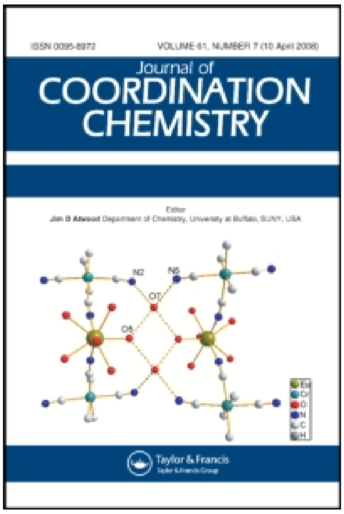


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Complexation and structure of anthranilic acid-derived *N,N,O*-terdentate ligands

G. R. Woodburn[a]; N. R. Lien[b]; A. Hoppe[c]; Y. Jahng[d]; J. R. Telford[e]
[a] Department of Science, Blaine High School, Blaine, MN 55434, USA [b] Department of Chemistry, Whitman College, Walla Walla, WA 99362, USA [c] College of Engineering, University of Iowa, Iowa City, IA 52242, USA [d] School of Pharmacy, Yeungnam University, Kyongsan, 712-749, South Korea [e] College of Liberal Arts and Sciences, Maryville University, St. Louis, MO 63141, USA

First published on: 20 October 2009

To cite this Article Woodburn, G. R. , Lien, N. R. , Hoppe, A. , Jahng, Y. and Telford, J. R.(2010) 'Complexation and structure of anthranilic acid-derived *N,N,O*-terdentate ligands', Journal of Coordination Chemistry, 63: 2, 185 — 195, First published on: 20 October 2009 (iFirst)

To link to this Article: DOI: 10.1080/00958970903349591

URL: http://dx.doi.org/10.1080/00958970903349591

Journal of Coordination Chemistry
Vol. 63, No. 2, 20 January 2010, 185–195

Complexation and structure of anthranilic acid-derived *N*,*N*,*O*-terdentate ligands

G.R. WOODBURN†, N.R. LIEN‡, A. HOPPE§, Y. JAHNG¶ and J.R. TELFORD*⊥

†Department of Science, Blaine High School, Blaine, MN 55434, USA
‡Department of Chemistry, Whitman College, Walla Walla, WA 99362, USA
§College of Engineering, University of Iowa, Iowa City, IA 52242, USA
¶School of Pharmacy, Yeungnam University, Kyongsan, 712-749, South Korea
⊥College of Liberal Arts and Sciences, Maryville University, St. Louis, MO 63141, USA

(*Received 26 May 2009; in final form 28 July 2009*)

Complexes of archetypal compounds 2-(2-amino-ethylamino)-benzoic acid (**1**) and 2-[(pyridin-2-ylmethyl)-amino]-benzoic acid (**2**) have been prepared with Co, Ni, and Cu. These complexes have been examined by UV-Vis and IR spectroscopy. The structure of [(Co · **2**)Cl] has been studied by X-ray crystallography.

Keywords: Crystal structure; *N*,*N*,*O*-terdentate; Anthranilic acid; Coordination polymer; Cobalt

1. Introduction

Anthranilic acid is a versatile ligand that can bind metal ions in a variety of ways. The amine can bind metals neutral or deprotonated, alone or as a bidentate chelate with the carboxylate. The carboxylic acid is usually deliberately deprotonated to promote ligation, but under some conditions it can also coordinate metals if it remains protonated [1]. One or both oxygens of the carboxylate can bind directly to a metal. In addition, in one study, anthranilic acid was found to form outer-sphere complexes with the hexa-aquomagnesium cation [2].

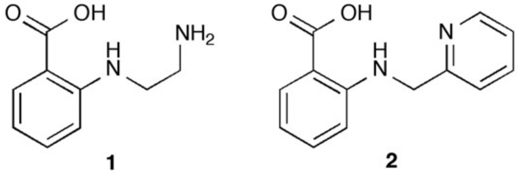
A survey of the literature suggests that anthranilic acid preferentially binds metals through carboxylate rather than chelating with the ortho-amine [1]. This may be due in part to deactivation of the nitrogen lone pair of electrons with the benzene ring. While acid–amide binding has been shown with heavier transition metals, few first row transition metals show this coordination [1]. In this study several different ligand groups were added to the amine in an attempt to modify the acidity of the nitrogen lone pair and thus to form terdentate *N*,*N*,*O* ligands.

