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Synthesis, structure, and ion-binding studies of cobalt(II) complexes with aza-crown substituted salicylaldimine Schiff base ligand

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Abstract

A series of cobalt(II) complexes with azacrown ether-containing salicylaldimine Schiff base ligand Co(L1), Co(L2)$_2$ and Co(L3)$_2$ has been successfully synthesized. The cation-binding properties of the complexes have been studied and the stability constants with alkali and alkaline earth metal cations determined. Synthesis of the complexes with monoaza-12-crown-4, Co(L1) and Co(L2)$_2$, allows for a direct comparison of the cation binding properties between the mono- and bis-Schiff base systems as well as with the complex containing the monoaza-15-crown-5 pendant, i.e. Co(L3)$_2$, which has a different crown size. The X-ray crystal structure of Co(L3)$_2$ has also been determined.

Keywords: Ion-binding; Cobalt(II) complexes; Aza-crown; Salicyladimine; Schiff base

1. Introduction

Synthetic oxygen carriers [1] are of great interest as models to mimic oxygen carrying metalloenzymes [2] and oxygenases, such as hemoglobin and cytochrome P-450 [3], which play important roles in the catalytic oxygenation mechanism of organic substrates [4]. Schiff bases represent one of the most successful classes of ligands for synthetic oxygen carriers due to their structural similarity to those found in biological systems [1,5]. The thermodynamic [5a], theoretical [6], and catalytic aspects [7] of this class of compounds have been extensively studied. Recently, Schiff bases containing a secondary site for coordination have attracted special attention. Crown ether-containing Schiff bases are known to bind cations in the crown ether cavity in addition to the coordination of a transition metal center through the N_2O_2 donor atoms. Co-complexation of a hard cation close to the transition-metal center is believed to play an important role in perturbing its oxygen-binding properties. Recent works by us [8] and others [9] have shown that Schiff base ligands with crown ether pendants are good receptors for alkali and transition metal guest cations. Stable dioxygen adducts of Co(II) complexes of (15-crown-5)salophen [10] and (18-crown-6)disalophen [11] have successfully been prepared. Oxygenation constants and thermodynamic parameters of transition metal complexes with (15-crown-5)salophen were measured and the complexes have been employed to catalyze the epoxidation of styrene [12]. Compared with the crown-free analogues, the dioxygen affinities and catalytic activities of those complexes with crown ethers are higher. However, up to date, all the Co(II) complexes with crown ether-containing Schiff base ligands are limited to those of oxacrown moieties. Recently, we became interested in crown systems other than that involving all oxygen donor atoms, such as the azaoxacrown systems as shown in Chart 1. Herein are described the synthesis and characterization of several azaoxacrown-containing Schiff base ligands and their complexes of cobalt(II). The cation-binding properties of these complexes have been studied. The complexes with monoaza-12-crown-4, i.e. Co(L1) and Co(L2)$_2$, together with the complex contain-

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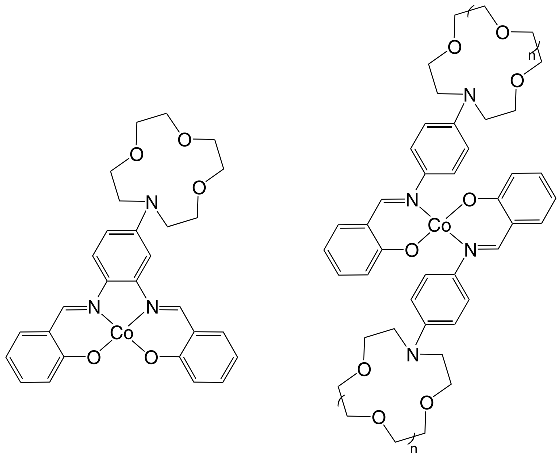


Co(L1)

$Co(L2)_2$ (n = 1)

$Co(L3)_2$ (n = 2)

Chart 1.

ing the monoaza-15-crown-5 pendant, $Co(L3)_2$, provide a direct comparison of the cation binding properties between the mono- and bis-Schiff base systems as well as those with different crown sizes. The X-ray crystal structure of $Co(L3)_2$ has also been determined.

2. Experimental

2.1. Reagents and materials

4-Aminoacetanilide, *N*-phenyldiethanolamine, reduced iron powder and salicylaldehyde were obtained from Lancaster Synthesis Ltd. Cobalt(II) acetate tetrahydrate was obtained from Merck. Tetra-*n*-butylammonium hexafluorophosphate ($^nBu_4NPF_6$) (Aldrich, 98%) was purified by recrystallization from hot ethanol three times and vacuum dried for 12 h before use. Lithium perchlorate, sodium perchlorate and potassium hexafluorophosphate were recrystallized from hot methanol and vacuum dried before use. The compounds *N*,*N*′-(4-nitro-1,2-phenylene)bisacetamide [13] and 1,11-diiodo-3,6,9-trioxaundecane [14] were synthesized according to literature procedures. Acetonitrile was distilled over calcium hydride before use. All other reagents and solvents were of analytical grade and were used as received.

2.2. Physical measurements and instrumentation

UV–Vis spectra were obtained on a Hewlett–Packard 8452A diode array spectrophotometer, and steady-state excitation and emission spectra on a Spex Fluorolog 111 spectrofluorometer equipped with a Hamamatsu R-928 photomultiplier tube. Low-temperature (77 K) spectra were recorded by using an optical Dewar sample holder. ^1H NMR spectra were recorded on a Bruker DPX-300 (300 MHz) Fourier-transform NMR spectrometer, while $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker DRX-500 Fourier-transform NMR spectrometer. Chemical shifts (ppm) of ^1H and ^{13}C NMR spectra were recorded relative to tetramethylsilane (Me_4Si). Electron-impact (EI) and positive-ion FAB mass spectra were recorded on a Finnigan MAT95 mass spectrometer. Elemental analyses of the newly synthesized compounds were performed on a Carlo Erba 1106 elemental analyzer at the Institute of Chemistry, Chinese Academy of Sciences.

