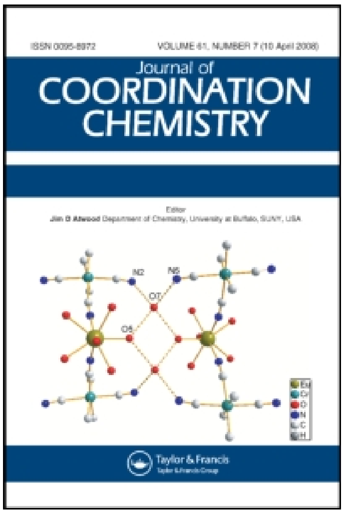

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Synthesis, Characterization, and Structure of Metal(II) (-)-Sparteine Complexes Containing Acetate Ligands

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SYNTHESIS, CHARACTERIZATION, AND STRUCTURE OF METAL(II) (–)-SPARTEINE COMPLEXES CONTAINING ACETATE LIGANDS

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The complexes [Co($C_{15}H_{26}N_2$)($C_2H_3O_2$)$_2$] (**1**), [Ni($C_{15}H_{26}N_2$)($C_2H_3O_2$)$_2$] (**2**), [Cu($C_{15}H_{26}N_2$)($C_2H_3O_2$)$_2$] (**3**) and [Zn($C_{15}H_{26}N_2$)($C_2H_3O_2$)$_2$] (**4**) were prepared from reaction of (–)-sparteine with the corresponding metal(II) acetates in ethanol at stoichiometric ligand to metal ratios. The complexes were characterized by UV–Vis and IR spectroscopies, and magnetic susceptibility measurements. The solid-state structures of **1**, **2** and **4** have been determined by X-ray crystallography. The Complexes **1** and **2** display a *pseudo*-octahedral structure around the metal center, where two acetate ligands coordinate to the metal center in a bidentate fashion, whereas the metal centers in **3** and **4** adopt a *pseudo*-tetrahedral structure and two acetate ligands in these complexes coordinate to the metal center in a monodentate fashion. The whole set of prepared complexes has been used for comparative structural and spectroscopic studies.

Keywords: (–)-Sparteine; Acetate; Jahn-Teller distortion; X-ray structure

INTRODUCTION

As a part of our interest in oxyanion ligands [1–6], we have attempted to prepare a series of metal(II) sparteine diacetate complexes by extending the previous work on nitrate [1], nitrite [2,4] and oxalate [5,6] oxyanion complexes.

Many studies of transition metal complexes with neutral alkaloids (–)-sparteine ($C_{15}H_{26}N_2$) were reported [1–12], and the crystal structures of complexes with Co(II) [4], Ni(II) [4], Cu(II) [1–3,7,8] and Pd(II) [9] with various anions have been determined. It has been recognized that the role of anions in these complexes is very important in the ultimate molecular structure. The chiral (–)-sparteine is naturally occurring, commercially available, and acts as a bidentate ligand, reacting with a metal ion to form a metal complex with two mono-anionic ligands occupying the remaining coordination

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sites to produce a four- [1,3], five- [1,2] or six- [4] coordinate complex depending on the type of anionic ligand and metal ion employed.

Acetate is known to interact with a metal ion as a unidentate ligand, symmetrical chelates and symmetrical bridging ligand [13]. The carboxylates are a very important class of oxyanion ligands, and the nature of bonding interaction between a metal ion and the side-chain carboxylate of proteins has been studied by many workers [14–16]; Ca^{2+} binds to more than three carboxylates of glutamate or aspartate, and at least one carboxylate coordinates to Ca^{2+} in a bidentate fashion [14,15]. Similar results are reported for Zn^{2+}, with carboxylate as both monodentate and bidentate ligands [16].

Our synthesis of Co(II), Ni(II), Cu(II) and Zn(II) complexes with acetate ligands was prompted by our interest in how the electronic structure of metal(II) ions (d^7–d^{10}) affects the coordination geometry and bonding parameters in these complexes. Another interest was comparison of the structural characteristics of these acetate complexes with those of other metal oxyanion complexes.

EXPERIMENTAL

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.

Synthesis

$Co(C_{15}H_{26}N_2)(C_2H_3O_2)_2$, (1)

The Complex $Co(C_{15}H_{26}N_2)(C_2H_3O_2)_2$, **1**, was prepared by direct reaction of cobalt(II) acetate tetrahydrate (1.00 g, 4.01 mmol) with a stoichiometric amount of (−)-sparteine (0.93 mL, 4.05 mmol) in ethanol–triethylorthoformate (4 : 1 v/v) solution. The solution was evaporated until the violet product started to precipitate. The polycrystalline precipitates formed were then isolated by filtration. The violet complex was purified by recrystallization in dichloromethane–triethylorthoformate (5 : 1 v/v). The yield was 1.27 g (76.89%). The violet single crystals were obtained by recrystallization at about 5°C in dichloromethane–triethylorthoformate (4 : 1 v/v) solution under carbon tetrachloride vapor. Anal. Calcd. for $Co(C_{15}H_{26}N_2)(C_2H_3O_2)_2$: C, 55.47; H, 7.84; N, 6.81. Found: C, 55.49; H, 7.88; N, 6.82.

