Bull. Chem. Soc. Jpn., ***69***, *2573—2579 (1996)*

Ion Pair Charge-Transfer Complexes of Dithiolatocobaltates with Cationic Copper or Nickel Macrocycles: Crystal Structure and Magnetic Properties

Georg Schmauch, Teiji Chihara, Yasuo Wakatsuki,* Masayuki Hagiwara, and Horst Kisch†

The Institute of Physical and Chemical Research (RIKEN), Wako, Saitama 351-01

†Institute of Inorganic Chemistry, University of Erlangen-Nürnberg, 91058 Erlangen, Egerlandstr. 1, Germany

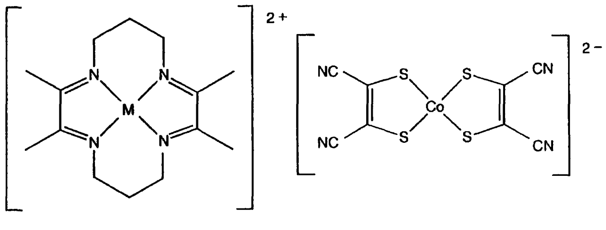
(Received April 26, 1996)

The complexes $\{[M(tim)]^{2+}[Co(mnt)_2]^{2-}\}$, (M = Ni (**NiCo**), Cu (**CuCo**), tim = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene, mnt^{2-} = *cis*-1,2-dicyano-1,2-ethylenedithiolato) have been isolated. **NiCo** and **CuCo** have isomorphous crystal structures ($P1$-), the basic feature of which is the presence of mixed donor–acceptor chains induced by short intrachain distances of 3.15 and 3.03 Å, respectively. For both **NiCo** and **CuCo**, an ion pair charge-transfer band is observed at 707 and 843 nm; application of the Hush model affords reorganization energies for electron transfer from the dianion to the dication of 89 and 104 kJ mol^{-1}, respectively. The magnetic properties of the powder samples have been studied in the temperature range of 2 K to 300 K. In **NiCo** the diamagnetic $[Ni(tim)]^{2+}$ acceptor induces antiferromagnetic coupling of the spin a half system $[Co(mnt)_2]^{2-}$ along the *a*-axis over a distance of 6.3 Å. From the exchange coupling constant of $J = -37$ cm^{-1} a Weiss temperature of 26 K is calculated. Contrary to that, the magnetic orbitals of $[Cu(tim)]^{2+}$ and $[Co(mnt)_2]^{2-}$ remain uncoupled in **CuCo**.

Within the last decade, new interest in metal dithiolato-containing systems has evolved. This is mainly due to the fact that these complexes offer a variety of interesting physical effects with the implication of technical applications. Special attention was given to square planar bis(1,2-dithiolato) transition metal complexes with regard to electrical conductivity,[1] superconductivity,[2] non-linear optics,[3] or electrooptics.[4] The ability of these plate-like dithiolatometalates to form charge-transfer complexes with organic or organometallic components is well known. In most cases, ion pairs were obtained, the structure of which consisted either of segregated[5] or mixed stacks.[6] In the latter case, paramagnetic ditholatometalates have been used successfully to built up systems exhibiting cooperative phenomena.[7] For example the mixed stack compounds $TTF[M(S_2C_2(CF_3)_2)_2]$ (M = Pt, Ni, and TTF = tetrathiafulvalene) are ferro- and ferrimagnetic chains[8] and the ion pair of decamethylferrocenium with $[Ni(dmit)_2]^-$ (dmit^{2-} = 2-thioxo-1,3-dithiole-4,5-dithiolate) exhibites a ferromagnetic transition.[9] Another strategy to model the magnetic properties of ionic CT systems is to combine two planar metal complex ions, but examples of this type are still rare. For the heterometallic assemblies $\{[Au(TPP)]^+[M(mnt)_2]^-\}$ (TPP = tetraphenylporphyrin, M = Ni, Pt, Au; mnt^{2-} = *cis*-1,2-dicyano-1,2-ethylenedithiolato) an alternate arrangement of both planar ions has been suggested.[10] However, in that case the paramagnetic anion was found to be magneticaly diluted.[10] Planar macrocyclic complexes of the tetraimine ligand, tim (tim = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene) and cyclam (cyclam = 1,4,8,11-tetraazacyclotetradecane), were also employed as planar components. For example in $[Cu(tim)]CuCl_4$, the dication is bridged by the tetrahedral $[CuCl_4]^{2-}$ in an unsymmetrical manner, resulting in an alteranating chain with antiferromagnetic and ferromagnetic couplings.[11] Combinations of octahedral $[M(cyclyam)(MeCN)_2]^{2+}$ with planar monoanionic $[Ni(dmit)_2]^-$ did not induce unusual magnetic interactions.[12] Finally, it was communicated that the complexes $\{[Ni(tim)]^{2+}[M(mnt)_2]^{2-}\}$ (M = Ni, Pd, Pt), which contain two planar ions, exhibit an ion pair change transfer (IPCT) band in the range of 820 to 840 nm.[13] In recent work we have shown that in the same type of IPCT complexes, wherein the cationic complex is replaced by a dipyridinium derivative, the electrical conductivity could be quantitatively controlled over eight orders of magnitude by modeling the CT-interaction through variation of the components' redox potential.[14] It seemed therefore worthwile to study whether this interaction would also influence magnetic properties when paramagnetic components are introduced. In the following we report on the isolation, solid state structure, and magnetism of $\{[M(tim)]^{2+}[Co(mnt)_2]^{2-}\}$ (**NiCo**: M = Ni, **CuCo**: M = Cu). (Scheme 1).