A series of ligands based on anthranilic acid has been reported using Ullmann-type arylamination without metal catalyst [3]. These terdentate *N*,*N*,*O* ligands bind with first

---

*Corresponding author. Email: jtelford@maryville.edu

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2010 Taylor & Francis
DOI: 10.1080/00958970903349591



1 **2**

Figure 1. Ligands studied herein.

row transition metals. We report here the preparation of coordination complexes with these ligands (figure 1). As the behavior of these complexes is similar, compounds **1** and **2** are presented in the interest of brevity to describe the behavior of these ligands and metal complexes. Complexes of **1** and **2** with Co, Cu, and Ni were prepared and studied by UV-Vis, IR, and fluorescence spectroscopy. The crystal structure of [(Co · **2**)Cl] is also presented.

2. Experimental

2.1. *Materials and reagents*

All reagents were obtained from commercial sources and used without purification. Solvents were dried over activated molecular sieves (4 Å). All NMR spectra were recorded on a Brüker DPX-400 spectrometer. IR measurements were obtained on an Avatar 360 FT-IR spectrometer. UV-Vis measurements were taken on an HP Agilent 8453A spectrometer. Water for UV-Vis measurements was purified to a resistance of 18.2 MΩ cm using a commercial Millipore (USA) Milli-Q purification system. All metal salts were used as received.

Caution! Perchlorate salts are potentially explosive oxidizing agents and should be handled in small amounts, without heating, and with caution.

2.2. *Synthetic methods*

Approximately 2.0 g of 2-iodobenzoic acid (approx. 8.3 mmol) was added to a 40-fold excess of neat amine. Three equivalents of K_2CO_3 were added and the mixture was heated to 100°C. After 12 h, 30 mL of H_2O was added to the reaction mixture. Evaporation of solvent by reduced pressure afforded a pale brown solid, which was dissolved in 30 mL of H_2O. Insoluble material was filtered off. The filtrate was acidified ($pH \approx 3$) by addition of concentrated HCl. The precipitate that formed was collected and washed with H_2O, cold methanol, and air dried to give the final product.

2.2.1. Synthesis of 2-(2-amino-ethylamino)-benzoic acid (1). White needles (CH_3OH): m.p. 253–254°C. ESI-MS (*m*/*z*) 181.1 (M + H). IR (KBr) ν 3334, 3022, 1660, 1574, 1512, 1430, 1320, 1256, 1220, 1165, 1150, 1012, 750, 745 cm^{-1}. ^1H NMR (DMSO-d_6, 400 MHz) $\delta = 12.6$ (br s, COOH), 8.31 (br s, NH), 7.89 (d, $J = 7.4$ Hz, H3), 7.34 (t, $J = 6.8$ Hz, 7H, H4), 6.87 (d, $J = 8.2$ Hz, H6), 6.59 (t, $J = 6.8$ Hz, H5), 3.56 (br s, 2H), 2.94 (br s, 2H). ^{13}C NMR (DMSO-d_6, 100 MHz) $\delta = 169.8$, 150.2, 134.5, 131.8, 114.8, 110.9, 39.5, 37.5.

