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Pendant-Arm Macrocycles Derived from the Cyclocondensation Reaction of Sodium 2,6-Diformyl-4-substitutedphenolates and Tris-(2-aminoethyl)amine Derivatives. Preparation, Characterization and Properties of their Dinuclear Copper(II) Complexes

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Abstract. A series of pendant-arm Schiff base macrocycles have been obtained *via* the cyclocondensation reaction between sodium 2,6-diformyl-4-substitutedphenolates and tris-(2-aminoethyl)-amine derivatives followed by transmetallation with $Cu(ClO_4)_2{\cdot}6H_2O$. The resulting dinuclear copper(II) complexes have been characterized by elemental analysis, infrared and mass spectra as well as magnetic moments at room temperature. All complexes have been electrochemically investigated, and two typical compounds have been studied with ESR spectra as well.

Key words: pendant-arm macrocycles, dinuclear macrocyclic copper(II) complexes, sodium template, Schiff base cyclocondensation

1. Introduction

There has been increasing interest in pendant-arm macrocyclic ligands and their metal complexes nowadays, and much attention has been focused on the mimicking of active biosites as well as the properties and applications of these macrocyclic complexes [1–8]. It is due to the fact that ligating groups attached to ring carbon and/or nitrogen atoms can offer additional donors to incorporate metal ions with high affinity apart from those on the macrocyclic skeleton. Generally pendant arms are bound to a ring in two ways: (i) connecting organic functional moieties to established macrocycles *via* electrophilic substitution or addition reactions; and (ii) combining donor species with macrocyclic precursors first and proceeding cyclization reactions subsequently. Tris-(2-aminoethyl)amine (tren) is a well known

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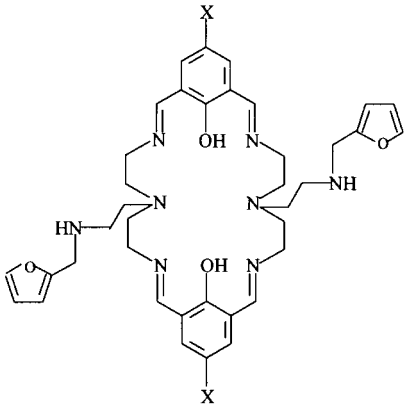
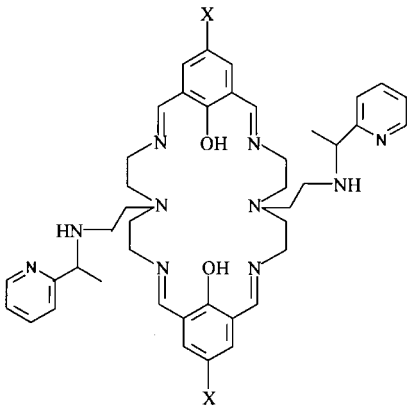
precursor for both monomacrocycles [9–12] and bimacrocycles [13–17], so we have applied tren derivatives (the reduced 1 : 1 Schiff base of tren with aromatic aldehydes or ketones) to produce pendant-arm macrocycles with 2,6-diformyl-4-substitutedphenolates by an *in situ* condensation reaction in the presence of sodium [18]. As part of our research, we herein report the synthesis and characterization of the following macrocyclic complexes.





Ligand	X	Ligand	X
H_2L^1	CH_3	H_2L^4	CH_3
H_2L^2	$C(CH_3)_3$	H_2L^5	$C(CH_3)_3$
H_2L^3	Cl	H_2L^6	Cl

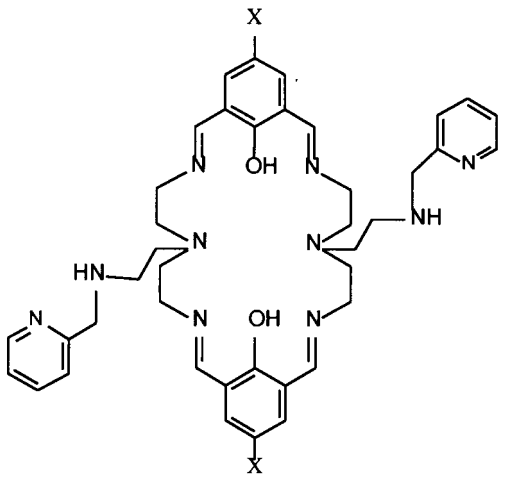
2. Experimental

2.1. STARTING MATERIALS

The sodium salt of 2,6-diformyl-4-X-phenolates [X = CH_3, $C(CH_3)_3$, Cl] was prepared according to the method reported before [19]. 2-Formylfuran, 2-acetylpyridine and 2-formylpyridine as well as tren are commercials from Aldrich and used without further purification.