Results and Discussion

The new complexes were obtained as black crystals by mixing an acetone solution of $(NBu_4)_2[Co(mnt)_2]$ with a DMSO solution of $[M(tim)]ZnCl_4$ (M = Cu, Ni), followed by crystallization of the resulting powder from DMSO/acetone/MeOH. X-Ray structural analyses revealed that **CuCo** and **NiCo** are isomorphous (Fig. 1, Table 4). All metal atoms are occupying centers of inversion and the cobalt atoms are



$[\mathrm{M(tim)}]^{2+}$; M=Cu, Ni **$[\mathrm{Co(mnt)_2}]^{2-}$**

Scheme 1.

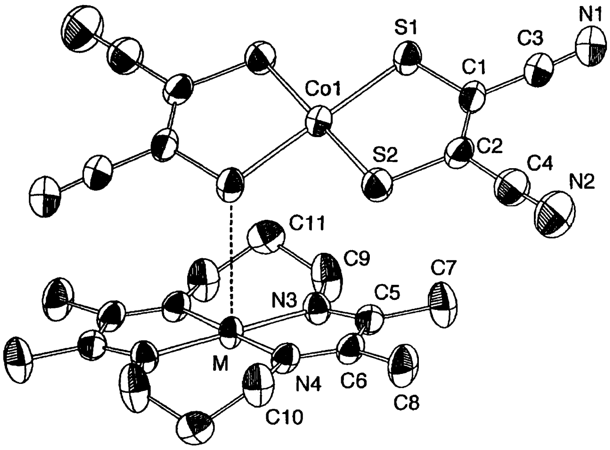


Fig. 1. Molecular structure of **NiCo** and **CuCo**.

therefore well sperated from each other by the lattice constants. Along the *a*-axis the donors and acceptors form an alternatively mixed arrangements where the Co–Cu or Co–Ni distance is equal to *a*/2. (Fig. 2). While there were sufficient structural data reported for $[\mathrm{Cu(tim)}]^{2+}$-containing systems,[11a,15] the first X-ray structure analysis of $[\mathrm{Ni(tim)}]^{2+}$ has been published very recently.[16] In $[\mathrm{M(tim)}]^{2+}$ (M = Cu, Ni) the metal atom has a planar coordination geometry and bond lengths and angles (Tables 1 and 2) agree with the literature values.[16] In both **CuCo** and **NiCo**, the cobalt atom is square planar coordinated by the sulfur atoms S(1), and S(2) and the bond lengths and angles of $[\mathrm{Co(mnt)_2}]^{2-}$ are in good agreement with the data reported for $(\mathrm{NBu_4})_2[\mathrm{Co(mnt)_2}]$[17]

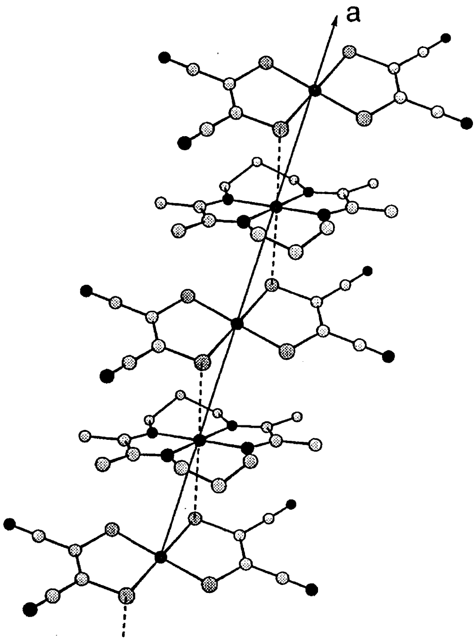


Fig. 2. Packing along the *a*-axis.

Table 1. Selected Bond Lengths (Å) for **CuCo** (M(1) = Cu) and **NiCo** (M(1) = Ni)

	CuCo	**NiCo**
M(1) -S(1)	3.034(2)	3.154(2)
M(1) -N(3)	1.954(3)	1.899(3)
M(1) -N(4)	1.954(2)	1.889(3)
N(3) -C(5)	1.272(4)	1.285(5)
N(4) -C(6)	1.265(4)	1.284(5)
N(3) -C(9)	1.472(4)	1.473(5)
N(4) -C(10)	1.478(4)	1.471(5)
C(5) -C(6)	1.517(4)	1.490(5)
C(5) -C(7)	1.494(5)	1.507(7)
C(6) -C(8)	1.494(5)	1.494(6)
C(9) -C(11)	1.505(5)	1.495(7)
Co(1) -S(1)	2.191(1)	2.171(1)
Co(1) -S(2)	2.186(2)	2.171(1)
S(1) -C(1)	1.736(3)	1.735(4)
S(2) -C(2)	1.730(4)	1.735(5)
C(1) -C(2)	1.366(4)	1.367(5)
C(1) -C(3)	1.417(5)	1.420(6)
C(2) -C(4)	1.426(5)	1.422(6)
C(3) -N(1)	1.137(6)	1.140(7)
C(4) -N(2)	1.138(5)	1.142(6)
C(7) -HC(71)	0.98(5)	
C(7) -HC(72)	0.96(6)	0.75(6)
C(7) -HC(73)	0.83(6)	
C(8) -HC(81)	1.02(7)	0.90(7)
C(8) -HC(82)	0.82(5)	0.97(7)
C(8) -HC(83)	0.90(6)	0.97(6)
C(9) -HC(91)	0.93(5)	0.91(6)
C(9) -HC(92)	1.01(6)	1.07(8)
C(10) -HC(101)	0.98(3)	0.90(5)
C(10) -HC(102)	0.95(6)	1.10(7)
C(11) -HC(111)	0.97(3)	0.94(5)
C(11) -HC(112)	0.91(5)	0.96(4)

