Synthesis of salicylaldimine Schiff bases cobalt (ii) complexes with benzo-10-aza-15-crown-5 pendant

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The azacrown-ether-substituted salicylaldimine Schiff bases ligands **HL^1–HL^5** have been prepared by the condensation of salicylaldehyde (or its derivatives) with the azacrown-ether-containing arylamine from benzo-10-aza-15-crown-5 (BN15C5). The cobalt (II) complexes **$CoL_2{}^1$–$CoL_2{}^5$** are readily synthesised by treatment of **HL^1–HL^5** with cobalt acetate; their structures were characterised by IR, MS, ^{1}H NMR, molar conductance and elemental analysis.

Keywords: cobalt (II) complexes, benzo-10-aza-15-crown-5, Schiff bases

Synthetic oxygen carriers[1] are of great interest as models to mimic oxygen-carrying metalloenzymes[2] for oxygen storage and transport. The cobalt (II) complexes of Schiff bases have been the first and the most extensively investigated due to their structural similarity to those found in biological systems.[3,4] It is well known that introduction of substituents into Schiff base ligands allows their complexes to form stable dioxygen adducts and avoid dimerisation and loss of activity.[5] In particular, crown ethers employed as the substituents have received much attention[6,7] because of their binding ability to alkali ions and special configuration. Recent works have indicated that oxa-crowned Schiff base transition-metal complexes are good receptors for alkali cations[8,9] and show much improved O_2-binding activity due to the special configuration and function of the crown ether ring.[10] Moreover, some of them can form stable Na(I) or K(I)/Co(II) hetero-nuclear complexes and solid dioxygen adducts.[11] We are investigating the effect of azacrown ether substituents, which possess special stereo configuration, on the function and O_2-binding activity of Schiff base cobalt (II) complexes, and herein are described the synthesis of salicylaldimine Schiff bases cobalt (II) complexes with benzo-10-aza-15-crown-5 pendant substituent. Their structures have been characterised by IR, MS, ^{1}H NMR, molar conductance and elemental analysis.

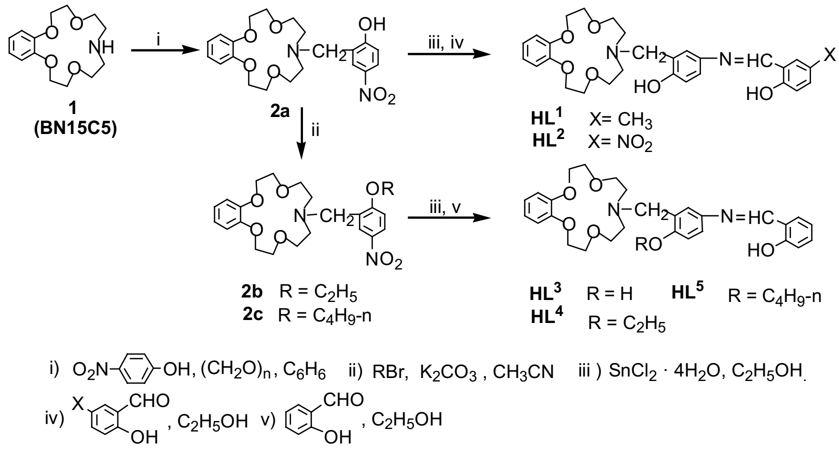
Result and discussion

As shown in Scheme 1, benzo-10-aza-15-crown-5 **(1)** underwent a Mannich reaction to give the key intermediates **2a**, which reacted with bromoethane or bromobutane to yield **2b** and **2c. 2a–c** were then reduced to the amino compounds by $SnCl_4 \cdot 4H_2O$, and since they were easily oxidised in the air, they were treated without further isolation and purification to directly condense with salicylaldehyde (or its derivatives) to give the ligands **HL**.

The elemental analysis and ESIMS of the complexes of these ligands, prepared by treatment of **HL** with cobalt acetate, (see Experimental) indicate that they are 1 : 2 (metal/ligand) complexes. Moreover, the observed molar conductances of all complexes in DMF solution (1.00×10^{-3} mol dm^{-3}) are in the range of 3.61–6.16 S cm^2 mol^{-1}. This suggests that the Co(II) complexes are non-electrolytes.[12] The IR spectra of the complexes show most ligand absorptions are still at the same frequency except the C=N stretches are shifted slightly (10–14 cm^{-1}) to lower frequencies and the OH stretches (3220–3225 cm^{-1}) disappeared after complex formation. The absorption at about 3440 cm^{-1} of **$CoL_2{}^1$–$CoL_2{}^3$** is attributed to the OH at the para-position of C=N. The structures of CoL_2 are shown in Scheme 2.