2.2. MEASUREMENTS

Elemental analyses were performed with a Perkin Elmer model 240C elemental analyzer. Infrared spectra were recorded as KBr pellets using a Nicolet 170SX-FT spectrophotometer (4000–600 cm^{-1}). Electrospray ionization mass spectra (ES-MS) were obtained on a Finnigan MAT SSQ710 spectrometer (solvent = 1 : 1 CH_3CN:H_2O). Positive ion FAB mass spectra were carried out on a VG-2AB-HS mass spectrometer (matrix solvent: 4-nitrobenzyl alcohol). Magnetic susceptibilit-



Ligand	X
H_2L^7	CH_3
H_2L^8	$C(CH_3)_3$
H_2L^9	Cl

ies were measured in the solid state at room temperature employing a CAHN-2000 magnetometer with $[Ni(en)_3]S_2O_3$ as a calibrant with data corrected by Pascal's constants. X-band ESR spectra were obtained utilizing a Bruker 200D-SRC spectrometer at 110 K. Cyclic voltammograms were recorded on a BAS 100B Electrochemical Analyzer (USA), measurements were carried out in DMF solutions (ca. 1×10^{-3} mol dm^{-3}) of complexes containing 0.1 mol dm^{-3} tetraethylammonium perchlorate (TEAP) as the supporting electrolyte. A three-electrode cell equipped with a glass carbon working electrode, a platinum wire as the auxiliary electrode and a saturated calomel electrode (SCE) as the reference was used.

2.3. PREPARATION OF MACROCYCLIC COMPLEXES

The cyclocondensation and transmetallation reaction was carried out by the following general procedure.

An ethanolic solution (50 cm^3) containing *tren* (1 mmol) and aromatic aldehyde or ketone (1 mmol) was stirred for 30 min, excess $NaBH_4$ (5.2 mmol) was added. The resulting suspension was kept stirring for 2 h, then dilute hydrochloric acid in ethanol was added to remove the excess $NaBH_4$ and the pH was adjusted to 10 by the addition of 2M NaOH. After filtration the concentrated filtrate (ca. 20 cm^3) was added into a suspension of the corresponding sodium 2,6-diformyl-4-X-phenolate (1 mmol) in ethanol (30 cm^3). The mixture was cooled in an ice-water bath and

kept on stirring. As the reaction progressed, the solution gradually became clear. After 8 h, $Cu(ClO_4)_2 \cdot 6H_2O$ (2 mmol) was added to the solution, then the mixture was heated under reflux for a further 1 h. The precipitate was collected and dried in *vacuo*. Yields and element analytical data for all complexes are given in Table I.

Caution: perchlorates which are potentially explosive should be handled with care!

3. Results and Discussion

3.1. SYNTHESIS

The synthetic route is shown in Scheme 1. The formation of 1 : 1 Schiff base has been strictly controlled by reacting a stoichiometric molar amount of *tren* with 2-formylfuran or 2-acetylpridine or 2-formylpyridine in ethanol, in which the C=N double bonds are then reduced by $NaBH_4$. The resulting diamino intermediate has been subsequently used to carry out the cyclocondensation reaction with sodium 2,6-diformyl-4-X-phenolate. As pointed out previously [19], dinuclear sodium macrocyclic compounds are generally unstable and difficult to isolate, hence *in situ* transmetallation by copper(II) perchlorate has been done to generate stable dinuclear copper(II) complexes with high yields. Microanalytical data are in agreement with the theoretical values. Moreover, experiments indicate that the non-reduction of C=N bonds will lead to a 2 : 3 Schiff base macrocycle rather than a pendant-arm one, because the 1 : 1 condensation reaction between *tren* and 2-formylfuran or 2-acetylpyridine or 2-formylpyridine is reversible [20]. Therefore it is noted that the reduction of C=N double bonds into C—N single bonds with sodium hydroborate should be completely finished, otherwise highly stable metal cryptates would occur.

