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Synthesis of *N*′-[4′-Benzo(15-Crown-5)]-4-Tolylaminoglyoxime and *N*′-[4′-Benzo(15-Crown-5)]-4-Chlorophenylaminoglyoxime and Their Complexes with Copper (II), Nickel (II) and Cobalt (II)

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Abstract

N′-[4′-benzo(15-crown-5)]-4-tolylaminoglyoxime (H_2L^1), the sodium chloride salt of H_2L^1 (H_2L^1·NaCl), *N*′-[4′-benzo(15-crown-5)]-4-chlorophenylaminoglyoxime (H_2L^2) and the sodium chloride salt of H_2L^2 (H_2L^2·NaCl) have been prepared from *p*-chlorophenylchloroglyoxime, *p*-tolylchloroglyoxime, 4′-aminobenzo[15-crown-5] and sodium bicarbonate or sodium bicarbonate and sodium chloride. Nickel (II), cobalt (II) and copper (II) complexes of H_2L and H_2L·NaCl have a metal-ligand ratio of 1 : 2 and the ligand coordinates through the two N atoms, as do most of the *vic*-dioximes. Their IR spectra and elemental analyses are given, together with ^{1}H NMR spectra of the ligands.

Introduction

The field of coordination chemistry of macrocyclic compounds has undergone spectacular growth during the past 35 years. This enormous growth has been due to the synthesis of a great number and variety of synthetic macrocycles that behave as coordinating agents for metal ions. On the other hand, the development of bioinorganic chemistry has also been another important factor in spurring the growth interest in complexes of macrocyclic compounds [1]. Macrocyclic ligands often exhibit unusual properties and sometimes mimic related natural macrocyclic compounds. There is considerable current interest [2] in complexes of polydentate macrocyclic ligands, because of the variety of geometrical forms available and the possible encapsulation of the metal ion [3].

The chemistry of transition metal complexes with vic-dioximes has been well studied and is the subject of several reviews [4]. Both the presence of mildly acidic hydroxy groups and slightly basic nitrogen atoms make (*E*, *Z*) dioximes amphoteric ligands which form corrin-type, MN_4, square-planer, square-pyramidal and octahedral complexes with transition metal ions such as copper(II), cobalt(II), nickel(II) and cobalt(III) as central atoms [5]. Vicinal dioximes have received considerable attention as model compounds to mimic biofunctions such as reduction of vitamin B_{12} [6]. Oxime metal chelates are biologically active [7] and are reported to possess semiconducting properties [8, 9]. Derivatives of monoaminoglyoxime, heterocyclic and macrocyclic vic-dioximes, tetraoximes and their complexes with transition metals have been described [4, 10–14].

The goal of the present study was to obtain and characterize new dioximes containing a macrocycle and prepare their metal complex.

Experimental

Benzo[15-crown-5] [15], 4′-nitrobenzo[15-crown-5] [16], 4′-aminobenzo[15-crown-5] [16, 17], isonitrosomethyl-*p*-tolyl ketone [18], *p*-tolylglyoxime [18, 19], *p*-tolylchloroglyoxime [18] isonitroso-*p*-chloroacetophenone [20], *p*-chlorophenylglyoxime [19, 20] and *p*-chlorophenylchloroglyoxime [20] were prepared according to the published methods. All remaining reagents were purchased from Merck (Germany) and were used without further purification. Melting points were determined on a Gallenkamp melting point apparatus and are uncorrected. Elemental analyses (C, H, and N) were determined using a Leco, CHNS-932 model analyzer. ^{1}H NMR spectra were recorded on a Bruker DPX-400 400 MHz High Performance Digital FT-NMR and IR spectra on a Perkin Elmer 1605 FTIR spectrometer in KBr pellets. The UV-visible spectra were recorded on a SHIMADZU 160A spectrometer. The metal analyses were determined using a UNICAM 929 AAS spectrometer.