$Ni(C_{15}H_{26}N_2)(C_2H_3O_2)_2$, (2)

The Complex $Ni(C_{15}H_{26}N_2)(C_2H_3O_2)_2$, **2**, was prepared by direct reaction of nickel(II) acetate tetrahydrate (1.00 g, 4.02 mmol) with a stoichiometric amount of (−)-sparteine (0.93 mL, 4.05 mmol) in ethanol–triethylorthoformate (5 : 1 v/v) solution. The solution was evaporated until the green product started to precipitate and the polycrystalline precipitates formed were isolated by filtration. The green complex was purified by recrystallization in dichloromethane–triethylorthoformate (5 : 1 v/v). The yield was 1.12 g (67.76%). Single crystals were obtained by recrystallization at about 5°C in dichloromethane–triethylorthoformate (4 : 1 v/v) solution under carbon tetrachloride vapor. Anal. Calcd. for $Ni(C_{15}H_{26}N_2)(C_2H_3O_2)_2$: C, 55.50; H, 7.84; N, 6.81. Found: C, 55.16; H, 7.83; N, 6.84.

$Cu(C_{15}H_{26}N_2)(C_2H_3O_2)_2$, (3)

The Complex $Cu(C_{15}H_{26}N_2)(C_2H_3O_2)_2$, **3**, was prepared by direct reaction of copper(II) acetate monohydrate with a stoichiometric amount of (–)-sparteine in ethanol–triethylorthoformate (5 : 1 v/v) solution as reported [3]. Anal. Calcd. for $Cu(C_{15}H_{26}N_2)(C_2H_3O_2)_2$: C, 54.85; H, 7.75; N, 6.73. Found: C, 54.80; H, 7.82; N, 6.65.

$Zn(C_{15}H_{26}N_2)(C_2H_3O_2)_2$, (4)

The Complex, $Zn(C_{15}H_{26}N_2)(C_2H_3O_2)_2$, **4**, was prepared by direct reaction of zinc(II) acetate dihydrate (1.00 g, 4.56 mmol) with a stoichiometric amount of (–)-sparteine (1.05 mL, 4.57 mmol) in ethanol–triethylorthoformate (4 : 1 v/v) solution. The solution was evaporated until the white product started to precipitate and then the polycrystalline precipitate formed was isolated by filtration. The colorless complex was purified by recrystallization in dichloromethane–triethylorthoformate (5 : 1 v/v). The yield was 1.24 g (65.14%). Single crystals were obtained by recrystallization at room temperature in dichloromethane–triethylorthoformate (3 : 1 v/v) solution. Anal. Calcd. for $Zn(C_{15}H_{26}N_2)(C_2H_3O_2)_2$: C, 54.61; H, 7.72; N, 6.70. Found: C, 54.60; H, 7.73; N, 6.74.

Physical Measurements

Infrared spectra were obtained as KBr pellets using a Mattson Instruments Polaris FT-IR spectrometer. Elemental analyses were carried out by using a Profile HV-3 Elemental Analyzer System. Electronic absorption spectra were obtained on a Shimadzu UV-3101PC spectrophotometer (190–3200 nm) and a Shimadzu UV-1601PC spectrophotometer (200–1100 nm). Magnetic susceptibility measurements were made on a powered sample over the temperature range of 5–300 K with a field calibrated at 10 000 G by using a 760R SRM SQUID (Superconducting Quantum Interference Device) Rock Magnetometer. The data were corrected for temperature independent paramagnetic and for the diamagnetic contribution of the constituent atoms using Pascal's constant.

Crystal Structure Determination

Crystals of Complexes **1**, **2** and **4** suitable for x-ray analysis were obtained by slow evaporation from the dichloromethane–triethylorthoformate solution. Crystals of **1**, **2** and **4** were mounted and aligned on a CAD-4 diffractometer [17]. The cell parameters were refined from setting angles of 25 reflections with $2.03° \leq \theta \leq 22.97°$ for **1**, 25 reflections with $2.03° \leq \theta \leq 24.97°$ for **2** and 22 reflections with $2.29° \leq \theta \leq 27.47°$ for **4**, 1586 independent reflections for **1** in an asymmetric unit in range $0 \leq h \leq 10$, $0 \leq k \leq 13$, $0 \leq l \leq 17$, 1969 independent reflections for **2** in an asymmetric unit in range $0 \leq h \leq 11$, $0 \leq k \leq 15$, $0 \leq l \leq 19$ and 2369 independent reflections for **4** in an asymmetric unit in range $-10 \leq h \leq 10$, $0 \leq k \leq 17$, $0 \leq l \leq 11$ were collected using graphite-monochromated Mo-$K\alpha$ radiation and ω scan mode, ω-scan width $= (1.20 + 0.35\tan\theta)°$,

$\theta_{\max} = 22.97$ for **1**, ω-scan width $= (1.50 + 0.35\tan\theta)^\circ$, $\theta_{\max} = 24.97^\circ$ for **2** and ω-scan width $= (0.51 + 0.35\tan\theta)^\circ$, $\theta_{\max} = 27.47^\circ$ for **4**.