2.2.2. Synthesis of 2-[(pyridin-2-ylmethyl)-amino]-benzoic acid (2). White needles (CH_3OH): m.p. 153–154°C. ESI-MS (*m*/*z*) 229.14 (M + H). IR (KBr) ν 3337, 3020, 1659, 1575, 1517, 1431, 1321, 1257, 1221, 1164, 1150, 1012, 754, 745 cm^{-1}. ^1H NMR (DMSO-d_6, 400 MHz) $\delta = 12.64$ (br s, COOH), 8.55 (dd, $J = 4.8$, 1.2 Hz, H6′), 7.82 (dd, $J = 8.0$, 1.6 Hz, H3′), 7.74 (ddd, $J = 8.0$, 7.8, 1.6 Hz, H4′), 7.35 (d, $J = 8.0$ Hz, H6), 7.30 (ddd, $J = 8.2$, 8.0, 1.6 Hz, H4), 7.26 (dd, $J = 8.0$, 4.8 Hz, H5′), 6.65 (d, $J = 8.4$ Hz, H3), 6.56 (ddd, $J = 8.2$, 8.0, 1.0 Hz, H5), 4.54 (s, 2H). ^{13}C NMR (DMSO-d_6, 100 MHz) δ 169.79, 158.36, 150.41, 149.03, 136.81, 134.38, 131.72, 122.21, 121.30, 114.54, 111.62, 110.51, 47.71.

2.3. *Preparation of solutions for UV-Vis and fluorescence studies*

2.3.1. Solution of Co · 1. A 1 : 1 metal : ligand solution was prepared by mixing 200 µL (0.100 M in DMSO) of **1** and 413 µL (0.0484 M) of $CoCl_2$. This solution was brought to a final volume of 1.00 mL using 0.100 M Hepes buffer (pH 7).

2.3.2. Solution of Cu · 1. A 1 : 1 metal : ligand solution was prepared by mixing 100 µL (0.100 M in DMSO) of **1** with 200 µL (0.0500 M) $CuSO_4 \cdot 6H_2O$. This solution was brought to a final volume of 1.00 mL using 0.100 M HEPES buffer (pH 7).

2.3.3. Solution of Co·2. A 1 : 1 metal : ligand solution was prepared by mixing 51.06 µL (0.195 M in DMSO) of **2** and 204.27 µL (0.0489 M) of $CoCl_2$. This solution was brought to a final volume of 1.00 mL using 0.100 M HEPES buffer (pH 7).

2.3.4. Solution of Cu · 2. A 1 : 1 metal : ligand solution was prepared by mixing 51.06 µL (0.195 M in DMSO) of **2** with 190.79 µL (0.0524 M) $CuSO_4 \cdot 6H_2O$. This solution was brought to a final volume of 1.00 mL using 0.100 M HEPES buffer (pH 7).

2.3.5. Solution of Ni · 2. The nickel complex was insoluble using HEPES buffer and methods used above. However, the 1 : 1 metal : ligand complex was prepared by adding 51 µL 0.195 M of **2** in DMSO, 201 µL of 0.0537 M $Ni(ClO_4)_2 \cdot 6H_2O$ in EtOH and 6.5 µL of diisopropylamine and diluting with 747 µL DMSO. A 500 µL aliquot was taken and diluted to 2 mL with DMSO to obtain a suitable spectrum.

2.4. *Preparation of compounds for IR spectroscopy*

An IR spectrum of Co · **2** was obtained by evaporating a methanolic solution of [Co(**2**)Cl] and making a nujol mull. The IR spectra of Cu · **2** and Ni · **2** were obtained by a thin film cast from acetone solution onto a KBr plate. Solid Co · **1** was prepared by evaporating a methanolic solution, re-dissolving in acetone, adding 1 eq. triethylamine, centrifuging to remove solid, and storing the supernatant liquid in a sealed vial until solids formed. The IR spectrum of this solid was obtained from a nujol mull. Solid Cu · **1** was not obtained because it decomposed in solution.

2.5. *Crystal structure determination*

A crystal of **2** complexed with Co suitable for X-ray crystallography was obtained by slow diffusion of acetone into a concentrated methanolic solution of [Co(**2**)Cl]. Data were collected from a single red crystal with dimensions of 0.32 mm × 0.10 mm × 0.10 mm at 191 K on a Nonius Kappa CCD diffractometer equipped with an Oxford Cryostreams 700 using graphite monochromated Mo-Kα radiation ($\lambda = 0.7107$ Å) by the ω–2θ method ($2.9° < 2\theta < 25°$). A total of 10,697 reflections were collected; 2889 of these were unique and used to solve the structure. The structure was solved using SHELXS-97 and refined using SHELXL-97 with WinGX used as an interface for data refinement [4, 5]. The structure was solved using direct methods and refined on F^2 using full-matrix least-squares methods. The two most disagreeable reflections (0,0,1 and 0,1,0) were removed during refinement after it was determined they were behind the beam stop.

