

Structural and Spectroscopic Properties of Neutral Cobalt(II) and Nickel(II) Complexes with Nitrite Chelating Ligands

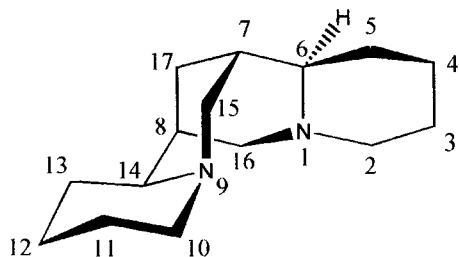
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Over the past two decades, several studies of the transition metal complexes of (-)-sparteine ($C_{15}H_{26}N_2$), a chiral alkaloid, were reported¹⁻⁹ and the crystal structures of its complexes with Co(II),^{3,9} Pd(II)⁷ and Cu(II)^{8,10,11} with various anions have been determined. It has been recognized that the role of anions in these compounds is important in the ultimate molecular structure, and has been always found, with an exception, that the coordination geometry around metal(II) center was four-coordinate and pseudo-tetrahedral. However, in sparteine copper(II) dinitrate crystals,¹⁰ one of two nitrate ligands can act as a bidentate ligand and the coordination geometry around the copper(II) center is distorted square-pyramidal. Recently we prepared and determined the crystal structure of (-)-sparteine copper(II) dinitrite and found that this compound is also distorted square pyramidal.¹²



(-)-sparteine (6R, 7S, 8S, 14S)

Our synthesis of the cobalt(II) and nickel(II) complexes with nitrite ligands was prompted by our interest in the preparation of higher coordination geometry around metal(II) center with bulky sparteine ligand being intact. Another interest of ours was to find how the electronic structure of metal(II) ions (d^7-d^9) affects the coordination geometry in these compounds.

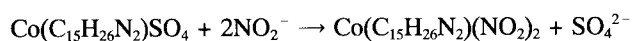
We chose the nitrite ion as the anionic ligand in preparing (-)-sparteine metal(II) complexes with higher coordination number since versatile nitrite may bind to the metal center in either monodentate or bidentate fashion, and the size of nitrite ion is relatively small.

Experimentals

Materials. All reagents and solvents were obtained commercially either from Fisher Scientific Co. or Aldrich Chemical Co. and were used without further purification except where noted. Anhydrous ethanol was distilled from calcium hydride and stored under argon. (-)-Sparteine was purchased from Sigma Chemical Company.

Preparation. The complex $Co(C_{15}H_{26}N_2)SO_4$ was prepared in a glove box by mixing a solution of cobalt

sulfate in 5:1 (by volume) ethanol/triethylorthoformate (TEOF) with a stoichiometric amount of (-)-sparteine under nitrogen atmosphere. The resulting violet precipitate was filtered, washed with cold absolute ethanol, and dried under vacuum. The complex, $Co(C_{15}H_{26}N_2)(NO_2)_2$, was prepared from the nucleophilic substitution reaction between $Co(C_{15}H_{26}N_2)SO_4$ and a stoichiometric amount of $NaNO_2$ in 5:1 ethanol/TEOF (yield: 72.4%).



The dark reddish-violet single crystals were obtained by recrystallization at about 5 °C in dichloromethane-TEOF (5:1 by volume) solution under carbon tetrachloride vapor. Anal. Calcd. for $Co(C_{15}H_{26}N_2)(NO_2)_2$: C, 46.76; H, 6.80; N, 14.54. Found: C, 46.05; H, 6.96; N, 14.41.