All non-H atoms were found by direct methods and their parameters were refined successfully with a full matrix least-squares procedure. The function minimized during least-squares refinement was $\Sigma\omega(|F_o| - |F_c|)^2$, where $\omega^{-1} = [\sigma^2(F_o)^2 + (0.0261P)^2 + 5.7525P]$ for **1**, $\omega^{-1} = [\sigma^2(F_o)^2 + (0.0076P)^2 + 9.2796P]$ for **2** and $\omega^{-1} = [\sigma^2(F_o)^2 + (0.0502P)^2]$ for **4**. H atoms were geometrically positioned and fixed. The absorption corrections for Complexes **1** and **2** were not applied for the *hkl* data because the crystal shape was uniform, whereas the empirical absorption corrections by using psi-scan for Complex **4** were applied to the intensity data ($T_{\max} = 0.7765$ and $T_{\min} = 0.5991$). Data collection: CAD-4 software [17]. Cell refinement: CAD-4 software. Data reduction: Xtal 3.2 Reference Manual [18] for Complexes **1** and **2**, and XCAD4 [19] for Complex **4**. Program used to solve structure: SHELXS97 [20]. Program used to refine structure: SHELXL97 [20]. Molecular graphics: ZORTEP [21] in NRCVAX [22] for Complexes **1** and **2**, and ORTEP-3 [23] for Complex **4**. Software used to prepare material for publication: SHELXL97 [20].

RESULTS AND DISCUSSION

Synthesis and Characterization

The metal(II) (−)-sparteine diacetate complexes, $[Co(C_{15}H_{26}N_2)(C_2H_3O_2)_2]$ (**1**), $[Ni(C_{15}H_{26}N_2)(C_2H_3O_2)_2]$ (**2**), $[Cu(C_{15}H_{26}N_2)(C_2H_3O_2)_2]$ (**3**) and $[Zn(C_{15}H_{26}N_2)(C_2H_3O_2)_2]$ (**4**) were prepared from reaction of (−)-sparteine ($C_{15}H_{26}N_2$) with the corresponding metal(II) diacetate in ethanol. Characterization of the complexes was conducted by IR and Vis/NIR spectroscopic methods, and magnetic measurements. Single crystal X-ray structures were obtained for Complexes **1**, **2** and **4**. The details of crystallographic data are listed in Table I, and perspective drawings of **1**, **2** and **4** appear in Figs. 1–3.

X-ray Crystallography

All three Complexes, **1**, **2** and **4**, contain a metal atom ligated by (−)-sparteine with two acetate groups occupying the remaining coordination sites. As predicted by previous work [1–5,7–9], the conformation of the coordinated (−)-sparteine in **1**, **2** and **4** 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. The conformation of the sparteine ring with respect to the metal is dictated by the absolute configuration at C6 and C14 as long as the two six-membered rings remain in the chair conformation.

Two acetate groups, in both Complexes **1** and **2**, coordinate to the metal ions in a bidentate fashion to produce *pseudo*-octahedral coordination complexes. In Complex **1**, two nitrogen donor atoms of (−)-sparteine and two oxygen atoms of acetate ligands [O1 and O4] constitute an equatorial plane for the elongated and distorted octahedron, and the Co–O2 and Co–O3 distances are shorter than the Co–O1 and Co–O4 distances by 0.158 Å and 0.357 Å, respectively.