Hydrogens on carbon atoms were placed in idealized positions with the exception of H14 [bonded to N(2)], which was found by direct methods during successive data refinements. Details of the data collection and refinement are provided in table 1. Selected bond lengths and angles are given in table 2. The monomer and atomic numbering scheme are given in figure 2.

3. Results and discussion

3.1. *UV-Vis and fluorescence*

Compound **2** exhibits absorption bands at 259 and 348 nm with extinction coefficients of 11,420 $M^{-1}cm^{-1}$ and 4750 $M^{-1}cm^{-1}$, respectively. This compound is fluorescent

Table 1. Crystallographic data and structural refinement for Co(**2**)Cl.

Empirical formula	$C_{13}H_{11}O_2N_2CoCl$
Formula weight	321.62
Crystal system	Monoclinic
Space group	*P2/c*
Unit cell dimensions (Å, °)	
a	9.8387(10)°
b	0.0628(17)°
c	7.8502(8)°
α	90.00
β	106.694(5)
γ	90.00
Volume (Å^3), Z	1262.3(2), 4
Calculated density (g cm^{-3})	1.692
Absorption coefficient (mm^{-1})	1.568
F(000)	652
Crystal size (mm^3)	0.32 × 0.10 × 0.10
θ range for data collection (°)	2.96–27.48
Limiting indices	$-12 \le h \le 12$, $-22 \le k \le 21$, $-10 \le l \le 10$
Reflections collected/unique	10,697/2889
Goodness-of-fit on F^2	1.041
Final R indices [$I > 2\sigma(I)$]	$R = 0.0575$, $wR_2 = 0.0791$

and emits at 410 nm upon irradiation at both 259 and 348 nm. The addition of one equivalent of metal (Cu, Ni, or Co) to **2** completely quenches the fluorescence.

Compound **2** readily forms complexes with Co and Cu in H_2O at pH 7.5. The Ni · **2** complex is formed in DMSO with a stoichiometric amount of triethylamine added to

Table 2. Selected bond lengths (Å) and angles (°) for Co(**2**)Cl.

Co–N(1)	2.0794(19)
Co–N(2)	2.1692(18)
Co–O(1)	2.0637(15)
Co–O(1)	2.1276(14)
Co–O(2)	2.3050(16)
O(1)–Co–N(1)	101.71(7)
O(1)–Co–O(1)	147.27(8)
N(1)–Co–O(1)	103.94(6)
O(1)–Co–N(2)	79.43(6)
N(1)–Co–N(2)	77.34(7)
O(1)–Co–N(2)	86.70(6)
O(1)–Co–O(2)	94.31(6)
N(1)–Co–O(2)	162.92(6)
O(1)–Co–O(2)	58.98(6)
N(2)–Co–O(2)	100.12(7)
O(1)–Co–Cl(1)	99.28(4)
N(1)–Co–Cl(1)	96.14(5)
O(1)–Co–Cl(1)	97.83(4)
N(2)–Co–Cl(1)	172.85(5)
O(2)–Co–Cl(1)	86.97(4)
N(2)···H(14)	0.85(2)
H(14)···Cl(1)	2.49(2)
N(2)···Cl(1)	3.3255(16)
N(2)–H(14)–Cl(1)	165.0(19)