Experimental

Melting points were determined on a Yanaco-500 micro-melting point apparatus and are uncorrected. IR spectra were recorded on a Nicolet-1705X IR spectrometer. ^{1}H NMR spectra were recorded on a Bruker AC-200 MHz spectrometer using tetramethylsilane as internal standard. Mass spectra were obtained on a Finnigan MAT 4510 spectrometer and Finnigan LCQ^{-DECA} spectrometer. Elemental analysis was performed on a Carlo Erbo-1160 elemental analyser. Molar conductances were obtained on a DDS-11A conductivity metre. The Co(II) content was measured by an IRIS-Advantage



Scheme 1

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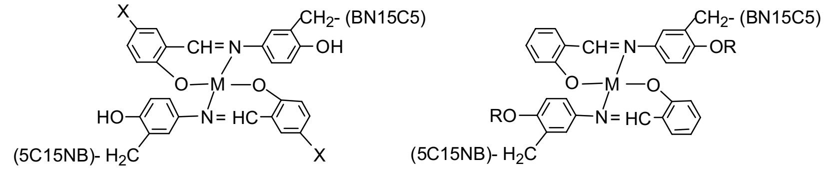

CoL_2^1 X= CH_3
CoL_2^2 X= NO_2

CoL_2^3 R = H
CoL_2^4 R= C_2H_5
CoL_2^5 R= C_4H_9-n

Scheme 2

ICP emission spectrometer. Silica gel (60H for TLC, Qingdao, China) was used for flash column chromatography. All other reagents are of analytical grade and are used without further purification. The synthetic routes of **HL^1–HL^5** are illustrated in Scheme 1.

Preparation of N-(2-hydroxy-5-nitrobenzyl)benzo-10-aza-15-crown-5 (**2a**): A mixture of **1** (2.67 g, 0.01 mol) in benzene (50 ml) was treated with 4-nitrophenol (1.39 g, 0.01 mol) and paraformaldehyde (0.3 g, 0.011 mol) under N_2 and refluxed for 20 h. The solvent was evaporated and the residual solid was crystallised from ethanol to give **2a** as yellow crystals, m.p. 146–148°C; yield 81%. IR (KBr, ν_{max}, cm^{-1}): 3423, 1625, 1332, 1257, 1136; ^1H NMR ($CDCl_3$) δ 8.07–7.89 (m, 4H, ArOH, ArH), 7.25–6.73 (m, 4H, ArH), 4.18–3.76 (m, 14H, OCH_2, NCH_2Ar), 2.86 (t, 4H, J = 5.5 Hz, NCH_2); Anal. Calcd. for $C_{21}H_{26}N_2O_7$: C60.3, H 6.2, N 6.7; Found: C 60.2, H 6.3, N 6.8; MS (*m/z*): 418 (M^+).

Preparation of N-(2-alkyloxy-5-nitrobenzyl)benzo-10-aza-15-crown-5 (**2b, 2c**): A mixture of **2a** (4.18 g, 0.01 mol) and the corresponding bromoethane or bromobutane (0.011 mol) in acetonitrile (30 ml) was refluxed in the presence of K_2CO_3 (1.52 g, 0.011 mol) for 20 h. The solvent was evaporated and the residual mass was chromatographed on a silica gel column (eluent: ethyl acetate) to afford the pure products. **2b:** Oil, yield 92%; ^1H NMR ($CDCl_3$) δ: 8.06–7.92 (m, 3H, ArH), 7.22–6.74 (m, 4H, ArH), 4.13–3.75 (m, 16H, OCH_2, NCH_2Ar), 2.81 (t, 4H, J = 5.5 Hz, NCH_2), 1.82–1.56(m, 3H, CH_3); IR (neat) ν_{max}: 1335, 1256, 1134 cm^{-1}; MS (*m/z*): 446 (M^+); Anal. Calcd for $C_{23}H_{30}N_2O_7$: C 61.9, H 6.7, N 6.3, found. C 61.7, H 7.85, N 6.03. **2c:** Oil, yield 88%,^1H NMR ($CDCl_3$) δ: 8.08–7.90 (m, 3H, ArH), 7.21–6.75 (m, 4H, ArH), 4.10–3.75 (m, 16H, OCH_2, NCH_2Ar), 2.81 (t, 4H, J = 5.5 Hz, NCH_2), 1.80–0.86 (m, 7H, CH_2, CH_3); IR (neat) ν_{max}: 1336, 1255, 1132 cm^{-1}; MS (*m/z*): 474 (M^+); Anal. Calcd for $C_{25}H_{34}N_2O_7$: C 63.3, H 7.2, N 5.9, found. C 63.5, H 7.0, N 6.1.