Electronic absorption spectral titration studies for binding constant determination were performed on a Hewlett–Packard 8452A diode array spectrophotometer at 25 °C, which was controlled by a Lauda RM6 compact low-temperature thermostat. Supporting electrolyte (0.1 mol dm^{-3} $^nBu_4NPF_6$) was added to maintain a constant ionic strength of the sample solution in order to prevent any changes arising from a change in the ionic strength of the medium. Binding constants for 1:1 complexation were obtained by a nonlinear least-squares fit [15] of the absorbance (X) versus the concentration of the metal ion added (c_M) according to:

$$X = X_0 + \frac{X_{\text{lim}} - X_0}{2c_0} \times [c_0 + c_M + 1/K_S - [(c_0 + c_M + 1/K_S)^2 - 4c_0c_M]^{1/2}] \quad (1)$$

where X_0 and X are the absorbances of complex Co(L1) at a selected wavelength in the absence and presence of the metal cation, respectively, c_0 is the initial concentration of complex Co(L1), c_M is the concentration of the metal cation M^{n+}, X_{lim} is the limiting value of absorbance in the presence of excess metal ion, and K_S is the stability constant.

2.2.1. Synthesis of *N*,*N*′-(4-amino-1,2-phenylene)bisacetamide

To boiling water (200 ml) in a 500 ml beaker was added in one portion the ground mixture of *N*,*N*′-(4-nitro-1,2-phenylene)bisacetamide (13.0 g, 0.055 mol) and reduced iron powder (5.0 g, 0.089 mol), with a few drops of acetic acid. The resulting mixtures were stirred and maintained at this temperature for 1 h. After which, to the solution was added ammonia solution (35%) until pH 8 was obtained. The solution was boiled and filtered while it was still warm. The filtrate was evaporated until solid appeared. After cooling, the white solid was collected by filtration. Yield: 10.25 g, 90%. ^1H NMR (300 MHz, CD_3COCD_3, 298 K, relative to Me_4Si): δ 1.91 (s, 6H, CH_3CO), 4.47 (s, 2H, NH_2), 6.27–6.31 (dd, 1H, $J = 8.4$ Hz and $J = 1.9$ Hz, C_6H_3), 6.90–6.93 (d, 2H, $J = 8.4$ Hz, C_6H_3), 8.55 (s, 1H, CONH), 8.71 (s, 1H, CONH). EI MS: (m/z): 207

$\{M^+\}$. Elemental analyses, Found: C, 57.78; H, 6.37; N, 20.24. Calc. for $C_{10}H_{13}N_3O_2$: C, 57.96; H, 6.32; N, 20.28%.

2.2.2. Synthesis of N-(3,4-diacetylphenyl)aza-12-crown-4

This was prepared by modification of a literature method for the related N-phenylaza-12-crown-4 [14]. A stirred solution of 1,11-diiodo-3,6,9-trioxaundecane (20.50 g, 0.05 mol) and N′,N′-(4-amino-1,2-phenylene)bisacetamide (10.35 g, 0.05 mol) in 700 ml dry acetonitrile containing suspended powdered anhydrous sodium carbonate (21.20 g, 0.20 mol) was heated to reflux under an atmosphere of nitrogen for 15 days. After cooling, the solid was filtered and washed with acetonitrile, and the filtrate was evaporated to dryness on a rotary evaporator. The residue was then dissolved in dichloromethane, purified by column chromatography on silica gel using $CHCl_3$ as eluent and the product was obtained as a white solid. Yield: 7.66 g, 42%. ^1H NMR (300 MHz, $CDCl_3$ 298 K, relative to Me_4Si): δ 2.09 (s, 3H, CH_3CO), 2.12 (s, 3H, CH_3CO), 3.51–3.67 (m, 12H, crown ether protons), 3.74–3.80 (m, 4H, crown ether protons), 6.54–6.57 (d, 1H, $J = 8.4$ Hz C_6H_3), 6.75 (s, 1H, C_6H_3), 7.02–7.05 (d, 1H, $J = 8.4$ Hz, C_6H_3), 8.00 (s, 1H, CONH), 8.35 (s, 1H, CONH). EI MS: m/z 365 $\{M^+\}$. Elemental analyses, Found: C, 59.48; H, 7.51; N, 11.44. Calc. for $C_{18}H_{27}N_3O_5$: C, 59.16; H, 7.45; N, 11.50%.

2.2.3. Synthesis of N-(3,4-diaminophenyl)aza-12-crown-4

In a 50 ml three-necked flask were placed N-(3,4-diacetylphenyl)aza-12-crown-4 (1.46 g, 4.00 mmol) and Claisen's alkali (40 ml). The mixture was stirred and allowed to heat to reflux for 24 h under a nitrogen atmosphere. The resulting mixture was concentrated under reduced pressure and extracted with dichloromethane. The solvent was evaporated to dryness and to give a brown-colored oil. Subsequent recrystallization from acetonitrile gave the product as brown crystals. Yield: 1.00 g, 89%. ^1H NMR (300 MHz, $CDCl_3$, 298 K, relative to Me_4Si): δ 3.38–3.44 (m, 4H, crown ether protons), 3.54–3.67 (m, 8H, crown ether protons), 3.78–3.86 (m, 4H, crown ether protons), 5.30 (s, 4H, NH_2), 6.22–6.23 (d, $J = 2.5$ Hz, 1H, C_6H_3), 6.59–6.62 (d, $J = 8.3$ Hz, 1H, C_6H_3), 6.74–6.78 (dd, $J = 8.3$ Hz and $J = 2.5$ Hz 1H, C_6H_3). EI MS: m/z 281 $\{M^+\}$. Elemental analyses, Found: C, 59.58; H, 8.27; N, 14.99. Calc. for $C_{14}H_{23}N_3O_3$: C, 59.76; H, 8.24; N, 14.94%.

