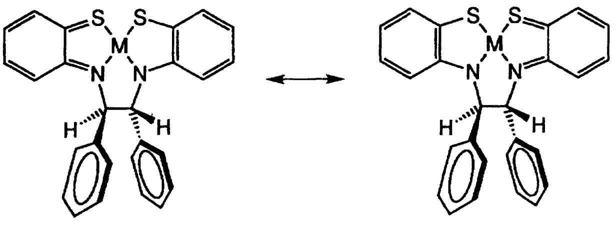


Fig. 7.

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45) [Co(phbt)$_2$] may also have the short Co$\cdots$H–C contact like the analogous tetrahedral distorted Zn complex with ferrocenyl groups (Ref. 19).