The complex, $Ni(C_{15}H_{26}N_2)Cl_2$, was initially prepared by mixing ethanol-TEOF (4:1 by volume) solution of nickel chloride hexahydrate with a stoichiometric amount of (-)-sparteine. The resulting violet precipitate was filtered, washed with cold absolute ethanol, and dried under vacuum. The complex, $Ni(C_{15}H_{26}N_2)(NO_2)_2$, was prepared from the substitution reaction between $Ni(C_{15}H_{26}N_2)Cl_2$ and stoichiometric amount of $NaNO_2$ in ethanol/TEOF (5:1 by volume) mixture solution (yield: 86.4%). The green crystals were obtained by recrystallization at about 5 °C in dichloromethane-TEOF (5:1 by volume) solution under carbon tetrachloride vapor. Anal. Calcd. for $Ni(C_{15}H_{26}N_2)(NO_2)_2$: C, 46.78; H, 6.81; N, 14.55. Found: C, 46.36; H, 6.81; N, 14.35.

Physical Measurements. Infrared spectra (4,000-400 cm^{-1}) were obtained as KBr pellets using a Mattson Instruments Polaris FT-IR spectrometer.

Electronic absorption spectra were measured on a Cary 17D UV/VIS/NIR spectrophotometer (200-1,500 nm). The sample solutions were purged with dry nitrogen before every measurement.

Elemental analyses were done by using a Carlo Erba Instruments E.A. 1108 Elemental Analyzer at Korea Basic Science Center (Seoul Branch).

Crystallography. Crystals of $Co(C_{15}H_{26}N_2)(NO_2)_2$ and $Ni(C_{15}H_{26}N_2)(NO_2)_2$ compounds suitable for an X-ray analysis were obtained by slow evaporation from dichloromethane/TEOF solution. Reddish-violet crystals of $Co(C_{15}H_{26}N_2)(NO_2)_2$ of approximate $0.26 \times 0.28 \times 0.23$ mm and green crystals of $Ni(C_{15}H_{26}N_2)(NO_2)_2$ of approximate $0.32 \times 0.38 \times 0.30$ mm were mounted and aligned on a CAD-4 diffractometer. The accurate cell parameters were refined from setting angles of 24 reflections with $11.4^\circ \leq \theta \leq 14.0^\circ$ for $Co(C_{15}H_{26}N_2)(NO_2)_2$ and 25 reflections with $11.4^\circ \leq \theta \leq 12.7^\circ$ for $Ni(C_{15}H_{26}N_2)(NO_2)_2$. 1611 independent reflections for $Co(C_{15}H_{26}N_2)(NO_2)_2$ in an asymmetric unit in range $0 \leq h \leq 13$, $0 \leq k \leq 20$, $0 \leq l \leq 9$

and 1464 independent reflections for $\text{Ni}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_2)_2$ in an asymmetric unit in range $0 \leq h \leq 13$, $0 \leq k \leq 20$, $-10 \leq l \leq 9$ were collected using graphite-monochromated Mo $K\alpha$ radiation and $\omega/2\theta$ scan mode, ω -scan width $= (0.8 + 0.35 \tan \theta)^\circ$, $\theta_{\max} = 24^\circ$ for $\text{Co}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_2)_2$ and $\theta_{\max} = 25^\circ$ for $\text{Ni}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_2)_2$. In general the reflections were strong. During data collection, one orientation reflection (5 3 -3) was monitored every 200 reflections and three standard reflections (5 3 -3), (-2 1 5) and (6 2 -3) measured at exposure intervals of 3 hours exhibited an average change of $\approx 1.0\%$, without apparent systematic trend, hence an exposure-dependent correction was not applied. All data were corrected for L-P with the program SDP,¹³ but no absorption corrections were made. The structure were solved by direct methods using SHELXS86.¹⁴ The best E maps gave the positions of the Co and Ni atoms. The remaining all non-H atoms were located from a difference Fourier synthesis. SHELX76 program¹⁵ was used for full-matrix least-square refinement with anisotropic thermal factors for all the non-H atoms. H-atoms were located in difference maps and were refined isotropically. The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where $w^{-1} = (\sigma^2 F + 0.0031 F^2)$ for $\text{Co}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_2)_2$ and $w^{-1} = (\sigma^2 F_o + 0.0008 F_o^2)$ for $\text{Ni}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_2)_2$. Scattering factors

Table 1. Crystallographic data of $\text{Co}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_2)_2$ and $\text{Ni}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_2)_2$