2.2.4. Synthesis of N′,N″-bis(2-hydroxyphenylmethylideneimino)-N-phenylaza-12-crown-4 (H_2L1)

This was prepared by modification of a literature procedure for 4′,5′-bis(2-hydroxyphenylmethylideneimino)benzo-15-crown-5 [16]. To a heated solution of N-(3,4-diaminophenyl)aza-12-crown-4 (1.00 g, 3.56 mmol) in 10 ml ethanol was added salicylaldehyde (0.87 g, 7.12 mmol) dissolved in 10 ml of the same solvent. The color of the solution immediately turned bright yellow. The solution was refluxed for 5 h and was then evaporated to dryness. Subsequent recrystallization from ethanol gave the product as bright yellow needles. Yield: 1.39 g, 80%. ^1H NMR (300 MHz, $CDCl_3$, 298 K, relative to Me_4Si): δ 3.62–3.65 (m, 12H, crown ether protons), 3.88–3.92 (m, 4H, crown ether protons), 6.52–7.40 (m, 11H, phenyl protons), 8.58 (s, 1H, –CH=N–), 8.63 (s, 1H, –CH=N–), 13.12 (s, 1H, –OH, disappeared upon D_2O exchange), 13.41 (s, 1H, –OH, disappeared upon D_2O exchange). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K, relative to Me_4Si): δ 160.88, 157.28, 147.11, 136.59, 131.94, 131.46, 122.41, 119.79, 118.79, 111.87, 71.35, 70.26, 70.16, 68.53, 52.72. IR (Nujol mull, KBr, ν cm^{-1}): 1618 ν(C=N). EI MS: m/z 489 $\{M^+\}$. Elemental analyses, Found: C, 67.22; H, 6.53; N, 8.44. Calc. for $C_{28}H_{31}N_3O_5 \cdot 1/2\ H_2O$: C, 67.45; H, 6.47; N, 8.43%.

2.2.5. Synthesis of N-(4-acetylphenyl)aza-12-crown-4

This was prepared by modification of a literature method for the related N-phenylaza-12-crown-4 [14]. A stirred solution of 1,11-diiodo-3,6,9-trioxaundecane (20.50 g, 0.05 mol) and 4-aminoacetanilide (7.50 g, 0.05 mol) in 700 ml dry acetonitrile containing suspended powdered anhydrous sodium carbonate (19.50 g, 0.18 mol) was heated under reflux under an atmosphere of nitrogen for 20 days. After cooling, the solid was filtered and washed with acetonitrile, and the filtrate was concentrated on a rotary evaporator. The residue was then dissolved in dichloromethane and purified by column chromatography on silica gel, using ethyl acetate as eluent. A white solid was obtained. Yield: 7.45 g, 42%. ^1H NMR (300 MHz, $CDCl_3$ 298 K, relative to Me_4Si): δ 3.50–3.74 (m, 12H, crown ether protons), 3.81–3.84 (t, 4H, $J = 5.0$ Hz, crown ether protons), 6.64–6.67 (d, 2H, $J = 8.8$ Hz, phenyl protons), 7.33–7.35 (d, 1H, $J = 8.8$ Hz, phenyl protons), 7.87 (s, 1H, NHCO). EI MS: m/z 355 $\{M^+\}$. Elemental analyses, Found: C, 62.67; H, 7.79; N, 9.22. Calc. for $C_{16}H_{24}N_2O_4$: C, 62.32; H, 7.84; N, 9.08%.

2.2.6. Synthesis of N′-(4-aminophenyl)aza-12-crown-4

In a 50 ml three-necked flask were placed N-(4-acetylphenyl)aza-12-crown-4 (1.77 g, 5.00 mmol) and Claisen's alkali (40 ml). The mixture was allowed to reflux while stirring for 24 h under a nitrogen atmosphere. The resulting mixture was concentrated under reduced pressure and extracted with dichloromethane. The solvent was removed to give a brown-colored oil. Subsequent recrystallization from acetonitrile gave the product as brown crystals. Yield: 1.09 g, 82%. ^1H NMR (300 MHz, $CDCl_3$, 298 K, relative to Me_4Si): δ 3.43–

3.46 (m, 4H, crown ether protons), 3.62–3.68 (m, 8H, crown ether protons), 3.77–3.81 (m, 4H, crown ether protons), 5.30 (s, 2H, NH_2), 6.64–6.68 (m, 4H, phenyl protons). EI MS: *m*/*z* 266 {M^+}. Elemental analyses, Found: C, 63.27; H, 8.29; N, 10.62. Calc. for $C_{14}H_{22}N_2O_3$: C, 63.13; H, 8.33; N, 10.52%.