Table 2. Selected Bond Angles (°) for **CuCo** (M(1) = Cu) and **NiCo** (M(1) = Ni)

	CuCo	**NiCo**
S(1)–Co(1) -S(2)	91.20(5)	91.45(5)
S(1)–Co(1) -S(2′)	88.80(5)	88.55(5)
Co(1)–S(1) -C(1)	103.3(1)	103.9(2)
Co(1) -S(2) -C(2)	103.8(1)	104.2(1)
S(1) -C(1) -C(3)	117.6(2)	117.2(3)
S(2) -C(2) -C(4)	118.5(3)	118.5(3)
C(1) -C(3) -N(1)	177.9(3)	177.3(4)
C(2) -C(4) -N(2)	178.9(7)	179.3(5)
N(3) -M(1) -N(4)	81.1(1)	82.2(1)
M(1) -N(3) -C(5)	115.7(2)	116.0(3)
N(3) -C(5) -C(6)	113.5(3)	112.5(4)
C(5) -C(6) -C(8)	120.7(3)	121.6(4)
N(3) -C(9) -C(11)	112.6(3)	112.8(4)

and $BQ[Co(mnt)_2]$.[14d] For $[M(mnt)_2]^{2-}$ (M = Ni, Pd) it was suggested that the bending out of the ligand cyano groups from the dithiolatometalate plane is due to crystal packing effects.[14c] In **CuCo** and **NiCo**, the corresponding atoms C(1) and C(2) are bent out of the plane defined by Co(1), S(1), and S(2) by 0.112(5) to 0.187(4) Å (Table 3). The crystal packing force which caused these deviations may be the result of a short *intrachain* contact observed in direction of the *a*-axis between S(1) of the donor and Cu or Ni of the acceptor (Figs. 1 and 2). The M–S(1) distances of 3.034(2) Å in **CuCo** and 3.154(2) Å in **NiCo** are distinctively shorter than the sum of the Van der Waals radii (3.2 Å for Cu–S and 3.43 Å for Ni–S),[18] but too long to suggest the presence of a chemical bond. For instance, the largest Ni–S distance that has been measured in a low spin nickel thiolato complex, is 2.45 Å.[19] Contrary to that, the Cu–S distance in $[Cu(tim)SCN]PF_6$ is 3.34 Å and the metal has a tetragonal–octahedral coordination geometry which gives rise to a polymeric solid state structure.[15]

The shortest *interchain* contacts in **CuCo** and **NiCo** are slightly longer than the sum of the van der Waals radii and are found between dianions and dications. In the *b*-direction, the shortest distance amounts to 3.506 Å for **CuCo** and 3.575(4) Å for **NiCo** between S(1) of the dianion and N(4) of the dication; in the direction of the *c*-axis, it is 3.727(7) Å for **CuCo** and 3.690(10) Å for **NiCo** between N(2) of the dianion and C(3) and C(7) of the dication, respectively.

While strong interactions lead to the formation of discrete dimeric structures, which is often the case for monoanionic dithiolatometalates,[20] the semi-coordination[21] of Cu in **CuCo** and Ni in **NiCo** by the dithiolato sulfer atoms suggests a mutual IPCT interaction and may be responsible for formation of the mixed-stack chain structure (Fig. 2). This interaction and steric hindrance between $[Co(mnt)_2]^{2-}$ and trimethylene groups of the tim-ligand may be responsible for the non-coplanar arrangement of the two ions; the resulting angle between the planes defined by Co–S(1)–S(2) and M–N(3)–N(4)–C(5)–C(6) is 32.02(8)° in **CuCo** and 29.83(11)° **NiCo**. Different from that, a coplanar arrangement was found for the comparable IPCT complexes of the type $\{MV^{2+}[M(mnt)_2]^{2-}\}$ (MV^{2+} = 1, 1′-dimethyl-4,4′-bipyridinium, M = Ni, Pd, Pt) consisting of a planar organic dication and a planar d^8-dithiolatometalate dianion.[14]

While for both of the new complexes no IPCT band could be detected in solution, this was possible in the diffuse reflectance spectra of the powders. For **NiCo** a maximum is observable at 843 nm (1.47 eV) (Fig. 3). In the case of the analogous compound $\{[Ni(tim)]^{2+}[Ni(mnt)_2]^{2-}\}$ (**NiNi**), which contains two d^8 centers instead of the d^8–d^7 combination present in **NiCo**, the corresponding band occurs at about the same wavelength (840 nm, 1.49 eV) but with an at least double intensity.[13] For **CuCo** an intense shoulder appears at 650 nm and from the corresponding difference spectrum the maximum is found at 707 (1.76 eV).