TABLE I Crystallographic data for the complexes **1**, **2** and **4**

	$Co(C_{15}H_{26}N_2)(C_2H_3O_2)_2$	$Ni(C_{15}H_{26}N_2)(C_2H_3O_2)_2$	$Zn(C_{15}H_{26}N_2)(C_2H_3O_2)_2$
Chemical formula	$CoC_{19}H_{32}N_2O_4$	$NiC_{19}H_{32}N_2O_4$	$ZnC_{19}H_{32}N_2O_4$
FW (amu)	411.40	411.18	417.84
Crystal description	Violet cube	Green cube	Colorless block
Crystal size (mm)	0.75 × 0.40 × 0.30	0.70 × 0.50 × 0.45	0.53 × 0.53 × 0.20
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_1$
T (K)	293(2)	293(2)	293(2)
Radiation(Mo-$K\alpha$) (λ/Å)	0.71073	0.71073	0.71073
a (Å)	9.5240(10)	9.4846(8)	8.3098(11)
b (Å)	12.6990(10)	12.742(2)	13.4251(11)
c (Å)	16.3080(10)	16.160(3)	8.9899(5)
V (Å^3)	1972.4(3)	1953.7(5)	993.86(16)
Z	4	4	2
$d_{\text{calcd.}}$ (mg m^{-3})	1.385	1.398	1.396
μ (mm^{-1})	0.896	1.019	1.261
F (0 0 0)	876	880	444
Intensity variation (%)	None	None	−2
Independent reflections	1586	1969	2369
Observed reflections	1297	1536	1714
Final R	0.048	0.057	0.046
ωR	0.105	0.109	0.092
Threshold expression	$I \geq 2\sigma(I)$	$I \geq 2\sigma(I)$	$I \geq 2\sigma(I)$
Parameters	235	230	245
$(\Delta/\sigma)_{\max}$	1.000	1.000	1.000
$\Delta\rho_{\max}$ (eÅ^{-3})	0.331	0.847	0.554
$\Delta\rho_{\min}$ (eÅ^{-3})	−0.379	−0.772	−0.279
Goodness of fit	1.327	1.229	1.043
Flack parameter [24]	0.02(5)	−0.03(5)	0.00(2)

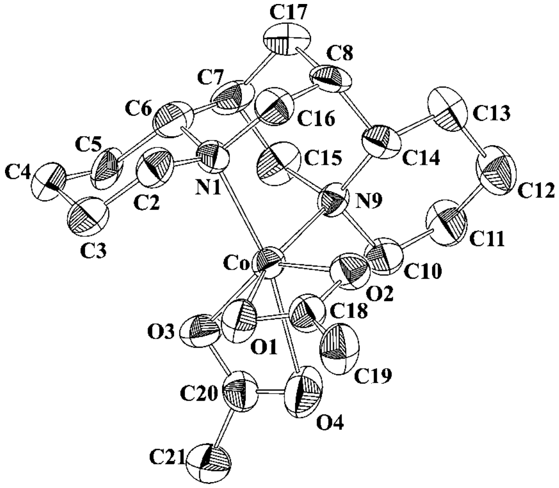

FIGURE 1 *ZORTEP* diagram of $Co(C_{15}H_{26}N_2)(C_2H_3O_2)_2$ showing the atom-numbering scheme and 40% probability ellipsoids. H atoms have been omitted for clarity.

In Complex **2**, the bidentate acetate ligands coordinate to the nickel(II) center almost symmetrically; two Ni–O distances of one chelated acetate are 2.145(6) Å and 2.080(6) Å, respectively and differ by only 0.065 Å and those of the other chelating acetate are 2.088(5) Å and 2.209(6) Å and differ by 0.121 Å. The carbon–oxygen bond

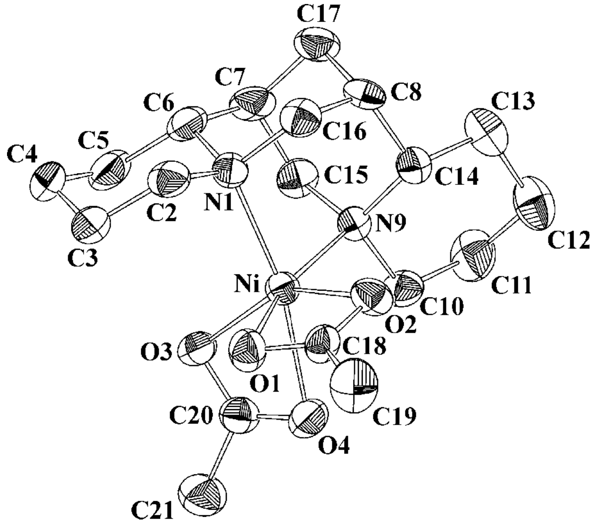

FIGURE 2 *ZORTEP* diagram of $Ni(C_{15}H_{26}N_2)(C_2H_3O_2)_2$ showing the atom-numbering scheme and 40% probability ellipsoids. H atoms have been omitted for clarity.

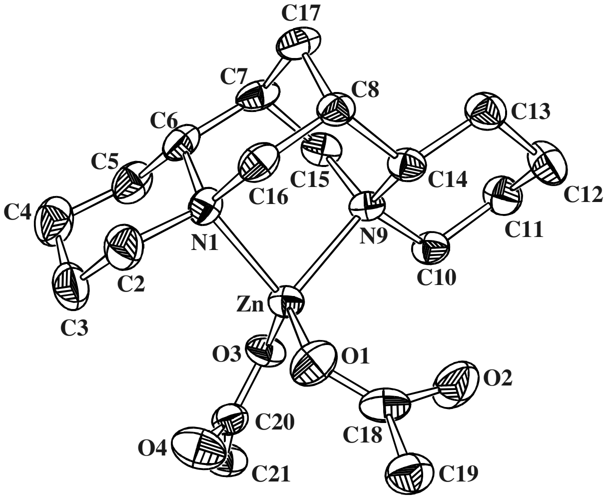

FIGURE 3 *ORTEP-3* diagram of $Zn(C_{15}H_{26}N_2)(C_2H_3O_2)_2$ showing the atom-numbering scheme and 40% probability ellipsoids. H atoms have been omitted for clarity.