2.2.7. Synthesis of N′-(2-hydroxyphenylmethylideneimino)-N-phenylaza-12-crown-4 (HL2)

This procedure was similar to that described for the synthesis of H_2L1, except that *N*′-(4-aminophenyl)aza-12-crown-4 (0.95 g, 3.56 mmol) was used in place of *N*-(3,4-diaminophenyl)aza-12-crown-4 to react with salicylaldehyde (0.435 g, 3.56 mmol) to give bright yellow needles. Yield: 1.12 g, 85%. ^1H NMR (300 MHz, $CDCl_3$, 298 K, relative to Me_4Si): δ 3.59–3.65 (m, 12H, crown ether protons), 3.86–3.89 (m, 4H, crown ether protons), 6.76–6.79 (d, 2H, $J = 9.0$ Hz, phenyl protons), 6.88–6.93 (t, 1H, $J = 7.4$ Hz, phenyl protons), 6.98–7.00 (d, 1H, $J = 8.3$ Hz, phenyl protons), 7.23–7.26 (d, 2H, $J = 9.0$ Hz, phenyl protons), 7.26–7.29 (d, 1H, $J = 8.3$ Hz, phenyl protons), 7.32–7.36 (t, 1H, $J = 7.4$ Hz, phenyl protons), 8.61 (s, 1H, CH=N), 13.77 (s, 1H, OH, disappeared upon D_2O exchange). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K, relative to Me_4Si): δ 155.46, 154.87, 149.52, 147.35, 138.89, 136.48, 124.23, 123.18, 121.34, 111.73, 71.35, 70.24, 70.15, 68.57, 52.73. IR (Nujol mull, KBr, ν cm^{-1}): 1616 (s) ν(C=N). EI MS: *m*/*z* at 370 {M^+}. Elemental analyses, Found: C, 67.98; H, 7.04; N, 7.54. Calc. for $C_{21}H_{26}N_2O_4$: C, 68.09; H, 7.07; N, 7.56%.

2.2.8. Synthesis of N-phenylaza-15-crown-5

This was prepared by modification of a literature procedure [17]. A two-necked flask equipped with a dropping funnel was evacuated and refilled with nitrogen, and then 300 ml dry THF and NaH (6.40 g, 0.16 mol) were added and refluxed. *N*-phenyldiethanolamine (13.57 g, 0.08 mol) and diethylene glycol ditosylate (34.39 g, 0.08 mol) were dissolved in 300 ml dry THF and then slowly added dropwise to the reaction mixture. Addition was completed in 3 h, and refluxing was continued for another 24 h. After cooling, the solid was filtered and washed with THF, and the filtrate was concentrated on a rotary evaporator. The red residue was then dissolved in dichloromethane and purified by column chromatography on silica gel, using diethyl ether as eluent. Yield, 7.45 g, 42%. ^1H NMR (300 MHz, $CDCl_3$ 298 K, relative to Me_4Si): δ 3.57–3.65 (m, 16H, crown ether protons), 3.68–3.77 (m, 4H, crown ether protons), 6.63–6.67 (m, 3H, phenyl protons), 7.17–7.25 (d, 1H, $J = 7.3$ Hz, phenyl protons). EI MS: *m*/*z* 295 {M^+}.

2.2.9. Synthesis of N-(4-nitrosophenyl)aza-15-crown-5

This was prepared by modification of a literature procedure [17]. *N*-Phenylaza-15-crown-5 (2.95 g, 10.00 mmol) was dissolved in 5 ml warmed hydrochloric acid (37%), and ice (8.00 g) was then added and the mixture was stirred at temperature below 5 °C. An aqueous solution of $NaNO_2$ (0.70 g, 10.00 mmol) in 2 ml H_2O was slowly added. After addition, the mixture was stirred for 20 min. The mixture separated into two layers upon addition of ice water (30 ml) and dichloromethane (20 ml). The mixture was adjusted to basic conditions upon vigorous stirring using saturated Na_2CO_3. The aqueous layer was extracted with dichloromethane several times. The dichloromethane extracts that were green in color were combined, and dried over anhydrous magnesium sulfate. After filtration, the solvent was evaporated to dryness, leaving behind a green residue. The residue was then dissolved in 15 ml warmed acetone, and 20 ml petroleum ether was quickly added. After cooling, green crystals were obtained. Yield: 2.50 g, 77%. ^1H NMR (300 MHz, $CDCl_3$, 298 K, relative to Me_4Si): δ 3.60–3.63 (m, 4H, crown ether protons), 3.67–3.70 (m, 8H, crown ether protons), 3.73–3.77 (m, 4H, crown ether protons), 3.79–3.85 (m, 4H, crown ether protons), 6.69–6.72 (m, 4H, phenyl protons). EI MS: *m*/*z* 324 {M^+}.

2.2.10. Synthesis of N-(4-aminophenyl)aza-15-crown-5

This was prepared by modification of a literature procedure [17]. $SnCl_2$ (2.60 g, 14.00 mmol) was dissolved in 3 ml hydrochloric acid (37%) and 1.6 ml water. *N*-(4-Nitrosophenyl)aza-15-crown-5 (1.60 g, 4.90 mmol) was then added in portions under stirring at 40 °C. Water (20 ml) was added to dilute the solution after 20 min and the mixture was allowed to continue stirring for another 30 min. After addition of NaOH (40%), the crude product appeared as a brown oil. The mixture was extracted with dichloromethane several times and the combined dichloromethane extracts were dried over anhydrous magnesium sulfate. After filtration, the solvent was evaporated to dryness leaving brown oils. Subsequent recrystallization from acetonitrile gave the product as brown crystals. Yield: 1.2 g, 78%. ^1H NMR (300 MHz, $CDCl_3$, 298 K, relative to Me_4Si): δ 3.42–3.50 (m, 4H, crown ether protons), 3.63–3.74 (m, 16H, crown ether protons), 5.30 (s, 2H, NH_2), 6.55–6.63 (m, 4H, phenyl protons). EI MS: *m*/*z* 310 {M^+}.