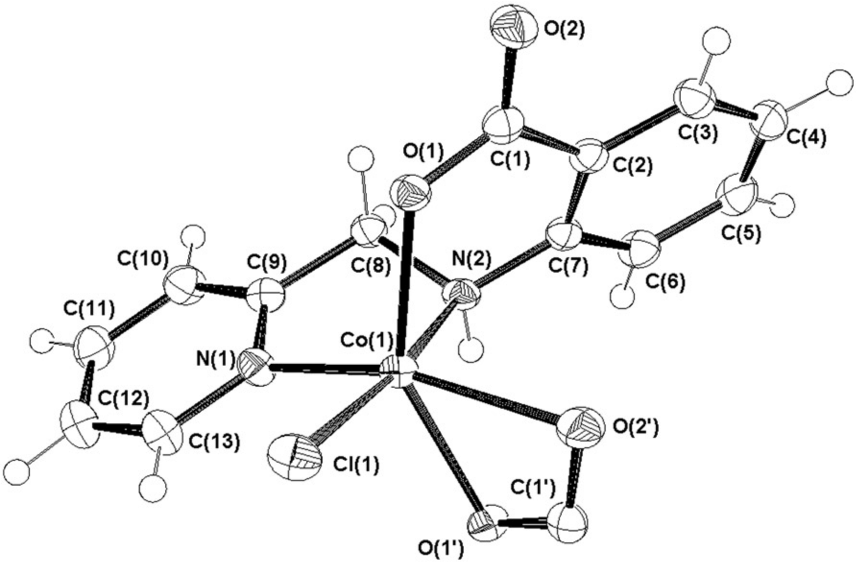


Figure 2. The asymmetric unit of [Co(**2**)Cl] expanded to show the complete metal coordination sphere. Atoms are drawn at 50% probability. Symmetry codes: x, $1/2-y$, $1/2+z$ and x, $1/2-y$, $-1/2+z$.

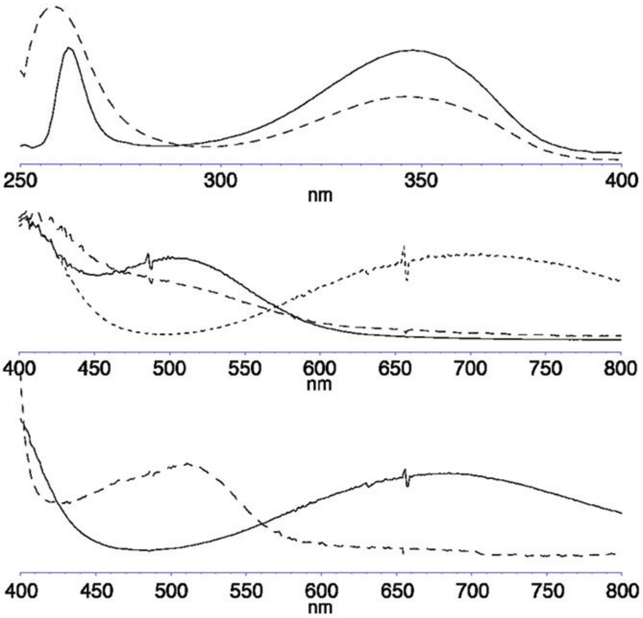


Figure 3. Top: Ligands **1**–solid line, and **2**–dashed line. Middle: Complexes Co · **22**–solid line, Ni · **2**–dashed line, and Cu · **2**–dotted line. Bottom: Complex Cu · **1**–solid line, and Co · **1**–dashed line.

Table 3. Charge transfer bands and extinction coefficients for complexes of first row transition metals with **2**.

	Co · **2**	Ni · **2**	Cu · **2**
λ_{max} (nm)	460 (sh)	515 (sh)	697
ε (L mol^{-1} cm^{-1})	n/a	n/a	63.2

n/a: extinction coefficient was not calculated as the peak was a shoulder.

deprotonate the carboxylic acid. The Co · **2** solution shows a charge transfer shoulder at approx. 460 nm that tails into multiple peaks in the UV. The complex is sluggish to form, initially the solution is light pink in color characteristic of tetrahedral Co, but turns orange–red after 48 h. No change of the UV-Vis spectrum was found after the initial 48 h. This slow initial change is likely due to slow kinetics of complexation of the Co^{2+} cation. The Ni · **2** solution shows a charge transfer shoulder at 515 nm, and the solution color is deep red. The dark green Cu · **2** solution shows a distinct metal-to-ligand charge transfer band at 697 nm with an extinction coefficient of 63.2 M^{-1} cm^{-1}. The absorption spectra of **1** and **2** and their complexes with Co^{2+}, Ni^{2+}, and Cu^{2+} are given in figure 3. Charge transfer band and extinction coefficient data for each complex are given in table 3. The fluorescence of **2** is quenched by formation of the Co^{2+}, Cu^{2+}, or Ni^{2+} complexes.