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Synthesis of
N′-[4′-benzo(15-crown-5)]-4-tolylaminoglyoxime
$C_{23}H_{29}O_7N_3$ (H_2L^1) and
N′-[4′-benzo(15-crown-5)]-4-chlorophenylaminoglyoxime
$C_{22}H_{26}O_7N_3Cl$ (H_2L^2)

To 4′-aminobenzo[15-crown-5] (1412 mg, 5 mmol) dissolved in absolute ethanol (15 cm^3) a solution of *p*-tolylchloroglyoxime (1063 mg, 5 mmol) or *p*-chlorophenylchloroglyoxime (1165 mg, 5 mmol) in absolute ethanol (10 cm^3) was added under N_2 atmosphere at 60 °C. The mixture was stirred efficiently and heated on a water-bath at ca. 60 °C for 3 h. The mixture was cooled to 0 °C and H_2L^1 or H_2L^2 was precipated by addition of cold diethyl ether with continuous stirring. The violet-coloured precipitate was filtered, washed with cold diethyl ether and dried.

H_2L^1: UV-VIS (EtOH): λ_{max}/nm ($\log\epsilon$); 212 (1.642), 250 (1.895), 304 (2.315), 488 (2.247).

^{1}H NMR ($CDCl_3$) δ (p.p.m.): 11.03 (s, 1H, OH), 10.26 (s, 1H, OH), 8.43 (s, 1H, NH), 7.19 (s, 1H, Ar—H), 7.33 (d, J: 7.46 Hz, 1H, Ar—H), 6.87 (d, J: 7.80 Hz, 1H, Ar—H), 6.39 (d, J: 7.90 Hz, 2H, Ar—H), 6.25 (d, J: 8.05 Hz, 2H, Ar—H), 3.82 (d, J: 3.89 Hz, 4H, O—CH_2—), 3.55 (s, 8H, O—CH_2—), 3.42 (s, 4H, O—CH_2—), 2.13 (s, 3H, —CH_3).

H_2L^2: UV-VIS (EtOH): λ_{max}/nm ($\log\epsilon$); 210 (1.499), 243 (1.754), 319 (2.818), 380 (2.395).

^{1}H NMR (DMSO-d_6) δ (p.p.m.): 12.12 (s, 1H, OH), 10.65 (s, 1H, OH), 8.16 (s, 1H, NH), 7.70 (s, 1H, Ar—H), 7.59 (d, J: 8.70 Hz, 1H, Ar—H), 7.55 (d, J: 8.49 Hz, 1H, Ar—H), 6.96 (d, J: 9.16 Hz, 2H, Ar—H), 6.65 (d, J: 6.18Hz, 2H, Ar—H), 3.82 (d, J: 6.05 Hz, 4H, O—CH_2—), 3.66 (s, 8H, O—CH_2—), 3.61 (s, 4H, O—CH_2—).

The ligands are soluble in EtOH, $CHCl_3$, DMF, DMSO, CH_2Cl_2 and MeOH. They are insoluble in CCl_4. The yields, melting points, elemental analyses and IR spectral data of the ligands are given Tables 1 and 2, respectively.

Sodium chloride salt of H_2L^1 $C_{23}H_{29}O_7N_3$·NaCl
(H_2L^1·NaCl and H_2L^2 $C_{22}H_{26}O_7N_3Cl$·NaCl (H_2L^2·NaCl)

A solution of *p*-tolylchloroglyoxime (1063 mg, 5 mmol) or *p*-chlorophenylchloroglyoxime (1165 mg, 5 mmol) in absolute ethanol (10 cm^3) was added to a solution of 4′-aminobenzo[15-crown-5] (1412 mg, 5 mmol) in absolute ethanol (15 cm^3) which also contained solid $NaHCO_3$ (840 mg, 10 mmol) and NaCl (292.5 mg, 5 mmol) added under an atmosphere of N_2 at 60 °C. The mixture was stirred efficiently and heated on a water-bath at ca. 60 °C for 3 h. After cooling to room temperature, the mixture was filtered and washed with ethanol (10 cm^3). The filtrate was cooled to 0 °C and H_2L^1·NaCl or H_2L^2·NaCl was precipated by addition of cold diethyl ether with continous stirring. The pink-coloured precipitate was filtered, washed with cold diethyl ether and dried. H_2L^1·NaCl : UV-VIS (EtOH): λ_{max}/nm ($\log\epsilon$); 208 (1.433), 243 (1.841), 309 (2.417), 351 (2.390).