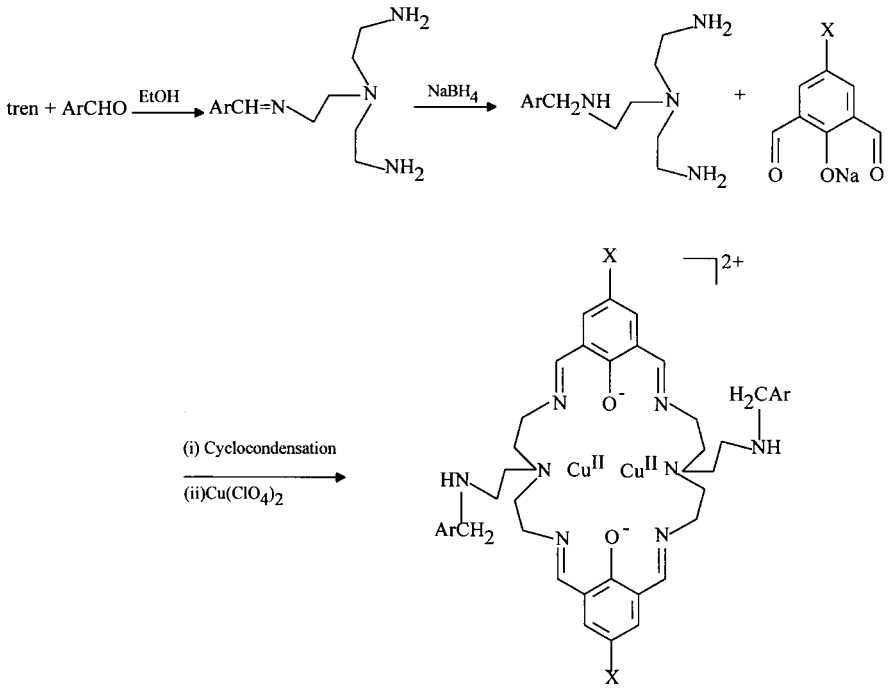
3.2. INFRARED, MASS AND ESR SPECTRAL CHARACTERIZATION

The main peaks of the infrared spectra of complexes **1**–**9**, presented in Table II, are very similar. The strong absorption of C=N double bond frequencies is found in the region of 1638 cm^{-1} and no bands ascribed to the stretching vibrations of C=O double bonds and primary amine species have indicated the formation of Schiff bases. On the other hand, a weak band in the range 3233–3272 cm^{-1} attributed to ν(NH) has been clearly observed in all complexes, confirming the existence of secondary amines. The presence of both ν(C=N) and ν(NH) suggests that the reaction has proceeded as expected, although no bands have been obviously assigned to the pendant arms due to the overlap of aromatic ring absorptions. All complexes exhibit a strong peak near 1100 cm^{-1}, which is assigned to uncoordinated perchlorate groups.

The ES mass spectral data of all complexes together with the FAB mass spectra of six complexes are listed in Table III. The parent molecular ion peak has not been found for each complex. However, peaks corresponding to $[Cu_2L]^{2+}$

Table I. Yields and microanalytical data with theoretical values in parentheses

No.	Complex	Formula	Yield (%)	C (%)	H (%)	N (%)
1	$[Cu_2L^1](ClO_4)_2{\cdot}4H_2O$	$C_{40}H_{58}Cl_2Cu_2N_8O_{16}$	75	43.3(43.4)	5.2(5.3)	10.5(10.1)
2	$[Cu_2L^2](ClO_4)_2{\cdot}H_2O$	$C_{46}H_{64}Cl_2Cu_2N_8O_{13}$	81	48.4(48.7)	5.4(5.6)	9.5(9.9)
3	$[Cu_2L^3](ClO_4)_2$	$C_{38}H_{44}Cl_4Cu_2N_8O_{12}$	73	42.7(42.5)	4.2(4.6)	10.2(10.4)
4	$[Cu_2L^4](ClO_4)_2{\cdot}2H_2O$	$C_{44}H_{60}Cl_2Cu_2N_{10}O_{12}$	79	47.5(47.2)	5.3(5.4)	12.5(12.5)
5	$[Cu_2L^5](ClO_4)_2{\cdot}2H_2O$	$C_{50}H_{72}Cl_2Cu_2N_{10}O_{12}$	85	49.9(50.0)	6.1(6.0)	12.0(11.7)
6	$[Cu_2L^6](ClO_4)_2{\cdot}H_2O$	$C_{42}H_{52}Cl_4Cu_2N_{10}O_{11}$	80	44.5(44.2)	4.7(4.6)	12.4(12.3)
7	$[Cu_2L^7](ClO_4)_2{\cdot}H_2O$	$C_{42}H_{54}Cl_2Cu_2N_{10}O_{11}$	73	47.3(47.0)	5.3(5.0)	12.9(13.0)
8	$[Cu_2L^8](ClO_4)_2{\cdot}3H_2O$	$C_{48}H_{70}Cl_2Cu_2N_{10}O_{13}$	76	48.8(48.3)	5.6(5.9)	11.4(11.7)
9	$[Cu_2L^9](ClO_4)_2{\cdot}H_2O$	$C_{40}H_{48}Cl_4Cu_2N_{10}O_{11}$	83	43.1(43.1)	4.7(4.3)	12.4(12.6)



Scheme 1. Cyclocondensation reaction of tren derivatives with sodium 2,6-di-formyl-4-substitutedphenolates and the subsequent transmetallation by copper perchlorate.