Compound **1** exhibits absorption bands at 262 nm ($\varepsilon = 4095$ M^{-1} cm^{-1}) and 348 nm ($\varepsilon = 3990$ M^{-1} cm^{-1}) and shows a fluorescence peak at 408 nm upon irradiation at both 262 and 348 nm.

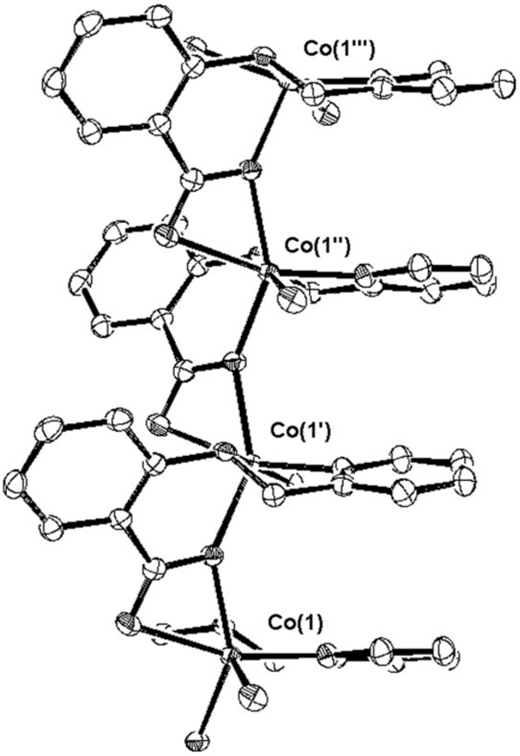


Figure 4. The extended coordination polymer of [Co(**2**)Cl].

Compound **1** readily forms complexes with Co and Cu in H_2O at pH 7.5. The Ni · **1** complex could not be obtained. The Co · **1** solution shows a CT peak at approx 511 nm ($\varepsilon = 7.20\,M^{-1}\,cm^{-1}$). This peak is a shoulder on the ligand absorption peaks. A very dilute solution of this complex shows that the ligand absorption band at 348 nm shifts to 328 nm. The solution is pale pink in color. Co · **1** shows a fluorescence peak at 427 nm upon irradiation at both 262 and 328 nm.

The Cu · **1** complex shows a CT peak at 685 nm ($\varepsilon = 51.96\,M^{-1}\,cm^{-1}$). A dilute solution of this complex shows that the ligand absorption band at 348 nm shifts to approximately 306 nm. The solution is bright turquoise. The ligand fluorescence in Cu · **1** is shifted from 408 to 438 nm upon irradiation at 262, 306, and 398 nm.

3.2. *Crystal structure*

The ORTEP diagram of [(Co · **2**)Cl] is given in figure 2. In the solid state, **2** forms a 1-D polymer where O1 of carboxylate bridges two cobalts and O2 binds to the neighboring Co. A view of the extended coordination sphere is given in figure 4. The crystal of [Co(**2**)Cl] is densely packed due to oxygen bridging two adjacent Co atoms. No solvent is present in the crystal. This illustrates the versatility in binding of the anthranilic acid derivative. N1, N2, and O1 bind in a facial arrangement. While N1 is an unfavorable binding orientation in anthranilic acid, the addition of the (2-methyl-pyridine) to N1