	$\text{Co}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_2)_2$	$\text{Ni}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_2)_2$
Crystal data		
Chemical formular	$\text{CoC}_{15}\text{H}_{26}\text{N}_4\text{O}_4$	$\text{NiC}_{15}\text{H}_{26}\text{N}_4\text{O}_4$
FW (amu)	385.33	385.11
color	Reddish Violet	Green
Crystal habit	Cube	Cube
Crystal size (mm)	$0.26 \times 0.28 \times 0.23$	$0.32 \times 0.38 \times 0.30$
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1$
T(K)	289	289
Radiation(MoK α) (λ , Å)	0.71069	0.71069
Scan mode	$\omega/2\theta$	$\omega/2\theta$
Cell dimensions		
a (Å)	12.143(4)	11.961(2)
b (Å)	17.819(3)	8.512(2)
c (Å)	8.061(1)	8.950(1)
angles ($^\circ$)	$\alpha = \beta = \gamma = 90$	$\alpha = \gamma = 90, \beta = 107.83(1)$
Volume (Å ³)	1744.1	867.5
Z	4	2
$d_{\text{calcd.}}$ (Mg m^{-3})	1.47	1.47
μ (mm^{-1})	0.98	1.12
F (0 0 0)	818	818
Intensity variation (%)	< 1.0	< 1.0
Refinement data		
Final R	0.056	0.025
ωR	0.057	0.025
Threshold expression	$F \geq \sigma(F)$	$F \geq \sigma(F)$
ω	$[\sigma^2 F + 0.0031 F^2]^{-1}$	$[\sigma^2 F + 0.0008 F^2]^{-1}$
parameters	291	320
$(\Delta/\sigma)_{\max}$	0.801	0.009
$\Delta\rho_{\max}$ ($\text{e}\text{Å}^{-3}$)	0.586	0.239
$\Delta\rho_{\min}$ ($\text{e}\text{Å}^{-3}$)	-0.512	-0.274
Goodness of fit	0.9574	0.8411

and anomalous-dispersion terms were taken from the usual sources.¹⁶ Details of the data collection together with structure refinement are summarized in Table 1. Geometric calculations on the crystal and molecular structure were done using GEOM program.¹⁷ All computations were carried out using the VAX-3400 computer at Chungnam National University.

Results and Discussion

The complexes, (dinitrito-O,O')[(*-*)-sparteine-N,N']cobalt(II), $[\text{Co}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_2)_2]$ and (dinitrito-O,O')[(*-*)-sparteine-N,N']nickel(II), $[\text{Ni}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_2)_2]$ were prepared and their crystal structures were determined. (*-*)-Sparteine, $\text{C}_{15}\text{H}_{26}\text{N}_2$ acts as a bidentate ligand reacting with cobalt(II) or nickel(II) in ethanol to form the title complexes. Both complexes contain a metal atom ligated by (*-*)-sparteine, with two nitrite groups occupying the remaining coordination sites. As predicted by previous works,^{7,8,10-12} the conformation of the coordinated (*-*)-sparteine of the dinitrito[(*-*)-sparteine]metal(II) complexes (M=Co and Ni) consists of one terminal ring folded down over the metal (endo) and the other terminal ring folded back away from the metal (exo) identical to the conformation of the free ligand. Two nitrite groups, both in $\text{Co}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_2)_2$ and $\text{Ni}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_2)_2$, coordinate to the metal ions in the bidentate fashion to produce pseudo-octahedral coordination