distances of acetate ions in Complex **2** are fairly symmetric, when the comparison is made with those of Complex **1**. The bond distances r_{M-O} and r_{M-N} of the prepared complexes are plotted against the number of *d*-electrons of the metal ions in Fig. 4. The four r_{M-O} values are scattered in the range of 2.00–2.40 Å, showing a high degree of distortion in Complex **1**. The severe distortion observed in Complex **1** is attributable to the Jahn-Teller effect operating on the d^7 configuration of cobalt(II). The Complex **2** is not subject to Jahn-Teller effects and the two acetate ligands chelate to nickel(II) almost symmetrically in a bidentate fashion.

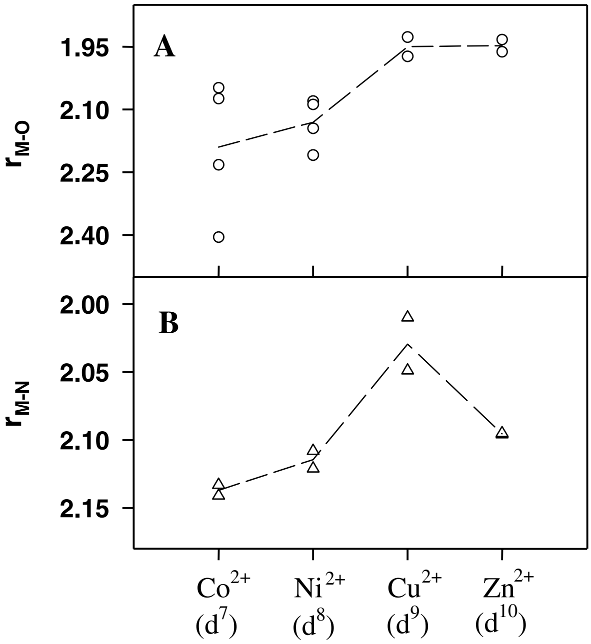

FIGURE 4 The values of metal–ligand bond distances (Å), r_{M-O} (A) and r_{M-N} (B) for metal(II) sparteine diacetate complexes plotted against number of d electrons of the metal ions. Both r_{M-O} and r_{M-N} distances decrease in the series $Co^{2+} \sim Cu^{2+}$. The average bond distances are connected by dotted lines in plots A and B.

Previously, we reported the crystal structures of metal(II) (–)-sparteine dinitrite complexes, $Ni(C_{15}H_{26}N_2)(NO_2)_2$ and $Co(C_{15}H_{26}N_2)(NO)_2$ [4] in which the metal(II) centers adopt a six coordinate, *pseudo*-octahedral geometry and the structural characteristics of these dinitrite complexes are similar to those of the corresponding diacetate Complexes **1** and **2**.

However, the metal–ligand bond distances in Complexes **1** and **2** are slightly longer than those in the corresponding dinitrite complexes. The cobalt–nitrogen distances [2.141(7) and 2.133(7) Å] in Complex **1** and the nickel–nitrogen distances [2.121(7) and 2.108(7) Å] in Complex **2** are slightly longer than those in $Co(C_{15}H_{26}N_2)(NO_2)_2$ [2.081(7) and 2.094(6) Å] and those in $Ni(C_{15}H_{26}N_2)(NO_2)_2$ [2.085(4) and 2.079(3) Å], respectively. The elongation of M–N and M–O distances in acetate complexes is attributable to the fact that acetate is larger than nitrite.

The crystal structure of Complex **3** was previously reported [3]; the copper(II) ion in Complex **3** is exclusively four-coordinate with a highly distorted tetrahedral geometry and the two acetate ions in it are monodentate. The Jahn-Teller effect operating on the cobalt(II) (d^7) is not severe enough to destroy the octahedral geometry of **1**, but this effect must strongly operate on the d^9Cu(II) center to make the fifth and sixth bonding interactions to the metal ion more difficult for acetate ligands.