General Procedure for the preparation of Schiff Bases Ligands **HL^1–HL^5**. A mixture of **2a–c** (0.01 mol), $SnCl_2·2H_2O$ (8.96, 0.04 mol) and ethanol (100 ml) was refluxed for 6 h under N_2 and cooled. The mixture was added to ice water and adjusted to pH 8 with 40% NaOH. After extraction (CH_2Cl_2, 3 × 20 ml), drying ($MgSO_4$) and evaporation of solvent, the residue dissolved in ethanol (20 ml) was immediately mixed with salicylaldehyde or *m*-substituted salicylaldehyde (0.01 mol) and stirred at room temperature under N_2 for 2 h. The precipitate was collected by suction filtration and washed with cold ethanol. The crude product was recrystallised from ethanol to give a pure sample.

HL^1: Yield 80%.Yellow crystals; m.p. 131–133°C. ^1H NMR ($CDCl_3$) δ: 13.42 (s, 1H, OH, D_2O exchangeable), 8.64 (s, 1H, OH, D_2O exchangeable), 8.55 (s, 1H, N=CH), 7.35–6.73 (10H, m, Ar–H), 4.18–3.75 (m, 14H, OCH_2, NCH_2Ar), 2.88 (t, J = 5.6 Hz, 4H, NCH_2), 2.43(s, 3H, Ar–CH_3); IR (KBr) ν_{max}: 3442, 3220, 1618, 1255, 1128 cm^{-1}; MS (*m/z*): 506 (M^+); Anal. calcd for $C_{29}H_{34}N_2O_6$: C 68.8, H 6.7, N 5.5; found C 68.5, H 6.9, N 5.7.

HL^2: Yield 75%, Yellow crystals; m.p. 198–200°C, ^1H NMR ($CDCl_3$) δ: 13.58 (s, 1H, OH, D_2O exchangeable), 8.65 (s, 1H, OH, D_2O exchangeable), 8.59 (s, 1H, N=CH), 7.36–6.78 (10H, m, Ar-H), 4.17–3.76 (m, 14H, OCH_2, NCH_2Ar), 2.89 (t, J = 5.6 Hz, 4H, NCH_2); IR (KBr) ν_{max}: 3445, 3220, 1620, 1253, 1122 cm^{-1}; MS (*m/z*): 537 (M^+); Anal. calcd for $C_{28}H_{31}N_3O_8$: C 62.57, H 5.77, N 7.82; found C 62.31, H 5.90, N 7.95.

HL^3: Yield 85%, Yellow crystals; m.p.128-130°C. ^1H NMR ($CDCl_3$) δ 13.49 (brs, 1H, OH, D_2O exchangeable), 8.62 (s, 8.56, 1H, OH, D_2O exchangeable), 8.56 (s, 1H, N=CH), 7.36–6.78 (m, 11H, ArH), 4.18–3.77 (m, 14H, OCH_2, NCH_2Ar), 2.89 (t, 4H, J = 5.6 Hz, NCH_2); IR(KBr) ν_{max}: 3445, 3222, 1618, 1256, 1128; Anal. Calcd. for $C_{28}H_{32}N_2O_6$: C 68.3, H 6.5, N 5.7; found: C 68.0, H 6.3, N 5.85; MS (*m/z*): 492 (M^+).

HL^4: Yield 79%, Yellow crystals; m.p. 106–108°C. ^1H NMR ($CDCl_3$) δ: 13.56 (s, 1H, OH, D_2O exchangeable), 8.62 (s, 1H, N=CH), 7.49–6.82 (11H, m, Ar–H), 4.15–3.77 (m, 16H, OCH_2, NCH_2Ar), 2.88 (t, J = 5.6 Hz, 4H, NCH_2), 1.59–1.38(m, 3H, CH_3); IR (KBr) ν_{max}: 3225, 1618, 1256, 1128 cm^{-1}; MS (*m/z*): 520 (M^+); Anal. calcd for $C_{30}H_{36}N_2O_6$: C 69.2, H 6.9, N 5.4; found C 69.0, H 6.8, N 5.5.