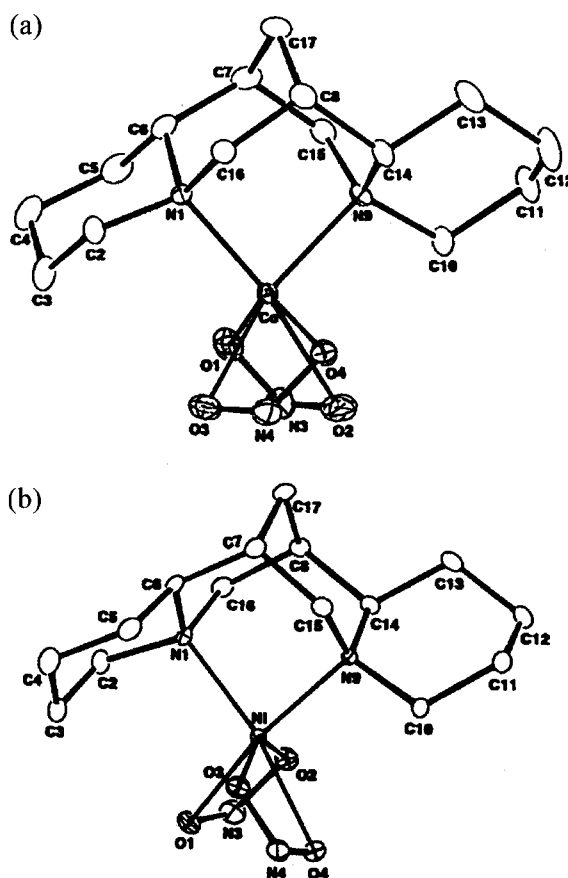


Figure 1. ORTEP diagrams of (a) $\text{Co}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_2)_2$ and (b) $\text{Ni}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_2)_2$. Non-H atoms are represented with 30% probability ellipsoids.

complexes.

A view of the molecular structure of two complexes are shown in Figure 1. Crystallographic data of both crystals are

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

(1) $\text{Co}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_2)_2$, $U_{\text{eq}} = (1/3)\sum_i U_{ii} a_i^2$				
	x	y	z	U_{eq}
Co	0.3726 (1)	0.1650 (1)	0.5187 (1)	0.038
N(1)	0.4314 (6)	0.2070 (4)	0.2947 (9)	0.041
C(2)	0.3995 (10)	0.2863 (6)	0.2646 (17)	0.060
C(3)	0.2788 (11)	0.2945 (9)	0.2453 (19)	0.092
C(4)	0.2324 (14)	0.2465 (10)	0.1075 (18)	0.104
C(5)	0.2722 (8)	0.1650 (9)	0.1257 (13)	0.079
C(6)	0.3966 (7)	0.1613 (7)	0.1468 (10)	0.056
C(7)	0.4418 (9)	0.0813 (6)	0.1564 (13)	0.064
C(8)	0.6026 (8)	0.1245 (6)	0.3072 (15)	0.058
N(9)	0.4504 (5)	0.0629 (3)	0.4658 (9)	0.041
C(10)	0.4257 (12)	0.0123 (7)	0.6064 (18)	0.060
C(11)	0.4939 (9)	-0.0607 (6)	0.6112 (20)	0.083
C(12)	0.6137 (11)	-0.0408 (7)	0.6199 (22)	0.099
C(13)	0.6447 (10)	0.0065 (8)	0.4728 (26)	0.078
C(14)	0.5722 (7)	0.0791 (5)	0.4635 (14)	0.049
C(15)	0.4082 (8)	0.0334 (6)	0.3062 (13)	0.052
C(16)	0.5554 (8)	0.2046 (5)	0.3102 (14)	0.053
C(17)	0.5678 (10)	0.0870 (8)	0.1511 (18)	0.068
O(1)	0.2054 (6)	0.1483 (5)	0.4988 (13)	0.091
O(2)	0.2575 (9)	0.1181 (5)	0.7269 (12)	0.093
O(3)	0.3516 (8)	0.2793 (4)	0.6428 (11)	0.080
O(4)	0.4705 (7)	0.2026 (4)	0.7096 (8)	0.064
N(3)	0.1737 (9)	0.1221 (5)	0.6329 (16)	0.081
N(4)	0.4284 (10)	0.2666 (6)	0.7400 (12)	0.071