The two acetate ligands in Complex **4** coordinate with the zinc(II) in a monodentate fashion to produce a *pseudo*-tetrahedral coordination complex. The molecular structure of Complex **4** shown in Fig. 3 is similar to that of **3**. The dihedral angle between the N–Zn–N and O–Zn–O planes is 74.0(3)°, and the geometry around zinc(II) is significantly distorted from a perfect tetrahedron although the extent of distortion is not as

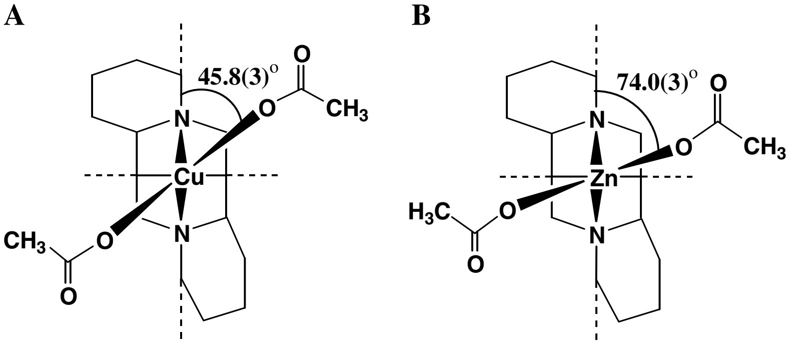

FIGURE 5 View showing dihedral angles between ∠N–M–N and ∠O–M–O planes (M = Cu(II) and Zn(II)) in complexes **3** (A) and **4** (B).

much as in **3** (see Fig. 5). The dihedral angle for a perfect tetrahedron is 90° and the twist of dihedral angle by 16° in **4** is caused by the steric effect exerted by the bulky (−)-sparteine ligand coordinated to the zinc(II) ion of d^{10} closed-shell system.

The dihedral angle between the N–Cu–N and O–Cu–O planes in Complex **3** is 45.8(3)°, much smaller than 74.0(3)°. The reduced dihedral angle in Complex **3** is definitely attributed to electronic effects since the copper(II) ion (d^9-configuration) favors the square-planar structure around the metal center over the tetrahedral structure. Unlike nitrite [2], the acetate [3] ligand coordinates to the copper(II) center exclusively as a monodentate ligand.

Selected bond distances and bond angles of the Complexes **1**–**4** are listed in Table II. The stability of complexes of the 3*d* metal ions with a given ligand is almost invariably in the order of $Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$ [25]. The plots in Fig. 4 exhibit a similar trend if it can be assumed that the stability of the complexes is inversely related to the metal–ligand bond distances.

IR Features of Coordinated Acetates

The bonding in metal carboxylates has often been distinguished by their IR spectra [13]. The "ionic" acetate or the "free" acetate ion has symmetric stretching frequency $\nu_s(COO^-)$ and asymmetric stretching frequency $\nu_a(COO^-)$ modes at ~1415 and 1570 cm^{-1}, respectively, and these frequencies can vary by $\pm 20\,cm^{-1}$ [13]. When a carboxylate group is unidentate, one of the C–O bonds should have enhanced double bond character and should give rise to a high frequency band. Symmetric bidentate coordination leaves the C–O bonds still equivalent, and the effect on the frequencies is not easily predictable.

Deacon and Phillips [26] carefully examined infrared spectra of many acetate and trifluoroacetate complexes having known X-ray crystal structures, and arrived at the following conclusions. First, monodentate complexes exhibit Å values $[\nu_a(COO^-) - \nu_s(COO^-)]$ which are much greater than ionic complexes. Secondly, chelating (bidentate) complexes exhibit Å values which are significantly less than the ionic values. The Å value for ionic acetate is 164 cm^{-1} [27]. Generally, monodentate complexes exhibit a Å value which is much greater than 200 cm^{-1}, and bidentate complexes exhibit a Å value which is less than 120 cm^{-1}.

TABLE II Selected bond distances (Å) and bond angles (°) with e.s.d's in parentheses for the complexes **1**–**4**