2.2.11. Synthesis of N′-(2-hydroxyphenylmethylideneimino)-N-phenylaza-15-crown-5 (HL3)

This procedure was similar to that described for the synthesis of H_2L1, except *N*′-(4-aminophenyl)aza-15-crown-5 (1.10 g, 3.56 mmol) was used in place of *N*-(3,4-diaminophenyl)aza-12-crown-4 to give bright yellow needles. Yield: 1.24 g, 84%. ^1H NMR (300 MHz,

$CDCl_3$, 298 K, relative to Me_4Si): δ 3.6 (m, 16H, crown ether protons), 3.8 (m, 4H, crown ether protons), 6.68–6.71 (d, 2H, $J = 8.9$ Hz, phenyl protons), 6.88–6.93 (t, 1H, $J = 7.5$ Hz, phenyl protons), 6.98–7.00 (d, 1H, $J = 8.2$ Hz, phenyl protons), 7.24–7.27 (d, 2H, $J = 8.9$ Hz, phenyl protons), 7.27–7.28 (d, 1H, $J = 8.2$ Hz, phenyl protons), 7.31–7.36 (t, 1H, $J = 7.5$ Hz, phenyl protons), 8.6 (s, 1H, CH=N), 13.8 (s, 1H, –OH, disappeared upon D_2O exchange). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K, relative to Me_4Si): δ 160.88, 157.28, 147.11, 136.59, 131.94, 131.46, 122.41, 119.79, 118.79, 111.87, 71.35, 70.26, 70.16, 68.53, 52.72. IR (Nujol mull, KBr, v cm^{-1}): 1616 v(C=N). EI MS: m/z at 414 $\{M^+\}$. Elemental analyses, Found: C, 63.57; H, 7.47; N, 6.34. Calc. for $C_{23}H_{30}N_2O_5 \cdot H_2O$: C, 63.87; H, 7.46; N, 6.48%.

2.2.12. *Synthesis of Co(L1)*

This complex was prepared by modification of a literature procedure for the related [Co(salen)] complexes [16]. $Co(OAc)_2 \cdot 4H_2O$ (51 mg, 0.20 mmol) dissolved in ethanol (100 ml) was added to H_2L1 (100 mg, 0.20 mmol) dissolved in 10 ml ethanol. The mixture was refluxed for 8 h under nitrogen atmosphere. After evaporation of the solvent, the red brown residue was dissolved in dichloromethane, and the solution was filtered through Celite to remove metallic cobalt. The filtrate was reduced in volume to 5 ml, and subsequent diffusion of diethyl ether vapor into the concentrated solution gave Co(L1) as red crystals. Yield: 95 mg, 87%. IR (Nujol mull, KBr, v cm^{-1}): 1614 (s) v(C=N). Positive FAB MS: m/z at 547 $\{M^+\}$. Elemental analyses, Found: C, 61.50; H, 5.27; N, 7.88. Calc. for $C_{28}H_{29}N_3O_5Co$: C, 61.54; H, 5.35; N, 7.69%.

2.2.13. *Synthesis of Co(L2)$_2$*

The procedure was similar to that described for the preparation of Co(L1) except HL2 (148 mg, 0.40 mmol) was used in place of H_2L1 to give red crystals. Yield: 116 mg, 73%. IR (Nujol mull, KBr, v cm^{-1}): 1610 (s) v(C=N). Positive FAB MS: m/z at 798 $\{M^+\}$. Elemental analyses, Found: C, 63.10; H, 6.43; N, 6.99. Calc. for $C_{42}H_{50}N_3O_5Co$: C, 63.23; H, 6.32; N, 7.02%.

2.2.14. *Synthesis of Co(L3)$_2$*

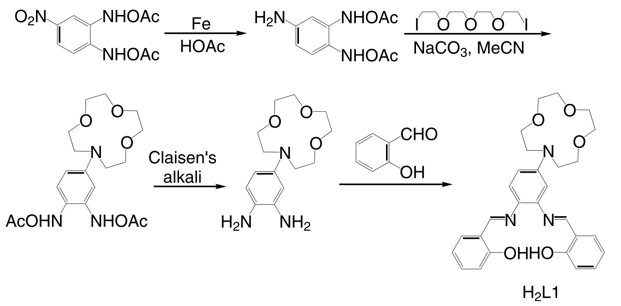
The procedure was similar to that described for the preparation of Co(L1), except HL3 (166 mg, 0.40 mmol) was used in place of H_2L1 to give red crystals. Yield: 133 mg, 75%. IR (Nujol mull, KBr, v cm^{-1}): 1610 (s) v(C=N). Positive FAB MS: m/z at 886 $\{M^+\}$. Elemental analyses, Found: C, 62.37; H, 6.73; N, 6.33. Calc. for $C_{46}H_{58}N_4O_{10}Co$: C, 62.36; H, 6.60; N, 6.32%.