From the redox potentials $E_{[Co(mnt)_2]^{-/2-}} = +0.04$ V,[22] $E_{[Ni(tim)]^{2+/+}} = -0.50$ V,[23] $E_{[Cu(tim)]^{2+/+}} = -0.64$ V,[24] and $E_{[Ni(mnt)_2]^{-/2-}} = +0.22$ V[25c] (in MeCN vs. SCE) the driving force of electron transfer from the dianion to the dication, ΔG_{12}, is calculated as 0.68, 0.54, and 0.72 eV for **CuCo**, **NiCo**, and **NiNi**, respectively. Through application of the modified Hush equation,[25] $E_{op} = \chi + \Delta G_{12}$, the reorganization energies χ are obtained as 104 kJ mol^{-1} (**CuCo**), 89 kJ mol^{-1} (**NiCo**), and 73 kJ mol^{-1} (**NiNi**). Apparently, χ increases each time by about 15 kJ mol^{-1} when the two diamagnetic ions in **NiNi** are successively substituted by the two paramagnetic ions Co(II) and Cu(II). A discussion of this interesting observation is deferred until it is corroborated by further experimental results.

The ESR spectrum of a powder sample of **CuCo** consisted of signals at $g = 2.51$ and 2.09 and corresponds to the superimposition of the signals of $[Co(mnt)_2]^{2-}[Cu(tim)]^{2+}$ as indicated by the signals at $g = 2.03$ and 2.73,[26] and at $g = 2.06$ obtained for $(NBu_4)_2[Co(mnt)_2]$ and $[Cu(tim)](PF_6)_2$, respectively. For **NiCo**, a pattern similar to that of $(NBu_4)_2[Co(mnt)_2]$ was found at $g = 2.94$ and 2.02. Low temperature experiments ($T = 5$ K)revealed that there is no significant change in line shape and position of the signals. Therefore there is no magnetic interaction detectable between the two ions.

There has been an early report about the temperature dependence of the molar magnetic moment ($\chi_M T$) of $(NBu_4)_2[Co(mnt)_2]$.[27] Typically for square planar Co(II) complexes, it decreases linearly with temperature.[28] A freshly prepared sample gave $\chi_M T = 0.63$ cm^3 mol^{-1} K at room temperature, 0.56 cm^3 mol^{-1} K at 77 K, and 0.54 cm^3 mol^{-1} K at 2 K. The deviation from Curie law may be explained by assuming spin-orbit coupling or the contribution of low-lying excited states. A plot of $\chi_M T$ vs. temperature shows that in the case of **CuCo** the magnetic behavior is paramagnetic (Fig. 4). Small humps at low temperature are due to traces of oxygen which has two phase transitions, one at around 20 K and another at around 50 K.[29] The drop of $\chi_M T$ below 13 K indicates the onset of weak antiferromagnetic coupling.

Contrary to the behavior of the tetrabutylammonium salt of the cobalt component, the $[Ni(tim)]^{2+}$ ion pair **NiCo** exhibits a continuous and enhanced decline of $\chi_M T$ with decreasing temperature, which indicates the presence of antiferromagnetic coupling (Fig. 4). Since $[Ni(tim)]^{2+}$ is diamagnetic, the magnetic moment is due to the $S = 1/2$ system of $[Co(mnt)_2]^{2-}$. The $\chi_M T$ value is 0.63 cm^3 mol^{-1}K at room temperature, 0.47 cm^3 mol^{-1} K at 77 K, and is tending towards zero when the temperature is lowered further (at 2

Table 3. Deviation [Å] from the Plane Defined by Co–S(1) –S(2) in $[Co(mnt)_2]^{2-}$ for **CuCo** and **NiCo**

	CuCo	NiCo
C(1)	0.187(4)	0.124(5)
C(2)	0.179(4)	0.112(5)
C(3)	0.383(5)	0.242(6)
C(4)	0.348(6)	0.237(7)
N(1)	0.547(6)	0.328(7)
N(2)	0.507(7)	0.342(8)

Table 4. Crystal Data and Refinement Details for **CuCo** and **NiCo**

Compound	**CuCo**	**NiCo**
Formula	$C_{22}H_{24}CoCuN_8S_4$	$C_{22}H_{24}CoN_8NiS_4$
Formula weight	651.21	646.37
Crystal system	Triclinic	Triclinic
Spece group (No.)	$P1$-(2)	$P1$-(2)
$a/\text{Å}$	8.942(5)	9.087(4)
$b/\text{Å}$	11.122(5)	11.013(4)
$c/\text{Å}$	7.591(4)	7.576(3)
$\alpha/°$	105.27(3)	104.93(2)
$\beta/°$	111.68(2)	111.96(2)
$\gamma/°$	93.63(3)	93.87(2)
$U/\text{Å}^3$	665.9(6)	667.9(5)
Z	1	1
$D_c/\text{g cm}^{-3}$	1.624	1.607
Crystal size/mm	0.64 × 0.35 × 0.14	0.04 × 0.13 × 0.60
Temperature/K	295	295
$\lambda(\text{Mo}\,K\alpha)/\text{Å}$	0.71073	0.71073
$F(000)$	332	331
μ/cm^{-1}	17.521	16.57
$2\theta_{\text{max}}/°$	58	55
Reflections measured	3735	3219
Reflections used	3164 ($F \geq 3\sigma$)	2362 ($F \geq 3\sigma$)
No. of parameters	215	207
Correction made	North-Phillips	North-Phillips
Transmission coeff.	0.7809 — 0.9982	0.9946 — 0.8161
Final R	0.0390	0.0414
Final R_W	0.0439 ($w=1$)	0.0433 ($w=1$)
Goodness of fit	0.7912	0.861
$\Delta/\sigma(\text{max.})$	0.169	0.48
$\Delta r_{\text{map}}/\text{eÅ}^{-3}$	0.90	1.21