^{1}H NMR ($CDCl_3$) δ (p.p.m.): 10.98 (s, 1H, OH), 9.69 (s, 1H, OH), 8.06 (s, 1H, NH), 7.57 (s, 1H, Ar—H), 7.42 (d, J: 8.06 Hz, 1H, Ar—H), 7.03 (d, J: 7.96 Hz, 1H, Ar—H), 6.62 (d, J: 8.57 Hz, 2H, Ar—H), 6.42 (d, J: 2.28 Hz, 2H, Ar—H), 3.96 (d, J: 4.43 Hz, 4H, O—CH_2—), 3.75 (s, 8H, O—CH_2—), 3.62 (s, 4H, O—CH_2—), 2.23 (s, 3H, —CH_3).

H_2L^2·NaCl: UV-VIS (EtOH): λ_{max}/nm ($\log\epsilon$); 212 (1.596), 240 (1.856), 311 (2.485), 351 (2.411).

^{1}H NMR (DMSO-d_6) δ (p.p.m.): 12.20 (s, 1H, OH), 10.65 (s, 1H, OH), 8.20 (s, 1H, NH), 7.83 (s, 1H, Ar—H), 7.71 (d, J: 8.49 Hz, 1H, Ar—H), 7.61 (d, J: 6.05 Hz, 1H, Ar—H), 6.99 (d, J: 8.61 Hz, 2H, Ar—H), 6.64 (d, J: 2.29 Hz, 2H, Ar—H), 3.82–3.55 (m, 16H, O—CH_2—).

The ligands are soluble in EtOH, $CHCl_3$, DMF, DMSO, CH_2Cl_2 and MeOH. They were insoluble in CCl_4.

The yields, melting points, elemental analyses and IR spectral data of the ligands are given in Tables 1 and 2, respectively.

Ni^{II}, Co^{II} and Cu^{II} complexes of the ligands

A solution of 0.25 mmol of metal salt [$NiCl_2·6H_2O$ (59 mg), $CoCl_2·6H_2O$ (60 mg), $CuCl_2·2H_2O$ (43 mg)] dissolved in EtOH (5 cm^3) was added to a stirred solution of H_2L^1 (230 mg, 0.5 mmol), H_2L^2 (240 mg, 0.5 mmol), H_2L^1·NaCl (259 mg, 0.5 mmol) or H_2L^2·NaCl (269 mg, 0.5 mmol) dissolved in EtOH (5 cm^3). The mixture was heated to 60 °C and NaOH (20 mg, 0.5 mmol) in ethanol (5 cm^3) was added dropwise. The reaction was allowed to continue for 3 h. at 60 °C. The mixture was allowed to stand one day at room temperature. The precipitated complexes were filtered, washed with EtOH and dried.

The yields, melting points, elemental analyses and IR spectral data of the compounds are given in Tables 1 and 2.

Results and discussion

By a method similar to that for the synthesis of *N*, *N′*-bis[4′-benzo(15-crown-5)]diaminoglyoxime [10], *N′*-(4′-benzo[15-crown-5]-4-tolylaminoglyoxime (H_2L^1), *N′*-[4′-Benzo(15-Crown-5)]-4-chlorophenylaminoglyoxime (H_2L^2), sodium chloride salt of H_2L^1 (H_2L^1·NaCl) and sodium chloride salt of H_2L^2 (H_2L^2·NaCl) were prepared by reaction of 4′-aminobenzo[15-crown-5] [16, 17] with *p*-tolylchloroglyoxime [18] and *p*-chlorophenylchloroglyoxime [20]. For H_2L^1·NaCl and H_2L^2·NaCl, $NaHCO_3$ was added into the reaction mixture in order to neutralize the HCl formed during the reaction, NaCl was produced as a byproduct and it complexed with the crown ether groups; therefore the ligand was obtained as a sodium chloride salt, H_2L^1·NaCl and H_2L^2·NaCl. No further attempt was made to isolate the free ligand, since H_2L·NaCl could be used to prepare the transition metal complexes. For H_2L^1 and H_2L^2, nothing was added into the reaction mixture in order to neutralize the HCl formed during the reaction.