2.3. *Crystal structure determination*

Crystal data for $Co(L3)_2$: formula = [$C_{46}H_{58}N_4O_{10}Co$], F.W. = 885.89, monoclinic, space group Cc, $a = 21.552(5)$ Å, $b = 19.148(4)$ Å, $c = 14.536(3)$ Å, $\alpha = 90°$, $\beta = 129.724(4)°$, $\gamma = 90°$, $V = 4613.9(18)$ Å^3, $Z = 4$, $D_{calc} = 1.275$ g cm^{-3}, μ(Mo Ka) = 4.32 cm^{-1}, $F(000) = 1876$, $T = 294(2)$ K; $R = 0.0616$, $wR = 0.1197$ for 9435 reflections with $I > 2\sigma(I)$, goodness-of-fit = 1.038. A crystal with dimensions of 0.16 × 0.14 × 0.10 mm was mounted on a Bruker CCD area detector diffractometer using Mo Ka radiation ($\lambda = 0.71073$ Å) from generator operating at 50 kV, 30 mA condition. The intensity data were collected in the range of $2\theta = 2.80$–$27.56°$; h: −27–27; k: −24–17; l: −18–17 with oscillation frames of ϕ and Ω in the range 0–180°. Frames of 1876 were taken in four shells. A self-consistent absorption correction of SADABS program [18] based on Fourier coefficient fitting was applied. The structure was determined by the direct method, which yielded the positions of part of the non-hydrogen atoms and subsequent difference Fourier syntheses were employed to locate all of the remaining non-hydrogen atoms, which did not show up in the initial structure. All non-hydrogen atoms were refined anisotropically with weight function $w = 1/[\sigma^2(F_0^2) + (0.0300p)^2 + 0.0000p]$ ($p = (F_0^2 + 2F_c^2)/3$), except the C and O atoms of the disordered aza-crown ethers which were refined isotropically. Hydrogen atoms were located based on difference Fourier syntheses coupled with geometrical analysis. All the analyses and computations were performed on a PC computer using the programs of Bruker Smart and Bruker SHELXTL package [18]. The final difference Fourier map was featureless, with maximum positive and negative peaks of 0.343 and −0.229 e Å^{-3}, respectively.

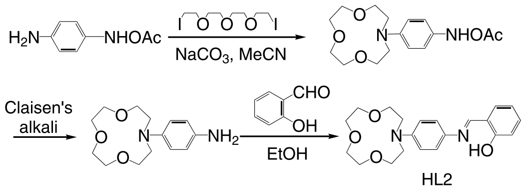
3. Results and discussion

Three new azacrown-ether substituted salicylaldimine Schiff base ligands, namely H_2L1, HL2 and HL3, have been synthesized, which represents an extension of the work on the all-oxygen crown ether ligands previously reported by Qin and co-workers [11,12,16]. For the synthesis of H_2L1, which consisted of a monoaza-12-crown-4, the first step was the reduction of the N,N'-(4-nitro-1,2-phenylene)bisacetamide using iron powder in the presence of a few drops of acetic acid as catalyst (Scheme 1). The incorporation of the monoaza-12-crown-4 pendant is simple and straightforward, involving the reaction between primary amines and 1,11-diiodo-3,6,9-trioxaundecane in acetonitrile solution containing Na_2CO_3. Cyclization of N,N'-(4-amino-1,2-phenylene)bisacetamide, followed by hydrolysis using the Claisen's alkali (KOH:H_2O:MeOH = 8:63:250)

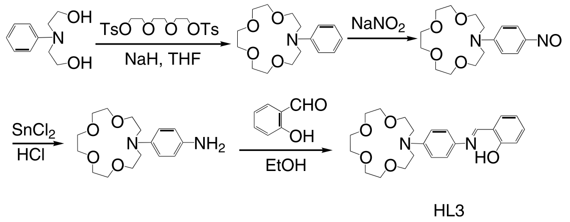


Scheme 1. Synthetic scheme of N',N''-bis(2-hydroxyphenylmethylideneimino)-N-phenylaza-12-crown-4 (H_2L1).

would give the key intermediate N-(3,4-diaminophenyl)aza-12-crown-4. The condensation of N-(3,4-diaminophenyl)aza-12-crown-4 with salicylaldehyde gave the ligand as an N_2O_2 donor with a monoaza-12-crown-4 unit. HL2 was similarly obtained (Scheme 2). For N'-(4-aminophenyl)aza-12-crown-4 and N-(3,4-diaminophenyl)aza-12-crown-4, the amino groups were first introduced into the benzene ring using mono-protected 4-aminoacetanilide or biprotected N,N'-(4-amino-1,2-phenylene)bisacetamide as the starting material. However, for N'-(4-aminophenyl)aza-15-crown-5, the amino group was introduced into the benzene ring after cyclization of N-phenyldiethanolamine. After cyclization of N-phenyldiethanolamine, direct nitration followed by a reduction of nitroaza-15-crown-5 according to modification of a literature method [17] gave the aminoaza-15-crown-5 (Scheme 3). The complexes Co(L1) was prepared in good yield from the reaction of $Co(OAc)_2 \cdot 4H_2O$ and the corresponding ligand in the ratio of 1:1 in ethanol under reflux condition. Reaction of $Co(OAc)_2 \cdot 4H_2O$ with the corresponding ligands in the ratio of 1:2 under the same condition gave $Co(L2)_2$ and $Co(L3)_2$. The IR, FAB mass spectra and elemental analyses of compounds Co(L1), $Co(L2)_2$ and $Co(L3)_2$ confirmed the formation of the cobalt(II) complexes with azacrown-ether substituted salicylaldimine Schiff base ligands. The IR spectra (KBr discs) of the complexes show bands that occur almost at the same frequencies as the ligand absorptions with the exception of the ν(C=N) stretch, which is shifted slightly (ca. 5–10 cm^{-1}) to lower frequency after complex formation.



Scheme 2. Synthetic scheme of N'-(2-hydroxyphenylmethylideneimino)-N-phenylaza-12-crown-4 (HL2).



Scheme 3. Synthetic scheme of N'-(2-hydroxyphenylmethylideneimino)-N-phenylaza-15-crown-5 (HL3).