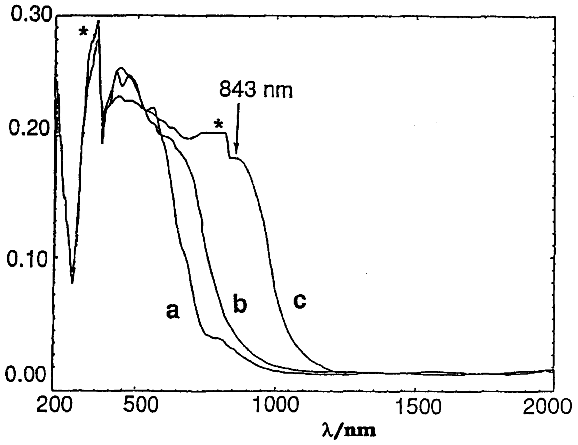


Fig. 3. Diffuse reflectance spectra of $(NBu_4)_2[Co(mnt)_2]$ (a), **CuCo** (b), and **NiCo** (c). (*) indicates technical artefact.

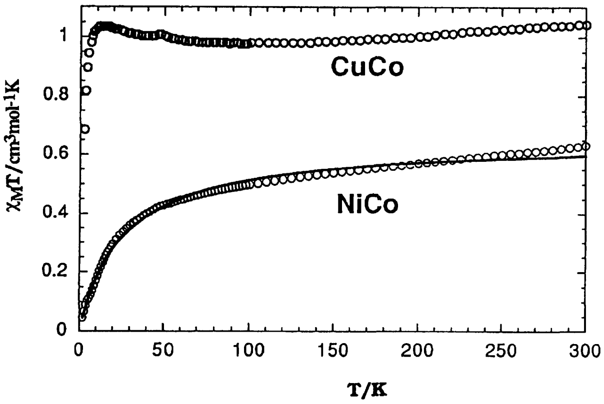


Fig. 4. Temperature dependence of the magnetic moments of **NiCo** and **CuCo**.

K $\chi_M T$ is 0.05 $\text{cm}^3\,\text{mol}^{-1}\,\text{K}$). From a fit of the experimental data of **NiCo** to the Curie–Weiss law over the whole temperature range by minimizing function $R=\sum(\chi_{\text{M(calcd)}}-\chi_{\text{M(obsd)}})^2/\sum(\chi_{\text{M(obsd)}})^2$ up to $R=7.8\times10^{-4}$, the following parameters were obtained by using the molecular field approximation and Hamiltonian $H=-J\sum S_iS_j$; $J=-37\ \text{cm}^{-1}$, $g=2.63$, and number of nearest neighbors $z=2$. From the interaction parameter J, the value of the Weiss temperature was calculated as 26 K. Since **CuCo** and **NiCo** are isomorphous and all intermolecular distance are nearly the same, it is the change from Cu(II) to Ni(II) that brings about the antiferromagnetic coupling. Extended Hückel MO calculations indicate that the HOMO of $[\text{Ni(tim)}]^{2+}$ has d_{z^2} character;[23] it is therefore directed towards the chain axis and capable of interacting with the dianion sulfur atoms (see Fig. 2). Thus, the diamagnetic nickel complex ion enables spin-coupling between the cobaltates over a distance of 6.3 Å. But for **CuCo**, SCF-Xα-SW calculations reveal that the SOMO of $[\text{Cu(tim)}]^{2+}$ has d_{xy}-character and is located in the molecular plane;[30] coupling along the a-axis is therefore not possible. This weaker interionic interaction in the case of **CuCo** is in accord with the higher reorganization energy of electron transfer as compared to **NiCo**.

Experimental

Synthesis. The starting materials [M(tim)]ZnCl$_4$ (M = Ni,[31) Cu[24)) and (NBu$_4$)$_2$[Co(mnt)$_2$][32) were synthesized according to the literature. All syntheses have been carried out under argon atmosphere.

Synthesis of [Cu(tim)][Co(mnt)$_2$] (CuCo). Into a solution of 275 mg (0.33 mmol) of (NBu$_4$)$_2$[Co(mnt)$_2$] in 50 ml of MeOH–acetone (1 : 1, v/v) was dropped a solution of [Cu(tim)]ZnCl$_4$ in 50 ml of DMSO. The precipitate was filtered after stirring for 2 h at room temperature. Washing with 3 ml of DMSO and 10 ml of MeOH : acetone (1 : 1, v/v) afforded a black powder (158 mg, 73%). Found: C, 40.43; H, 3.69; N, 17.03; S, 19.62%. Calcd for $C_{22}H_{24}CoCuN_8S_4$: C, 40.58; H, 3.71; N, 17.21; S, 19.70%. IR ν(C=N) 1586, 1701 cm^{-1}.

Synthesis of [Ni(tim)][Co(mnt)$_2$] (NiCo). Into a solution of 255 mg (0.31 mmol) of (NBu$_4$)$_2$[Co(mnt)$_2$] in 20 ml of acetone was dropped a solution of [Ni(tim)]ZnCl$_4$ (160 mg = 0.31 mmol) in 10 ml of DMSO. Then 20 ml of acetone was added. The precipitate was filtered after stirring for 15 min at room temperature and washed with 3 ml of DMSO and 5 ml of acetone. Black powder (155 mg, 78%). Found: C, 40.50; H, 3.83; N, 17.07; S, 19.71%. Calcd for $C_{22}H_{24}CoN_8NiS_4$: C, 40.88; H, 3.74; N, 17.34; S, 19.84%. IR ν(C=N) 1601, 1653 cm^{-1}.