In the ^{1}H NMR spectra of the ligands, two peaks are present for the —OH protons of the oxime groups. These two deuterium-exchangeable singlets correspond to two non-equivalent —OH protons which also indicate the

Table 1. Formula weights, m.p., yields and elemental analytical results for the ligands and their complexes

Compound		Formula weights	Mp/°C	Yield (%)	Analysis (%) calculate[a]			
					C	H	N	M
H_2L^1	$C_{23}H_{29}O_7N_3$	459.492	–	74	60.12	6.36	9.15	–
					(59.94)	(6.14)	(9.02)	
$(HL^1)_2Ni$	$C_{46}H_{56}O_{14}N_6Ni$	975.662	284	78	56.63	5.79	8.61	6.02
					(56.44)	(5.74)	(8.52)	(6.11)
$(HL^1)_2Co$	$C_{46}H_{56}O_{14}N_6Co$	975,902	>300	60	56.61	5.78	8.61	6.04
					(56.55)	(5.68)	(8.54)	(5.87)
$(HL^1)_2Cu$	$C_{46}H_{56}O_{14}N_6Cu$	980.514	>300	38	56.35	5.76	8.57	6.48
					(56.26)	(5.72)	(8.67)	(6.54)
$H_2L^1{\cdot}NaCl$	$C_{23}H_{29}O_7N_3{\cdot}NaCl$	517.934	192	69	53.34	5.64	8.11	–
					(53.29)	(5.54)	(7.92)	
$(HL^1)_2Ni{\cdot}2NaCl$	$C_{46}H_{56}O_{14}N_6Ni{\cdot}2NaCl$	1092.547	>300	70	50.57	5.17	7.69	5.37
					(50.48)	(4.9)	(7.65)	(5.39)
$(HL^1)_2Co{\cdot}2NaCl$	$C_{46}H_{56}O_{14}N_6Co{\cdot}2NaCl$	1092.787	74	74	50.56	5.17	7.69	5.39
					(50.39)	(5.01)	(7.53)	(5.15)
$(HL^1)_2Cu{\cdot}2NaCl$	$C_{46}H_{56}O_{14}N_6Cu{\cdot}2NaCl$	1097.399	>300	88	50.35	5.14	7.66	5.79
					(50.40)	(5.20)	(7.47)	(5.60)
H_2L^2	$C_{22}H_{26}O_7N_3Cl$	479.910	–	58	55.06	5.46	8.76	–
					(54.92)	(5.30)	(8.64)	
$(HL^2)_2Ni$	$C_{44}H_{50}O_{14}N_6Cl_2Ni$	1016.498	>300	88	51.99	4.96	8.27	5.77
					(51.87)	(4.85)	(8.16)	(5.68)
$(HL^2)_2Co$	$C_{44}H_{50}O_{14}N_6Cl_2Co$	1016.738	>300	54	51.98	4.96	8.27	5.80
					(51.76)	(4.92)	(8.14)	(5.69)
$(HL^2)_2Cu$	$C_{44}H_{50}O_{14}N_6Cl_2Cu$	1021.351	>300	82	51.74	4.93	8.23	6.22
					(51.71)	(4.81)	(8.03)	(5.99)
$H_2L^2{\cdot}NaCl$	$C_{22}H_{26}O_7N_3Cl{\cdot}NaCl$	538.353	144	79	49.08	4.87	7.81	–
					(48.82)	(4.75)	(7.76)	
$(HL^2)_2Ni{\cdot}2NaCl$	$C_{44}H_{50}O_{14}N_6Cl_2Co{\cdot}2NaCl$	1133.383	>300	56	46.63	4.45	7.42	5.18
					(46.50)	(4.34)	(7.31)	(5.01)
$(HL^2)_2Co{\cdot}2NaCl$	$C_{44}H_{50}O_{14}N_6Cl_2Ni{\cdot}2NaCl$	1133.623	>300	71	46.62	4.45	7.41	5.20
					(46.44)	(4.35)	(7.28)	(5.26)
$(HL^2)_2Cu{\cdot}2NaCl$	$C_{44}H_{50}O_{14}N_6Cl_2Cu{\cdot}2NaCl$	1138.236	>300	82	46.43	4.43	7.38	5.58
					(46.41)	(4.31)	(7.22)	(5.37)

[a] Found values are in parentheses.