3.1. Crystal structure determination

Single crystals of $Co(L3)_2$ were obtained by vapor diffusion of diethyl ether into a concentrated dichloromethane solution of the complex. The perspective drawing of $Co(L3)_2$ with atomic numbering is depicted in Fig. 2. The crystal structure determination data are summarized in Table 1 and selected bond distances and angles tabulated in Table 2. During the structure determination, attempts to select a space group of higher symmetry (*C*2/*c*) have been made because of the symmetric nature of the molecular structure. However, the highly disordered nature of the atoms in the aza-crown ether moieties and the unusually high *R* value (ca. 0.32) obtained, indicate that the *C*2/*c* space group was not appropriate, and a space group of lower symmetry (*Cc*) was chosen instead. The bond lengths

Table 1
Crystal and structure determination data for $Co(L3)_2$

Formula	$C_{46}H_{58}N_4O_{10}Co$
Formula weight	885.89
Temperature (K)	294(2)
a (Å)	21.552(5)
b (Å)	19.148(4)
c (Å)	14.536(3)
α (°)	90
β (°)	129.724(4)
γ (°)	90
V (Å^3)	4613.9(18)
Crystal system	monoclinic
Space group	*Cc*
Z	4
F(000)	1876
D_{calc} (g cm^{-3})	1.275
Crystal dimensions (mm)	0.16 × 0.14 × 0.10
λ (Å) (graphite monochromated, Mo Kα)	0.71073
μ (Mo Kα) (cm^{-1})	4.32
Collection range (°)	2.80–27.56 (h: −27–27; k: −24–17; l: −18–17)
Number of data collected	15 335
Number of unique data	9435
Number of data used in refinement, m	9435 [$R_{int} = 0.0487$]
Number of parameters refined, p	635
R^a	0.0616
R_w^a	0.1197
Goodness-of-fit, S	1.038
Residual extrema in final difference map (e Å^{-3})	+0.343 and −0.229

Table 2
Selected bond lengths (Å) and bond angles (°) for $Co(L3)_2$

Co–N(1)	1.9086(19)	Co–N(2)	2.0329(19)
Co–O(1)	1.898(2)	Co–O(2)	1.883(2)
O(1)–C(1)	1.2938(19)	O(2)–C(24)	1.316(2)
N(1)–C(7)	1.299(2)	N(1)–C(8)	1.496(3)
N(2)–C(30)	1.307(2)	N(2)–C(31)	1.408(3)
C(6)–C(7)	1.532(4)	C(29)–C(30)	1.375(4)
C(1)–C(6)	1.398(3)	C(24)–C(29)	1.395(3)
N(1)–Co–N(2)	110.54(7)	O(1)–Co–O(2)	116.87(7)
O(1)–Co–N(1)	96.49(8)	O(1)–Co–N(2)	118.27(10)
O(2)–Co–N(1)	118.63(10)	O(2)–Co–N(2)	97.30(8)
Co–O(1)–C(1)	126.40(17)	Co–O(2)–C(24)	124.26(18)
Co–N(1)–C(7)	125.7(2)	Co–N(2)–C(30)	117.46(19)
O(1)–C(1)–C(2)	117.6(2)	O(2)–C(24)–C(25)	119.0(2)
O(1)–C(1)–C(6)	125.1(2)	O(2)–C(24)–C(29)	125.3(2)

Table 3
Electronic absorption spectral data for crown ether-containing cobalt(II) complexes in acetonitrile at 298 K

Compound	Absorption λ (nm) ε ($dm^3\ mol^{-1}\ cm^{-1}$)
H_2L1	262 (21 000), 346 (14 600), 396 (17 900)
Co(L1)	256 (30 000), 320 (9700), 390 (12 400), 428(11 600)
HL2	251 (24 700), 332 (7400), 392 (24 700)
$Co(L2)_2$	251(41 600), 331 (16 500), 414 (33 900)
HL3	250 (15 200), 330 (7650), 390 (24 280)
$Co(L3)_2$	250 (22 120), 330 (9100), 408 (17 830)

from both nitrogen atoms to the cobalt center are slightly different [Co–N(1) 1.9086 Å, Co–N(2) 2.0329 Å]. Similar findings were observed for those found from both oxygen atoms [Co–O(1) 1.898 Å, Co–O(2) 1.883 Å]. The six bond angles, N(1)–Co–N(2), O(1)–Co–O(2), O(1)–Co–N(1), O(1)–Co–N(2), O(2)–Co–N(1) and O(2)–Co–N(2), are 110.54, 116.87, 96.49, 118.27, 118.63 and 97.30°, respectively. The coordination geometry at the cobalt atom of $Co(L3)_2$ may best be described as distorted tetrahedral with two bidentate Schiff base ligands containing crown ether pendants coordinated to the metal center. This is different from that of the Schiff base cobalt complexes bridged by ethylenediamine [19], in which the coordination about the cobalt is essentially squared planar with the two salicylideneiminate residues approaching approximate coplanarity. However, the plane formed by Co–O(1)–C(1) in $Co(L3)_2$ is approximately perpendicular to the plane formed by Co–O(2)–C(24). The molecular structure of $Co(L3)_2$ shown in Fig. 1 indicates that the two Schiff base ligands with crown ether pendants are linked by cobalt atom to form a rare butterfly structure.

3.2. Absorption spectra

The UV–Vis spectral dates for the free and complexed azacrown-ether substituted salicylaldimine Schiff base are shown in Table 3. All the compounds show low-energy absorption bands at approximately 390–430 nm and high energy bands at approximately 250–262 nm. With reference to Khalaf et al. [20], the electronic absorption spectra of the cobalt(II) complexes are dominated by the ligand-centerd π–π* and n–π* transitions of the Schiff base ligands.