Table 5. Atomic Coordinates (× 10^4) and Equivalent Temperature Factors (Å^2) for **CuCo**

Atom	x	y	z	B_{eq} a)
Cu(1)	5000(0)	0(0)	0(0)	2.5
Co(1)	0(0)	0(0)	0(0)	2.4
S(1)	2262(1)	−728(1)	1180(1)	2.9
S(2)	−1271(1)	−1877(1)	−2077(1)	3.4
N(1)	3784(5)	−3722(3)	1186(6)	5.0
N(2)	−781(6)	−5251(4)	−3107(8)	6.9
N(3)	6425(3)	−930(2)	1575(4)	2.4
N(4)	4499(3)	−1616(2)	−2085(4)	2.4
C(1)	1672(4)	−2351(3)	11(5)	2.8
C(2)	132(4)	−2853(3)	−1419(5)	3.1
C(3)	2828(5)	−3129(3)	636(6)	3.3
C(4)	−371(5)	−4186(4)	−2372(7)	4.3
C(5)	6413(4)	−2063(3)	629(5)	2.6
C(6)	5251(4)	−2470(3)	−1552(5)	2.5
C(7)	7406(5)	−2961(4)	1478(6)	3.9
C(8)	5060(5)	−3779(3)	−2879(6)	4.1
C(9)	7466(5)	−357(3)	3710(5)	3.6
C(10)	3342(5)	−1822(3)	−4162(5)	3.3
C(11)	7988(4)	1052(3)	4276(5)	3.1
HC(71)	692(6)	−387(5)	83(7)	6.5
HC(72)	753(7)	−271(5)	284(8)	8.1
HC(73)	835(7)	−271(5)	157(8)	8.7
HC(81)	494(7)	−450(6)	−230(9)	9.4
HC(82)	412(7)	−408(5)	−370(9)	9.0
HC(83)	600(7)	−405(5)	−281(8)	8.6
HC(91)	837(5)	−75(4)	406(6)	4.9
HC(92)	668(6)	−45(4)	435(7)	6.3
HC(101)	282(5)	−271(4)	−483(6)	3.6
HC(102)	395(6)	−159(5)	−485(7)	6.7
HC(111)	883(4)	130(3)	562(5)	3.1
HC(112)	859(5)	121(4)	358(6)	4.6

a) $B_{eq} = 4/3(\sum_i \sum_j B_{ij} a_i b_j)$.

Measurements. The magnetic susceptibilities of powdered samples were measured with a SQUID magnetometer (Quantum Design, MPMS2) in the temperature range of 2 to 300 K with an applied field of 0.1 T. The samples were prepared under a dry nitrogen atmosphere in a glove box. Experimental susceptibility data were corrected for the underlying diamagnetism using Pascal's constants.[33) Diffuse reflectance spectra were measured relative to corundum with a Shimadzu Model 3101 spectrometer equipped with an integrating sphere unit. Infrared spectra (KBr pellets) were recorded on a Perkin–Elmer model 1600 FT-IR instrument. the powder X-band ESR spectra were recorded at various temperatures between 5 and 300 K with a JEOL JES-FE3AX spectrometer equipped with a standard cavity and an Oxford Instruments liquid helium continuous-flow cryostat. To study the influence of oxygen, one sample was exposed for one hour to a pure oxygen atmosphere. By this treatment $\chi_M T$ increased to 0.77 cm^3 mol^{-1} K at room temperature (0.63 cm^3 mol^{-1} K at 77 K and 0.56 cm^3 mol^{-1} K at 2 K). This observation shows that the magnetic moment of [Co(mnt)$_2$]$^{2-}$ in particular in the high temperature range is sensitive to oxygen.

Structure determination. Crystal and data collection. Black shiny single crystals of **CuCo** and **NiCo** were obtained by slow diffusion of [M(tim)](ZnCl$_4$) (M = Cu, Ni) dissolved in DMSO into an acetone–MeOH(1 : 1, v/v) solution of (NBu$_4$)$_2$[Co(mnt)$_2$] at room temperature. Intensity data were collected by use of a

Table 6. Atomic Coordinates (×10^4) and Equivalent Temperature Factors (Å^2) for **NiCo**

Atom	x	y	z	B_{eq} a)
Ni(1)	5000(0)	0(0)	0(0)	2.4
Co(1)	0(0)	0(0)	0(0)	2.6
S(1)	2193(1)	−734(1)	1240(2)	3.1
S(2)	−1271(1)	−1885(1)	−2034(2)	3.6
N(1)	3783(6)	−3710(4)	1203(8)	5.5
N(2)	−784(7)	−5293(4)	−3131(10)	7.6
N(3)	6422(4)	−887(3)	1532(5)	2.7
N(4)	4476(4)	−1573(3)	−2037(5)	2.7
C(1)	1629(5)	−2369(4)	55(6)	3.0
C(2)	112(5)	−2877(4)	−1398(7)	3.3
C(3)	2799(5)	−3137(4)	668(7)	3.6
C(4)	−392(5)	−4215(5)	−2367(8)	4.6
C(5)	6390(5)	−2051(4)	608(6)	2.8
C(6)	5242(5)	−2452(3)	−1535(6)	2.9
C(7)	7400(6)	−2951(5)	1483(7)	4.4
C(8)	5023(6)	−3765(4)	−2893(7)	4.4
C(9)	7533(6)	−330(5)	3651(6)	4.4
C(10)	3331(6)	−1803(4)	−4118(6)	3.8
C(11)	8033(5)	1087(4)	4245(6)	3.5
H(72)	750(6)	−283(5)	255(8)	5.4
H(81)	421(7)	−431(5)	−295(8)	7.1
H(82)	506(7)	−370(5)	−413(9)	7.3
H(83)	596(7)	−417(6)	−249(9)	8.1
H(91)	833(6)	−78(5)	403(8)	6.3
H(92)	678(7)	−46(6)	441(9)	7.6
H(101)	303(6)	−263(5)	−486(8)	5.8
H(102)	403(6)	−142(5)	−484(8)	5.8
H(111)	851(5)	137(4)	348(6)	3.0
H(112)	874(5)	134(4)	565(7)	4.4