(2) $\text{Ni}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_2)_2$, $U_{\text{eq}} = (1/3)[U_{22} + 1/\sin^2\beta(U_{11} + U_{33} + 2U_{13} \cos\beta)]$

	x	y	z	U_{eq}
Ni	0.2545 (0)	-0.1282 (0)	0.3456 (0)	0.032
N(1)	0.1912 (3)	0.1004 (5)	0.3423 (4)	0.036
C(2)	0.1418 (5)	0.1589 (6)	0.1766 (6)	0.059
C(3)	0.0342 (5)	0.0678 (8)	0.0867 (7)	0.072
C(4)	-0.0607 (5)	0.0774 (9)	0.1670 (8)	0.079
C(5)	-0.0126 (4)	0.0311 (7)	0.3377 (7)	0.063
C(6)	0.0986 (4)	0.1201 (5)	0.4231 (5)	0.043
C(7)	0.1495 (4)	0.0832 (6)	0.5984 (5)	0.045
C(8)	0.3423 (4)	0.1720 (5)	0.5997 (5)	0.042
N(9)	0.3026 (2)	-0.1178 (6)	0.5891 (3)	0.031
C(10)	0.3502 (5)	-0.2753 (6)	0.6466 (6)	0.043
C(11)	0.4143 (6)	-0.2845 (7)	0.8226 (7)	0.054
C(12)	0.5125 (5)	-0.1655 (7)	0.8689 (6)	0.058
C(13)	0.4648 (5)	-0.0026 (7)	0.8199 (6)	0.046
C(14)	0.3963 (5)	0.0078 (6)	0.6449 (6)	0.036
C(15)	0.1976 (4)	-0.0827 (5)	0.6395 (5)	0.041
C(16)	0.2940 (4)	0.2006 (5)	0.4248 (6)	0.045
C(17)	0.2452 (4)	0.2007 (7)	0.6726 (6)	0.051
O(1)	0.2691 (3)	-0.1291 (8)	0.1091 (3)	0.062
O(2)	0.4119 (3)	-0.0751 (4)	0.3045 (3)	0.056
O(3)	0.1166 (3)	-0.2863 (4)	0.3117 (4)	0.058
O(4)	0.2783 (4)	-0.3786 (4)	0.3178 (4)	0.063
N(3)	0.3758 (4)	-0.0967 (7)	0.1573 (5)	0.065
N(4)	0.1706 (5)	-0.4068 (6)	0.2971 (6)	0.063

summarized in Table 1 and atomic coordinates are given in Table 2. Selected bond distances and angles are presented in Table 3.

The chelating nitrite ligands in $\text{Co}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_2)_2$ are less symmetrically coordinated to the metal(II) center compared with those in $\text{Ni}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_2)_2$. In $\text{Co}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_2)_2$, two nitrogen donor atoms of sparteine and two oxygen atoms of nitrite ligands [O(1) and O(4)] constitute equatorial plane for the elongated and distorted octahedron, and the Co-O(1) and Co-O(4) distances are shorter than the Co-O(2) or Co-O(3) distances by 0.25-0.28 \AA . In $\text{Ni}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_2)_2$, the bidentate nitrite ligand coordinates to the Ni (II) center almost symmetrically and the Ni-O distances differ by only 0.1 \AA . The severe distortion observed in $\text{Co}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_2)_2$ is definitely attributed to the Jahn-Teller effect operating on the d^7 configuration of cobalt(II). The M-N distances [2.081 \AA and 2.094 \AA] in $\text{Co}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_2)_2$ are slightly longer than those in $\text{Co}(\text{C}_{15}\text{H}_{26}\text{N}_2)\text{Cl}_2$ [2.040 \AA and 2.068 \AA].⁵ The elongation of M-N distance is naturally required to accommodate two more donor atoms around their coordination sphere.

As reported earlier,¹² the copper(II) in $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_2)_2$ adopts a highly distorted square pyramidal geometry which is expected to be caused by strong Jahn-Teller effect operating on the d^9 configuration. Jahn-Teller effect operating on the cobalt(II) (d^7) is not severe enough to destroy octahedral geometry of $\text{Co}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_2)_2$, but the coordination structure of this compound is highly distorted when the comparison is made with that of $\text{Ni}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_2)_2$.