3.3. Cation-binding studies

Upon addition of $LiClO_4$ to a solution of Co(L1) in acetonitrile (0.1 mol dm^{-3} $^{n}Bu_4NPF_6$), the electronic absorption spectra showed UV–Vis spectral changes with well-defined isosbestic points (Fig. 2), while the addition of $NaClO_4$ and KPF_6 caused only minor changes in the absorption spectra. This suggests the

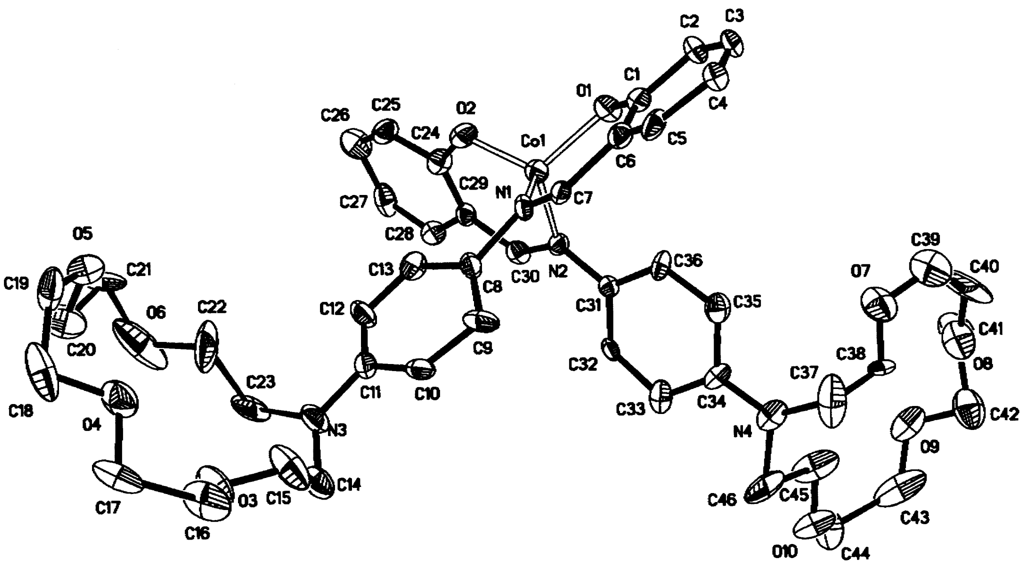


Fig. 1. Perspective drawing of $Co(L3)_2$ with atomic numbering. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids were shown at the 40% probability level.

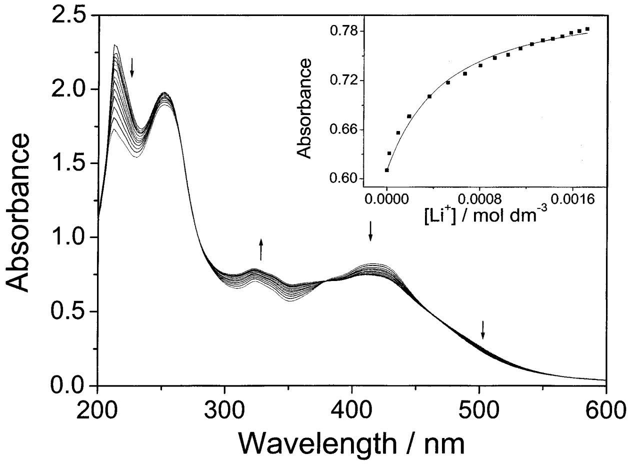


Fig. 2. UV–Vis spectral changes of Co(L1) upon addition of various concentrations of lithium ions in acetonitrile (0.1 mol dm^{-3} $^nBu_4NPF_6$). Insert: absorbance at 326 nm (■) as a function of Li$^+$ concentration with theoretical (——) fits.

preferential binding of Li$^+$ ions to Co(L1). As the diameter of Li$^+$ (1.36 Å) [21] provides a good match for the cavity size of 12-crown-4 (1.2–1.5 Å) [21], formation of a 1:1 adduct is anticipated. The insert in Fig. 2 shows the changes of absorbance at 326 nm as a function of lithium ion concentration. The close agreement of the experimental data with the theoretical fit to equation 1 is supportive of a 1:1 stoichiometry. For Li$^+$, a log K_s of 3.37 was obtained. In contrast, the diameters of Na$^+$ (1.90 Å) [21] and K$^+$ (2.66 Å) [21] are too large to fit into the cavity size of 12-crown-4. For the bis(azacrown ether)s cobalt(II) complexes Co(L2)$_2$ and Co(L3)$_2$, the UV–Vis absorption spectra resulted in a specific change upon addition of alkali and alkaline earth metal ions in acetonitrile (0.1 mol dm^{-3} $^nBu_4NPF_6$). No clean isosbestic points were observed, indicating that, most probably, both adducts of stoichiometries of 1:1 and 2:1 [M^+: Co(L2)$_2$ or Co(L3)$_2$] were formed.

The ion-binding studies have further been confirmed by positive ESI MS. For Co(L2)$_2$ and Co(L3)$_2$ with two azacrown ether moieties, both 1:1 and 2:1 [M^+: Co(L2)$_2$ or Co(L3)$_2$] adducts were observed, while for Co(L1) with one azacrown ether moiety, only 1:1 [M^+: Co(L1)] adducts were observed.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 181593 for compound Co(L3)$_2$. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgements

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