Table 2. Characteristic IR bands of the ligands and their complexes[a] (KBr pellets)

Bileşik	NH	OH	CH_{Ar}	O···H—O	C=N	NH	C=C	C_{Ar}—O—C	C—O—C	N—O	Other
H_2L^1	3430	3228	2926	–	1642	1606	1508	1271–1236	1135–1045	936	1452 (CH_3—)
$(HL^1)_2Ni$	3448	–	2934	1717	1636	1624	1510	1247–1226	1125–1056	936	1458 (CH_3—)
$(HL^1)_2Co$	3447	–	2926	1717	1636	1612	1508	1260–1226	1126–1050	938	1456 (CH_3—)
$(HL^1)_2Cu$	3448	–	2925	1717	1636	1616	1508	1259–1227	1126–1053	937	1450 (CH_3—)
$H_2L^1{\cdot}NaCl$	3382	3235	2922	–	1641	1612	1508	1246–1228	1127–1044	942	1436 (CH_3—)
$(HL^1)_2Ni{\cdot}2NaCl$	3447	–	2925	1717	1636	1617	1508	1260–1221	1125–1048	936	1436 (CH_3—)
$(HL^1)_2Co{\cdot}2NaCl$	3448	–	2920	1717	1636	1617	1508	1260–1228	1128–1052	942	1436 (CH_3—)
$(HL^1)_2Cu{\cdot}2NaCl$	3448	–	2912	1717	1636	1617	1508	1250–1222	1119–1058	940	1436 (CH_3—)
H_2L_2	3413	3105	2931	–	1638	1617	1514	1272–1239	1113–1045	938	694 (C—-Cl)
$(HL^2)_2Ni$	3448	–	2926	1717	1636	1617	1510	1260–1227	1127–1056	940	694 (C—Cl)
$(HL^2)_2Co$	3422	–	2925	1717	1636	1624	1508	1259–1226	1126–1052	941	673 (C—Cl)
$(HL^2)_2Cu$	3421	–	2926	1717	1636	1616	1510	1259–1227	1127–1056	940	688 (C—Cl)
$H_2L^2{\cdot}NaCl$	3345	3212	2937	–	1642	1616	1514	1249–1226	1127–1046	944	690 (C—Cl)
$(HL^2)_2Ni{\cdot}2NaCl$	3423	–	2915	1717	1642	1599	1508	1259–1222	1127–1014	940	692 (C— Cl)
$(HL^2)_2Co{\cdot}2NaCl$	3422	–	2916	1717	1636	1616	1508	1260–1223	1126–1014	942	674 (C— Cl)
$(HL^2)_2Cu{\cdot}2NaCl$	3448	–	2930	1717	1636	1624	1508	1244–1223	1126–1014	945	674 (C— Cl)

[a] cm^{-1}.

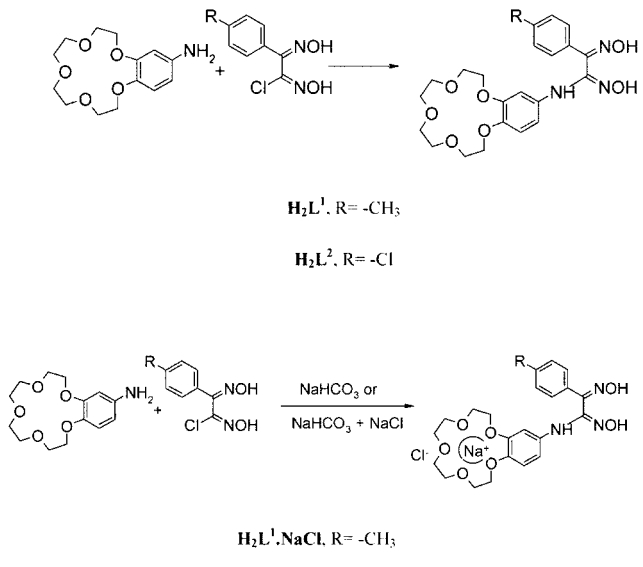

Figure 1. General formulas of ligands.