Octahedral or pseudooctahedral cobalt(II) complexes normally exhibit three transitions¹⁸ (ν_1 ; ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ (near-ir), ν_2 ; ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}$ (near-ir), ν_3 ; ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ (visible)), where the energy difference ($\nu_2 - \nu_1$) is equal to $10Dq$. The

Table 3. Selected geometry parameters (\AA , $^\circ$)

(1) $\text{Co}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_2)_2$			
Co-O(1)	2.058(7)	Co-O(4)	2.057(7)
Co-O(2)	2.338(10)	Co-N(1)	2.081(7)
Co-O(3)	2.283(8)	Co-N(9)	2.094(6)
O(1)-Co-O(2)	54.2(4)	O(2)-Co-N(1)	163.0(3)
O(1)-Co-O(3)	93.0(4)	O(2)-Co-N(9)	96.0(3)
O(1)-Co-O(4)	132.5(4)	O(3)-Co-O(4)	56.4(3)
O(1)-Co-N(1)	108.8(4)	O(3)-Co-N(1)	95.6(3)
O(1)-Co-N(9)	107.7(3)	O(3)-Co-N(9)	156.2(3)
O(2)-Co-O(3)	86.4(3)	O(4)-Co-N(1)	109.5(3)
O(2)-Co-O(4)	85.7(3)	O(4)-Co-N(9)	100.1(3)
		N(1)-Co-N(9)	88.9(3)
(2) $\text{Ni}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_2)_2$			
Ni-O(1)	2.177(3)	Ni-O(4)	2.175(3)
Ni-O(2)	2.076(3)	Ni-N(1)	2.085(4)
Ni-O(3)	2.078(3)	Ni-N(9)	2.079(3)
O(1)-Ni-O(2)	58.8(1)	O(2)-Ni-N(1)	98.0(1)
O(1)-Ni-O(3)	98.8(2)	O(2)-Ni-N(9)	101.6(1)
O(1)-Ni-O(4)	80.4(2)	O(3)-Ni-O(4)	58.3(2)
O(1)-Ni-N(1)	97.3(2)	O(3)-Ni-N(1)	109.5(1)
O(1)-Ni-N(9)	160.1(1)	O(3)-Ni-N(9)	97.7(1)
O(2)-Ni-O(3)	146.9(1)	O(4)-Ni-N(1)	166.6(1)
O(2)-Ni-O(4)	92.0(2)	O(4)-Ni-N(9)	99.1(2)
		N(1)-Ni-N(9)	87.6(2)

v_2 transition is normally very weak and is rarely unequivocally observed. For most octahedral cobalt(II) complexes, a band around 8,000-10,000 cm^{-1} is usually assigned to the ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ transition while a multiple structured band observed near 20,000 cm^{-1} is assigned to ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$. The ${}^4A_{2g}$ transition appears as a very weak band around 12,000-14,000 cm^{-1} . The optical absorption spectrum of $\text{Co}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_2)_2$ exhibit two bands at 9,615 cm^{-1} and 18,330 cm^{-1} , and the electronic spectral assignments of $\text{Co}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_2)_2$ are made tentatively as follow; 9,615 cm^{-1} (v_1 ; ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$) and 18,330 cm^{-1} (v_3 ; ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$). The optical absorption spectrum of $\text{Ni}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_2)_2$ exhibits the characteristic spectral features of octahedral nickel(II) complexes. For octahedral nickel(II) complexes, three spin-allowed transitions are expected from the energy level diagram of d^8 ions¹⁸ and three observed bands may thus be assigned; 9,852 cm^{-1} (v_1 ; ${}^3A_{2g} \rightarrow {}^3T_{2g}$), 15,220 cm^{-1} (v_2 ; ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$), 25,550 cm^{-1} (v_3 ; ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$).