$Co(C_{15}H_{26}N_2)$- $(C_2H_3O_2)_2$		$Ni(C_{15}H_{26}N_2)$- $(C_2H_3O_2)_2$		$Cu(C_{15}H_{26}N_2)$- $(C_2H_3O_2)_2$[a]		$Zn(C_{15}H_{26}N_2)$- $(C_2H_3O_2)_2$	
Co–O1	2.232(6)	Ni–O1	2.145(6)	Cu–O1	1.927(5)	Zn–O1	1.962(6)
Co–O2	2.074(6)	Ni–O2	2.080(6)	Cu–O2	3.062(5)	Zn–O2	2.64 (5)
Co–O3	2.048(6)	Ni–O3	2.088(5)	Cu–O3	1.973(4)	Zn–O3	1.933(5)
Co–O4	2.405(7)	Ni–O4	2.209(6)	Cu–O4	2.701(5)	Zn–O4	2.814(6)
Co–N1	2.141(7)	Ni–N1	2.121(7)	Cu–N1	2.010(6)	Zn–N1	2.096(6)
Co–N9	2.133(7)	Ni–N9	2.108(7)	Cu–N9	2.049(6)	Zn–N9	2.095(6)
O1–C18–O2	117.5(9)	O1–C18–O2	117.7(8)	O1–C18–O2	124.9(8)	O1–C18–O2	129.7(18)
O3–C20–O4	121.2(9)	O3–C20–O4	122.6(6)	O3–C20–O4	124.0(5)	O3–C20–O4	122.2(7)
N1–Co–N9	86.2(2)	N1–Ni–N9	86.5(3)	N1–Cu–N9	90.1(2)	N1–Zn–N9	87.7(2)
N1–Co–O1	96.2(2)	N1–Ni–O1	96.2(3)	N1–Cu–O1	151.8(2)	N1–Zn–O1	96.2(2)
N1–Co–O2	102.7(3)	N1–Ni–O2	98.9(3)	N1–Cu–O3	91.7(2)	N1–Zn–O3	123.4(2)
N1–Co–O3	111.4(2)	N1–Ni–O3	107.2(2)	N9–Cu–O1	103.1(3)	N9–Zn–O1	116.0(3)
N1–Co–O4	167.7(3)	N1–Ni–O4	167.3(3)	N9–Cu–O3	142.9(3)	N9–Zn–O3	101.0(3)
N9–Co–O1	159.2(2)	N9–Ni–O1	161.2(2)	O1–Cu–O3	92.4(3)	O1–Zn–O3	126.8(2)
N9–Co–O2	99.2(2)	N9–Ni–O2	99.3(3)				
N9–Co–O3	102.4(3)	N9–Ni–O3	99.6(2)				
N9–Co–O4	100.7(3)	N9–Ni–O4	99.6(3)				
O1–Co–O2	60.1(2)	O1–Ni–O2	62.0(2)				
O1–Co–O3	95.9(3)	O1–Ni–O3	97.3(2)				
O1–Co–O4	81.0(3)	O1–Ni–O4	81.6(3)				
O2–Co–O3	140.5(2)	O2–Ni–O3	148.4(2)				
O2–Co–O4	86.4(2)	O2–Ni–O4	91.1(2)				
O3–Co–O4	57.3(2)	O3–Ni–O4	60.9(2)				

[a] Ref. [3].

For Complex **1**, the Å values are in the range of 125–135 cm^{-1} [$\nu_a(COO^-)$ at 1581 and 1577 cm^{-1}, and $\nu_s(COO^-)$ at 1452 and 1446 cm^{-1}]. These values are slightly larger than 120 cm^{-1} but much smaller than that for free acetate. X-ray crystal structural data show that both acetate ligands are bidentate. However, the chelating acetate ligands are quite asymmetrically coordinated to the cobalt(II) center, and one oxygen–cobalt bond is extremely elongated.

The infrared spectrum of Complex **2** shows four bands originating from the acetate ligands; $\nu_a(COO^-)$ at 1558 and 1567 cm^{-1}, and $\nu_s(COO^-)$ at 1449 and 1458 cm^{-1}, respectively. The Å values are in the range of 100–118 cm^{-1}. These results indicate that both acetate ions of Complex **2** chelate to the nickel(II) center almost symmetrically in good agreement with X-ray crystallographic results.

The Å values of Complexes **3** and **4** are in the range of 208–297 cm^{-1}, indicating that the acetate ligands in these complexes coordinate to the metal center in a monodentate fashion. The infrared spectral features of the coordinated acetate ligand are assigned on the basis of crystallographic results, and are summarized in Table III.

Magnetic Behavior and Electronic Spectral Features

The magnetic susceptibility data of Complexes **1**–**3** were collected from 300 down to 5 K and the effective magnetic moments of these three complexes were evaluated from the relationship $\mu_{eff} = 2.828(\chi_M \times T)^{1/2}$. All three complexes exhibit effective magnetic moment values expected for monomeric Co(II), Ni(II) and Cu(II) complexes. The effective magnetic moments at 300 K and the Curie–Weiss parameters of these complexes are summarized in Table IV.

TABLE III Infrared spectral features of carboxyl group for metal(II) (–)-sparteine diacetate complexes

Complex	$\nu_a(COO^-)$ cm^{-1}	$\nu_s(COO^-)$ cm^{-1}	Δ^a cm^{-1}
$CH_3COO^-Na^{+b}$	1578 (vs)	1414 (vs)	164
$Co(C_{15}H_{26}N_2)(C_2H_3O_2)_2$	1581 (vs) 1577 (vs)	1452 (vs) 1446 (vs)	125 ~ 135
$Ni(C_{15}H_{26}N_2)(C_2H_3O_2)_2$	1567 (vs) 1558 (vs)	1449 (vs) 1458 (vs)	100 ~ 118
$Cu(C_{15}H_{26}N_2)(C_2H_3O_2)_2$	1606 (vs) 1585 (vs)	1377 (vs) 1325 (vs)	208 ~ 281
$Zn(C_{15}H_{26}N_2)(C_2H_3O_2)_2$	1624 (vs) 1616 (vs)	1392 (vs) 1327 (vs)	224 ~ 297

[a] Difference between $\nu_a(COO^-)$ and $\nu_s(COO^-)$; [b] Ref. [27].