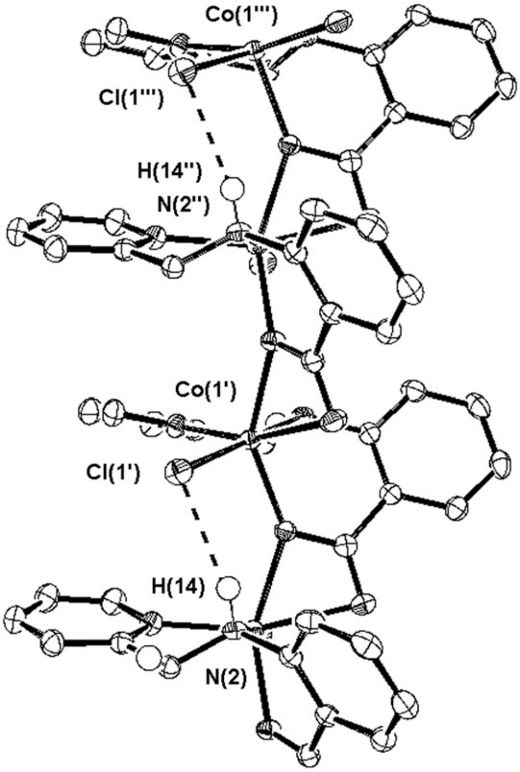


Figure 5. The N−H ··· Cl hydrogen bond within the extended coordination sphere framework of [Co(**2**)Cl].

has forced it into a favorable geometry for binding. The angle formed between the planes of the anthranilic ring and the pyridine ring in the ligand is 67.28°.

The geometry around the cobalt is distorted octahedral with the small bite angle of the bidentate carboxylate (58.97°) the most significant deviation from idealized geometry. This is not surprising, as the rigidity of the anthranilic acid does not allow O1 to occupy a position more consistent with octahedral geometry.

Several nonbonding interactions are present in the crystal structure. Within each 1-D polymer, a N–H ··· Cl hydrogen bond exists (figure 5), supplementing the coordination interactions and maintaining the 1-D polymer. A π–π interaction exists between anthranilic rings of neighboring ligands in neighboring polymer chains (figure 6). The interplanar distance between the rings is 3.409 Å; the distance between the centroids of each ring is 3.606 Å. This interaction is responsible for maintaining the 2-D structure. The facial coordination of the ligand is different from that of the solid-state structures of similar Schiff-base ligands; in the structure by Mukhopadhyay, the ligands are nearly planar [6].

3.3. *IR spectroscopy*

The antisymmetric COO^- stretching of **2** at 1575 cm^{-1} shifts to lower frequencies for cobalt and nickel complexes and to higher frequencies for the copper complex. This is consistent with the pattern observed for copper and nickel complexes of β-alanine,