a) $B_{eq} = 4/3(\sum_i \sum_j B_{ij} a_i b_j)$.

Enraf–Nonius CAD4 four-circle automated diffractometer with a graphite-monochromatized Mo K_α radiation. Crystal data and experimental detailes are given in Table 4. Structure analysis and refinement for **CuCo** and **NiCo**. Survey of the data set and the systematic extinction indicated a triclinic class with a space group $P\bar{1}$. Data were corrected for absorption.[34)] The analytical form of the scattering factor[35)] for the appropriate neutral atom was corrected for the real (*Df*) components of anomalous dispersions.[36)] The structure was solved by direct methods MULTAN,[37)] and all non-hydrogen atoms were located from subsequent difference Fourier synthesis. Twelve hydrogen atoms were found for **CuCo** and ten for **NiCo** by Fourier analysis. Refinement was done by the block-diagonal least-squares method[38)] with anisotropic thermal parameters for all non-hydrogen atoms. Final positional parameters are listed in Tables 5 and 6. The complete $F_o - F_c$ data are deposited as Document No. 96048 at the Office of the Editor of Bull. Chem. Soc. Jpn.

This work was partially supported by the "MR Science Research Program" from RIKEN and by a Grant-in-Aid for Scientific Research from the Japanese Ministry of Education, Science and Culture. We are indebted to M. Lemke for measuring the diffuse reflectance spectra.

References

1) a) P. I. Clemenson, *Coord. Chem. Rev.*, **106**, 171 (1990); b) A. E. Underhill and M. M. Ahmad, *J. Chem. Soc., Chem. Commun.*, **1981**, 67; c) A. E. Underhill, R. A. Clark, I. Marsden, M. Allan, R. H. Friend, H. Tajima, T. Naito, M. Tamura, and H. Kuroda, *J. Phys.: Condens. Matter*, **3**, 933 (1991); d) Y. Sakamoto, G. Matsubayashi, and T. Tanaka, *Inorg. Chim. Acta*, **113**, 137 (1986); e) L. Alcacer and H. Novais, " Linear Chain 1,2-Dithiolene Complexes. In Extended Linear Chain Compounds, " ed by J. S. Miller, Plenum Press, New York and London (1980), Vol. 3, p. 319; f) M. R. Bryce and M. C. Petty, *Nature*, **374**, 771 (1995).

2) a) M. Bousseau, L. Valade, J.-P. Legros, P. Cassoux, M. Garbauskas, and L. V. Interrante, *J. Am. Chem. Soc.*, **108**, 1908 (1986); b) P. Cassoux, L. Valade, H. Kobayashi, A Kobayashi, R. A. Clark, and A. E. Underhill, *Coord. Chem. Rev.*, **110**, 115 (1991).

3) a) M. G. Paradopoulos, J. Waite, C. S. Winter, and S. N. Oliver, *Inorg. Chem.*, **32**, 277 (1993); b) C. S. Winter, S. N. Oliver, J. D. Rush, R. J. Manning, C. Hill, and A. E. Underhill, " Materials for NLO, Chemical Perspectives," ed by S. R. Marder, J. E. Sohn, and G. D. Stucky, ACS-Series 455, Washington DC (1991), p. 616; c) S. B. Wilkes, I. R. Butler, A. E. Underhill, M. B. Hursthouse, D. E. Hibbs, and K. M. Abdul Malik, *J. Chem. Soc., Dalton Trans.*, **1995**, 897.

4) A. P. Abbott, P. R. Jenkins, and N. S. Khan, *J. Chem. Soc., Chem. Commun.*, **1994**, 1935.

5) a) B. L. Ramakrishna and P. T. Manoharan, *Inorg. Chem.*, **22**, 2113 (1983); b) P. T. Manoharan, J. H. Noordik, E. de Boer, and C.P. Keijizers, *J. Chem. Phys.*, **74**, 1980 (1981).

6) J. W. Bray, H. R. Hart, L. V. Interrante, I. S. Jacobs, J. S. Kasper, G. D. Watkins, S. H. Wee, and J. C. Bonner, *Phys. Rev. Lett.*, **35**, 744 (1975).

7) J. S. Miller and A. J. Epstein, *Angew. Chem., Int. Ed. Engl.*, **33**, 385 (1994).

8) I. S. Jacobs, H. R. Hart, L. V. Interrante, J. W. Bray, J. S. Kasper, G. D. Watkins, D. E. Prober, W. P. Wolf, and J. C. Bonner, *Physica*, **86-88b**, 655 (1977).

9) W. E. Broderick, J. A. Thompson, M. R. Godfrey, M. Sabat, and B. M. Hoffman, *J. Am. Chem. Soc.*, **111**, 7656 (1989).