The infrared spectrum of $\text{Ni}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_2)_2$ shows strong NO_2 stretching bands ($\nu_{\text{a NO}_2}$ and $\nu_{\text{s NO}_2}$) at 1307 cm^{-1} and 1196 cm^{-1} , and a weak deformation band (δ_{NO_2}) at 872 cm^{-1} . These data are in good agreement with the crystallographically determined molecular structure in which the NO_2^- groups¹⁹ are almost symmetrically bidentated with nickel(II) center utilizing two oxygen donor atoms. The infrared spectra of $\text{Co}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_2)_2$ shows strong stretching bands ($\nu_{\text{a NO}_2}$ and $\nu_{\text{s NO}_2}$) at 1273 cm^{-1} and 1177 cm^{-1} , and a weak deformation band (δ_{NO_2}) at 857 cm^{-1} . The infrared spectral data of $\text{Co}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_2)_2$ are also in agreement with the crystallographic results.

Supplementary Data

Tables of (1) H-atom coordinates and isotropic thermal parameters, (2) anisotropic thermal parameters for non-hydrogen atoms, and (3) observed and calculated structure factors with estimated standard deviations are available from IHS.

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References

1. Choi, S.-N.; Bereman, R. D.; Wasson, J. R. *J. Inorg.*

Nucl. Chem. **1975**, *37*, 1087.

- Mason, S. F.; Peacock, R. D. *J. Chem. Soc., Dalton Trans.* **1973**, 226; and references therein.
- Boschmann, E.; Weinstock, L. M.; Carmack, M. *Inorg. Chem.* **1974**, *13*, 1297; and references therein.
- Fraenkel, G.; Appleman, B.; Ray, J. G. *J. Am. Chem. Soc.* **1974**, *96*, 5113; and references therein.
- Kuroda, R.; Mason, S. F. *J. Chem. Soc., Dalton Trans.* **1977**, 371.
- Boschmann, E.; Nypaver, G. A.; Majors, J. P.; Ealy, S. M.; van Horn, M. *J. Coord. Chem.* **1978**, *7*, 141.
- Togni, A.; Rihs, G.; Pregosin, P. S.; Ammann, C. *Helv. Chim. Acta* **1990**, *73*, 723.
- Childers, L. S.; Folting, K.; Merritt, L., Jr.; Streib, W. *Acta Cryst.* **1975**, *B31*, 924.
- Kuroda, R.; Mason, S. *J. Chem. Soc., Dalton Trans.* **1979**, 727.
- Choi, S.-N.; Kwon, M.-A.; Kim, Y.; Bereman, R. D.; Singh, P.; Knight, B.; Seff, K. *J. Coord. Chem.* **1995**, *34*, 241
- Lopez, S.; Muravyov, I.; Pulley, S. R.; Keller, S. W. *Acta Cryst.* **1998**, *C54*, 355.
- Lee, Y.-M.; Choi, S.-N.; Suh, I.-H.; Bereman, R. D. *Acta Cryst.* **1998**, *C54*, 1582.
- Enraf-Nonius, Structure Determination Package, Enraf-Nonius, Delft, The Netherlands, 1985.
- Sheldrick, G. M. 'SHELX86', Program for Crystal Structure Determination, Univ. of Cambridge, England, 1986.
- Sheldrick, G. M. 'SHELX76', Program for Crystal Structure Determination, Univ. of Cambridge, England, 1976.
- Ibers, J. A.; Hamilton, W. C. *International Tables for X-ray Crystallography*; Vol. IV; Table 2.2A, Table 2.3.1., The Kynoch Press, Birmingham, England, 1974.
- Shin, W. 'GEOM', Seoul National University, Korea, 1978.
- Lever, A. B. P. *Inorganic Electronic Spectroscopy*; 2nd' Elsevier, 1984.
- Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; 4ed., John Wiley & Sons: 1986, pp. 221-227; and references therein.

Adsorbate Substitution and Electrochemical Behavior in Self-Assembled Monolayer of 2-Mercaptomethylhydroquinone (MH₂Q) on Gold

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Quinone/hydroquinone derivatives¹ take part in several biologically important oxidation-reduction processes. These redox-active molecules play key roles in electron/energy

transfer occurring onto biological membrane which they are bound. This type of electron transfer in membrane systems can be mimicked by self-assembled monolayers² containing