HL^5: Yield 885%, Yellow crystals; m.p. 95–97°C. ^1H NMR ($CDCl_3$) δ: 13.53 (s, 1H, OH, D_2O exchangeable), 8.60 (s, 1H, N=CH), 7.44–6.80 (11H, m, Ar-H), 4.16–3.75 (m, 16H, OCH_2, NCH_2Ar), 2.89 (t, J = 5.6 Hz, 4H, NCH_2), 1.82–0.86(m, 7H, $CH_2CH_2CH_3$); IR (KBr) ν_{max}: 3223, 1618, 1253, 1122 cm^{-1}; MS (*m/z*): 548 (M^+); Anal. Calcd for $C_{32}H_{40}N_2O_6$: C 70.1, H 7.3, N 5.1; found C 70.2, H 7.1, N 5.3

General procedure for the preparation of Schiff Bases cobalt (II) complexes **CoL_2^1–CoL_2^5**. A solution of **HL** (1.0 mol) and $Co(OAc)_2·4H_2O$ (0.5 mol) in EtOH (15 cm^3) was stirred for 2 h under N_2 at reflux temperature, then the mixture was cooled, filtered, the solid was washed with MeOH, then with H_2O to give the cobalt complexes. The pure product was obtained after recrystallisation from EtOH.

CoL_2^1: Dark brown, 68% yield, m.p. 236–238°C. IR (KBr) ν_{max}: 3440, 1606, 1255, 1125 cm^{-1}; Anal. calcd for $C_{58}H_{66}N_4O_{12}Co$: C 65.1, H 6.2, N 5.2; found C 65.3, H 6.0, N 5.5. Λ_m(S cm^2 mol^{-1}): 5.12.

CoL_2^2: Dark brown, 69% yield, m.p..>300°C. IR (KBr) ν_{max}: 3445, 1606, 1251, 1127 cm^{-1}; Anal. calcd for $C_{56}H_{60}N_6O_{16}Co$: C 59.4, H 5.3, N 7.2; found C 59.6, H 5.1, N 7.5. Λ_m(S cm^2 mol^{-1}): 3.61.

CoL_2^3: Dark brown, m.p.252–254°C. IR (KBr) $\nu_{max:}$ 3440, 1607, 1155, 1123 cm^{-1}; Anal. Calcd for $C_{56}H_{62}N_4O_{12}Co$: C 64.55, H 6.0, N, 5.4; found C 64.7, H 6.1, N 5.4; Λ_m(S cm^2 mol^{-1}): 6.16.

CoL_2^4: Dark brown, 69% yield, 230–232°C. IR (KBr) ν_{max}: 1606, 1255, 1123 cm^{-1}; Anal. Calcd for $C_{60}H_{70}N_4O_{12}Co$: C 65.6, H 6.4, N 5.1; found C 65.4, H 6.2, N 5.3. Λ_m(S cm^2 mol^{-1}): 5.63.

CoL_2^5: dark brown, 76% yield, 225–227°C. IR (KBr) ν_{max}: 1606, 1254, 1124 cm^{-1}; Anal. Calcd for $C_{64}H_{78}N_4O_{12}Co$: C 66.6, H 6.8, N 4.9; found C 66., H 7.0, N 4.6. Λ_m(S cm^2 mol^{-1}): 3.84.

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References

1 R.D. Jones, M.D.A. Summerville and F. Basolo, *Chem. Rev.*, 1979, **79**, 139.
2 M. Momenteau and C.A. Reed, *Chem. Rev.,* 1994, **94**, 659.
3 T. Tsumaki, *Bull Chem. Soc. Jpn*., 1938, **13**, 252.
4 M.J. Gunter and P Turner,. *Coord. Chem. Rev.,* 1991, **108,** 115.
5 E.V. Rybak-Akimova, W. Otto, P. Deardorf, R. Roesner, D.H. Busch, *Inorg. Chem.*, 1997, **36**, 2746.
6 A. Gül, A.I. Okur, A. Cihan, N. Tan, Ö Bekâroðlu, *Synth. React. Inorg. Met-Org. Chem.,* 1986, **16**, 871.
7 A.V. Bordunov, J.S. Bradshaw, V.N. Pastushok, X.X. Zhang, X. Kou, N.K. Dalley, Z. Yang, P.B. Savage and R.M Izatt, *Tetrahedron,* 1997, **53,** 17585.
8 V.W.W. Yam, Y.L. Pui, W.P. Li, K.K.W. Lo, K.K. and Cheung, *J. Chem. Soc., Dalton Trans.*, 1998, **21,** 3615.
9 U. Casellato, S. Tamburin, P. Tomasin, P.A. Vigato and B.M. Silvio, *Inorg. Chem.,* 1999, **38**, 2906.
10 W. Zeng, H.B. Li, R.L. Xiang, X.Y. Wei, and S.Y. Qin, *Chin. J. Chem.* 2003, **21**, 510.
11 X.X. Lu and S.Y. Qin, *Acta Chim. Sin.,* 1999, **57,** 1364.
12 W.J. Geary, *Coord. Chem. Rev*., 1971, **7**, 81.