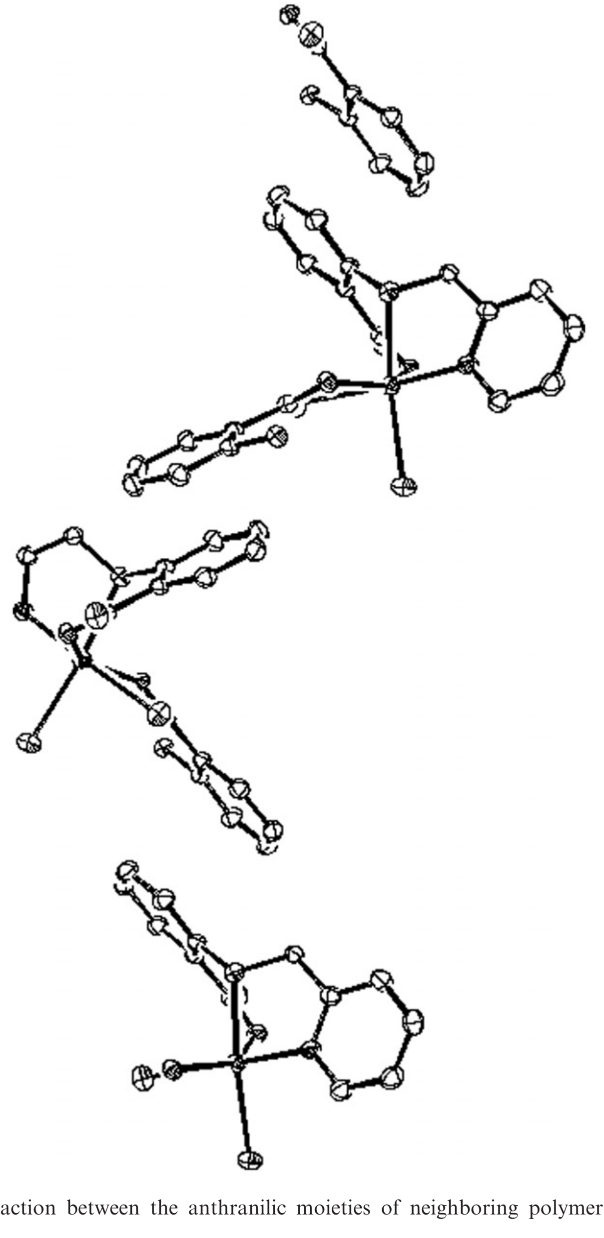


Figure 6. π–π interaction between the anthranilic moieties of neighboring polymers. Atoms have been removed for clarity.

which have a similar N–O binding motif [2]. A higher frequency stretch (ranging from 1605 to 1659 cm^{-1}) was assigned to N–H bending. This vibration shifted to lower frequencies for all complexes (table 4).

3.4. *Stoichiometry*

In the solid state, the two nitrogens and one oxygen from the carboxylate bind the metal. However, the carboxylate is still free to form a bidentate chelate, which it does,

Table 4. Selected IR stretching and bending frequencies of **1**, **2**, and metal complexes.

	1	Co · **1**	**2**	Co · **2**	Ni · **2**	Cu · **2**
Carbonyl stretch	1574	1556	1575	1559	1558	1581
N–H bend	1660	1638	1659	1605	1605	1611

to create a 1-D polymeric structure. Due to these multiple coordination modes, multimers may exist in solution as well. Job's plots with either Co · **2** and Cu · **2** were inconclusive. It is likely that a mixture of stoichiometries is present.

4. Conclusions

N-(ω-aminoalkyl)- and *N*-(azaheteroarylalkyl)-anthranilic acids were investigated as potential *N*,*N*,*O*-terdentate ligands for first row transition metals. Compound **2** binds in a facial arrangement, allowing the ligand to be employed as capping ligands for models of the metal centers of proteins. Due to the possibility of hydrogen bonding to the carbonyl oxygen, these ligands are capable of extending the coordination sphere of metal compounds; this could be utilized to probe the secondary coordination effects of metal complexes. The facile and straightforward synthetic procedure opens the possibility of a wide range of *N*,*N*,*O* -terdentate facially capping and bridging ligands for future analysis.

Supplementary materials

Crystallographic data for the structure reported in this article have been deposited in the Cambridge Crystallographic Data Center, CCDC No. 617484. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

Acknowledgements

This work was supported by a grant from the ACS Petroleum Research Fund (40348-G3). JRT would also like to acknowledge support from the DOE (DOE#4532A). YJ would like to acknowledge a research grant from Yeungnam University for support (2002). AH contributed to this effort while working as a summer 2005 student apprentice. She would like to thank the Academy of Applied Science REAP program (US Army Research Office #W911NF-04-1-0226) for support. The authors would like to thank Dr Dale Swenson for his help in collecting data and for his many helpful discussions.

References

[1] S.M. Humphrey, C. Redshaw, K.E. Holmes, M.R.J. Elsegood. *Inorg. Chim. Acta*, **358**, 222 (2005).
[2] K. Nakamoto, Y. Morimoto, A.E. Martell. *J. Am. Chem. Soc.*, **83**, 4528 (1961).
[3] Y. Jahng, J.R. Telford. *Bull. Korean Chem. Soc.*, **26**, 1614 (2005).
[4] L.J. Farrugia. *J. Appl. Cryst.*, **32**, 837 (1999).
[5] G.M. Sheldrick. *Acta Cryst.*, **A64**, 112 (2008).
[6] A. Mukhopadhyay, S. Pal. *J. Chem. Crystallogr.*, **35**, 737 (2005).