TABLE IV The effective magnetic moments and Curie–Weiss parameters of complexes **1**–**3**

Complex	μ_{eff} ^{a} (B.M.)	*Curie–Weiss parameters*	
		C^b	θ^b
$Co(C_{15}H_{26}N_2)(C_2H_3O_2)_2$	4.77	2.867	– 5.88
$Ni(C_{15}H_{26}N_2)(C_2H_3O_2)_2$	3.40	1.289	– 1.26
$Cu(C_{15}H_{26}N_2)(C_2H_3O_2)_2$	1.98	0.453	– 0.50

[a] The effective magnetic moments were calculated by $\mu_{eff} = 2.828(\chi_M \times T)^{1/2}$ at 300 K; [b] The values of Curie–Weiss parameters calculated by $\chi_M = C/(T - \theta)$ were obtained in the range 5–100 K.

The effective magnetic moments evaluated for Complexes **1–3** are 4.77, 3.40 and 1.98 B.M. at 300 K, respectively. These results indicate that cobalt(II) in Complex **1** has three unpaired electrons in a high spin system, and nickel(II) in Complex **2** has two unpaired electrons with some degree of orbital contribution. The copper(II) complex with a single unpaired electron exhibits μ_{eff} value of 1.98 B.M. as expected. However, μ_{eff} value of **1** and **2** decreases slightly at low temperature, likely due to single ion anisotropy.

The electronic spectra recorded in the Vis-NIR region were resolved into Gaussian components by using the PeakFit (version 4.0) of micro-program of Microcal Software Inc. and the results are summarized in Table V. The electronic spectrum of Complex **1** exhibits three bands of intensity 48–77 LM^{-1} cm^{-1} in the region of 490–600 nm and another three spin-forbidden bands of intensity 2–3 LM^{-1} cm^{-1} in the region of 950–1450 nm. The characteristic transitions of most high-spin octahedral and *pseudo*-octahedral cobalt(II) complexes consist of two principal regions; a band near 1000–1250 nm of intensity 1–10 LM^{-1} cm^{-1} is usually assigned to $^4T_{2g} \leftarrow {}^4T_{1g}$ and a multiple structured band in the region near 500 nm with an intensity of ~20 LM^{-1} cm^{-1} is usually assigned to $^4T_{1g}(P) \leftarrow {}^4T_{1g}$ [28]. The electronic spectrum of Complex **1** is very complicated and is not unequivocally interpretable on the basis of a $^4T_{1g}$ ground state for the high-spin system. The complication might arise from the low symmetry of Complex **1** and the admixture of spin-forbidden transitions to the doublet states. The low symmetry from Complex **1** might split $^4T_{1g}$ ground state into A and E states, leaving E as the ground state. This is compatible with the crystallographic results of Complex **1** because the Jahn-Teller effect will operate on a high-spin system only with an E ground state for an octahedral cobalt(II) complex.

TABLE V Analyses of electronic absorption spectral data for the complexes **1**–**3**

Complex	*Peak position*		
	λ_{max} (nm)	$\nu_{\max}$ (nm)	ε (LM^{-1}cm^{-1})
$Cu(C_{15}H_{26}N_2)(C_2H_3O_2)_2$	274	36490	3232
	310	32250	2831
	675	14810	127
	786	12720	174
	932	10730	80
$Ni(C_{15}H_{26}N_2)(C_2H_3O_2)_2$	391	25575	26
	425	23529	16
	686	14577	11
	766	13055	8
	1113	8985	7
	1312	7622	3
$Co(C_{15}H_{26}N_2)(C_2H_3O_2)_2$	499	20040	77
	552	18115	48
	590	16949	60
	962	10395	3
	1124	8897	2
	1409	7097	3

The electronic spectrum of Complex **2** shows six resolved *d*–*d* bands in the region of 390–1350 nm with intensities of 3–26 LM^{-1}cm^{-1}.

The ligand field transition bands of Complex **3** in the region of 600–1000 nm were resolved into three components and tentatively assigned to d_{xz}, $d_{yz}(^2E) \leftarrow d_{x^2-y^2}(^2B_2)$, $d_{xy} \leftarrow d_{x^2-y^2}(^2B_2)$, and $d_{z^2}(^2A_1) \leftarrow d_{x^2-y^2}(^2B_2)$, respectively. These results are expected when a planar copper(II) center is distorted toward the tetrahedral structure of D_{2d} or C_{2v} symmetry [29]. The strong intensities of these bands are attributable both to the metal centered *p*–*d* mixing expected for nonsymmetric complexes and covalency effects [29].

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Supplementary Material

A table of magnetic moment parameters, and the figures of IR spectra, temperature dependence of magnetic susceptibilities and electronic spectra for the complexes prepared (PDF) are available from S.-N.C. Crystallographic data (excluding structure factors) for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-179652, CCDC-179653 and CCDC-179654. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk]

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