10) Z. J. Zhong, H. Okawa, R. Aoki, and S. Kida, *Inorg. Chem. Acta*, **144**, 233 (1988).

11) a) I. Vasilevesky, N. R. Rose, R. Stenlamp, and R. D. Willett, *Inorg. Chem.*, **30**, 4082 (1991); b) J. J. Borrás-Almenar, E. Coronado, J. Curely, R. Georges, and J. C. Gianduzzo, *Inorg. Chem.*, **33**, 5171 (1994).

12) H. Oshio, *Inorg. Chem.*, **32**, 4123 (1993).

13) A. Vogler and H. Kunkely, *J. Chem. Soc., Chem. Commun.*, **1986**, 1616.

14) a) H. Kisch, *Comments Inorg. Chem.*, **16**, 113 (1994); b) H. Kisch, A. Fernandez, Y. Wakatsuki, and Y. Yamazaki, *Z. Naturforsch., Sect. B*, **40**, 292 (1995); c) M. Lemke, F. Knoch, and H. Kisch, *Acta Crystallogr., Sect. C*, **49**, 1630 (1993); d) G. Schmauch, F. Knoch, and H. Kisch, *Chem. Ber.*, **128**, 303 (1995).

15) a) M. J. Maroney and N. J. Rose, *Inorg. Chem.*, **23**, 2252 (1984); b) A. E. Elia, E. C. Lingaferlter, and V. Schomaker, *Croat. Chem. Acta*, **57**, 653 (1984).

16) D. J. Szalda, E. Fujita, R. Sanzenbacher, H. Paulus, and H. Elias, *Inorg. Chem.*, **33**, 5855 (1994).

17) J. D. Forrester, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, **3**, 1500 (1964).

18) A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).

19) J. J. Wilker, A. Gelasco, M. A. Pressler, R. O. Day, and M. J. Maroney, *J. Am. Chem. Soc.*, **113**, 6342 (1991).

20) a) J. V. Rodrigues, I. C. Santos, V. Gama, R. T. Henriques, J. C. Waerenborgh, M. T. Duarte, and M. Almeida, *J. Chem. Soc., Dalton Trans.*, **1994**, 2655; b) G. N. Schrauzer, V. P. Mayweg, H. W. Finck, and W. Heinrich, *J. Am. Chem. Soc.*, **88**, 4604 (1966); c) S. Alvarez, R. Vicente, and R. Hoffmann, *J. Am. Chem. Soc.*, **107**, 6253 (1985).

21) D. S. Brown, J. D. Lee, B. G. A. Melsom, B. J. Hathaway, I. M. Procter, and A. A. G. Tomlinson, *J. Chem. Soc., Chem. Commun.*, **1967**, 369.

22) J. A. McCleverty, *Prog. Inorg. Chem.*, **10**, 49 (1968).

23) L. R. Furenlid, M. W. Renner, D. J. Szalda, and E. Fujita, *J. Am. Chem. Soc.*, **113**, 833 (1991).

24) R. R. Gagné, J. L. Allison, and D. M. Ingle, *Inorg. Chem.*, **18**, 2767 (1979).

25) a) N. S. Hush, *Prog. Inorg. Chem.*, **8**, 391 (1967); b) R. A. Marcus and N. S. Sutin, *Comments Inorg. Chem.*, **5**, 119 (1986); c) I. Nunn, B. Eisen, R. Benedix, and H. Kisch, *Inorg. Chem.*, **33**, 5079 (1994).

26) See also: A. H. Maki, N. Edelstein, A. Davison, and R. H. Holm, *J. Am. Chem. Soc.*, **86**, 4580 (1964).

27) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *J. Am. Chem. Soc.*, **85**, 3049 (1963).

28) a) R. Havemann, W. Haberditzl, and K.-H. Mader, *Z. Physik. Chem.(Leibzig)*, **218**, 71 (1961); b) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, **1959**, 338.

29) E. Kanda, T. Haseda, and A. Otsubo, *Sci. Rep. Res. Inst. Tohoku Univ., Ser. A*, **A7**, 1 (1955).

30) M. J. Maroney and N. J. Rose, *Inorg. Chem.*, **23**, 2261 (1984).

31) A. M. Tait and D. H. Busch, *Inorg. Synth.*, **18**, 23 (1978).

32) a) H. B. Gray, R. Williams, I. Bernal, and E. Billing, *J. Am. Chem. Soc.*, **84**, 3596 (1962); b) A. Davison and R. H. Holm, *Inorg. Synth.*, **10**, 8 (1967).

33) R. R. Gupta, "Landolt-Börnstein, New Series II," ed by K.-H. Hellwege and A. M. Hellwege, Springer, Berlin (1986), Vol. 16, pp. 3 and 402.

34) A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Cryst-*

allogr., Sect. A, **24**, 351 (1968).

35) D. T. Cromer and J. T. Waber, in "International Tables for X-Ray Crystallography," ed by J. A. Ibers and W. C. Hamilton, Kynoch Press, Birmingham (1974), Vol. IV, p. 71.

36) D. T. Cromer, in "International Tables for X-Ray Crystallography," ed by J. A. Ibers and W. C. Hamilton, Kynoch Press, Birmingham (1974), Vol. IV, p. 148.

37) P. Main, S. E. Hull, L. Lessiger, G. Germain, J.-P. Declerq, and M. M. Woolfson, "MULTAN 78," University of York, York, England (1978).

38) Sakurai and K. Kobayashi, *Rikagaku Kenkyusho Hokoku*, **55**, 69 (1979).