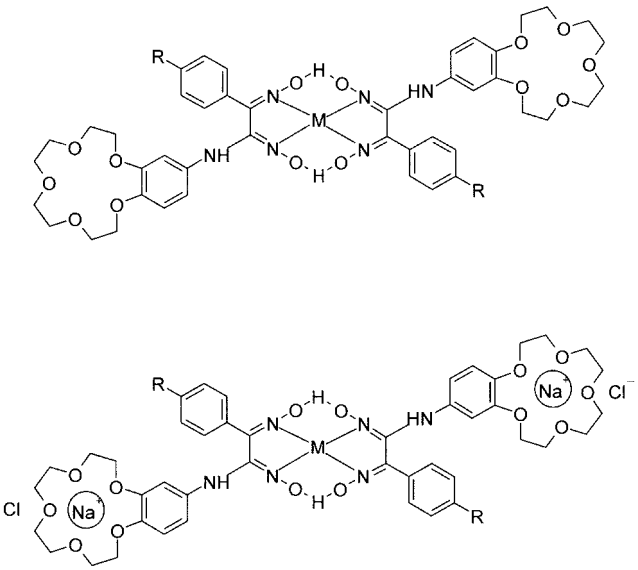

Figure 2. Square-planer metal complexes of ligands. (a) H_2L, (b) $H_2L{\cdot}NaCl$, R: CH_3—, —Cl.

anti-configuration of the —OH groups relative to each other [10, 11, 14, 22, 23] (Figure 1). The singlet chemical shifts, belonging to the hydroxyimino protons, indicate that the oxime groups are of the (E, E) structure [24, 25]. When the chemical shifts of the two —OH groups in the two different sets of ligands are compared, the ones at lower field quite closely resemble each other [11.03, 12.12 (for H_2L), 10.98, 12.20 (for $H_2L{\cdot}NaCl$) p.p.m.] whereas a considerable difference is observed for the shift at the higher field (10.26, 10.65, 9.69, 10.65 p.p.m.). The D_2O exchangeable —NH— protons of the aminoglyoximes were observed at 8.43, 8.16, 8.06, 8.20 p.p.m., —O—CH_2— protons at 3.96–3.42 p.p.m.. Addition of D_2O causes the disappearance of the —NH— and —OH peak.

The ligands, —NH (3430, 3382, 3413, 3345 cm^{-1}), —OH (3228, 3235, 3105, 3212 cm^{-1}), C=N— (1642, 1641, 1638, 1642 cm^{-1}) and NO (936, 942, 938, 944 cm^{-1}) exhibit stretching frequencies as for substituted aminoglyoximes [10, 14, 21].

The Cu(II), Ni(II) and Co(II) complexes of the four new ligands were prepared in ethanol by the addition of 0.1 M NaOH solution. The complexes were characterized by IR and elemental analyses, the data are shown in Tables 1 and 2, respectively. The complexes of H_2L^1, H_2L^2, $H_2L^1{\cdot}NaCl$ and $H_2L^2{\cdot}NaCl$ support the structures shown in Figure 2 by the weak bending vibration of the O—H$\cdots$O bridges etc. 1717 cm^{-1} [10, 14, 19, 21]. The IR spectra of the metal ion complexes exhibit ν(C=N) absorptions at 1636 cm^{-1} for metal complexes. These values are lower than those for the free ligand [10, 14, 19, 21].

As is the case for most anti-dioximes, H_2L forms complexes with Cu(II), Co(II) and Ni(II) with a metal-ligand ratio of 1 : 2 [4, 10, 11, 21, 24]. As with most vic-dioximes [4, 10, 11, 21], the nickel(II) complex of anti-H_2L^2 is planar. N′-coordination is verified by the diamagnetism of this compound, since it is known that a d^8 metal complex does not have unpaired electrons in a square planar field.

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