Table II. Principal IR absorptions (cm^{-1}) and their assignments

Complex	ν(NH)	ν(C=N)	ν(aromatic ring)	$\nu(ClO_4^-)$
1	3233(w)	1640(s)	1543(vs)	1089(vs)
2	3260(w)	1638(vs)	1554(s)	1100(vs)
3	3256(w)	1638(vs)	1554(s)	1101(vs)
4	3272(w)	1638(vs)	1544(s)	1099(vs)
5	3270(w)	1637(vs)	1553(s)	1098(vs)
6	3263(w)	1640(vs)	1539(s)	1100(vs)
7	3275(w)	1638(vs)	1558(s)	1099(vs)
8	3248(w)	1629(vs)	1537(s)	1091(vs)
9	3205(w)	1639(vs)	1537(s)	1088(vs)

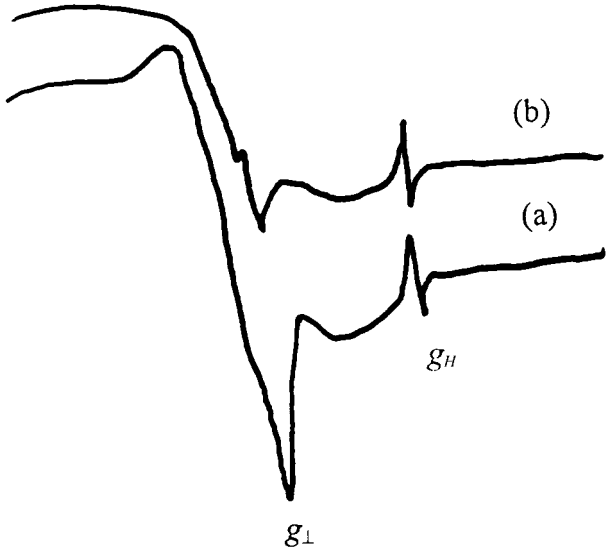


Figure 1. ESR spectra of complexes **1** (a) and **4** (b) in frozen DMF solutions (1×10^{-2} mol dm^{-3}) at 110 K.

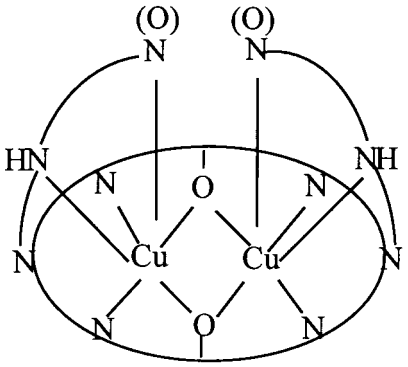
and/or $[Cu_2HL(ClO_4)]^{2+}$ have been observed as double-charged species in the ES mass spectra of all complexes. In addition, complexes **4**, **5**, **7** and **9** have also shown peaks assigned to triple-charged species such as $[Cu_2H_2L(ClO_4)]^{3+}$ and $[Cu_2H_3L(ClO_4)_2]^{3+}$, exhibiting the unique feature of ES mass spectra.[21] In order to provide more evidence, complexes **1**, **2**, **4**, **7**, **8** and **9** have been measured using the FAB-MS spectroscopic technique. Complex cations, $[Cu_2L(ClO_4)]^+$, have all been observed among these six compounds, indicating that the expected pendant-armed macrocycles have been formed as their copper(II) complexes as well.

Complexes **1** and **4** have been typically investigated by ESR spectroscopy. No ESR signals have been observed with solid samples and DMF solutions of both complexes at room temperature. The 110 K ESR spectra of two complexes in frozen DMF solutions (displayed in Figure 1) all give $g_\perp = 2.06$ and $g_\parallel = 2.00$. The fact of $g_\perp > g_\parallel \approx 2.00$ is in agreement with the compressed octahedral stereochemistry for Cu^{II} systems [22], but the half-field transition is not observed at $g = 4.3$. Thus it is suggested that each Cu atom is six-coordinated by two phenoxy anions and two imine nitrogen atoms as well as the ligating groups on the arm, namely, the secondary amine nitrogen atom and the attaching pyridine or furan moiety. The coordination geometry of each Cu atom would be a distorted octahedron, which is illustrated below.

Table III. Main ES-MS peaks (m/z) and their relative intensities (%) in parentheses

Complex	$[Cu_2L(ClO_4)]^{+}$*	$[Cu_2L]^{2+}/2$	$[Cu_2HL(ClO_4)]^{2+}/2$	$[Cu_2H_2L(Cl\ O_4)_2]^{2+}/2$	$[Cu_2H_2L(ClO_4)]^{3+}/3$	$[Cu_2H_3L(ClO_4)_2]^{3+}/3$
1	934	467(100)				
2	1017	458(62)	508(64)			
3	–	437(70)	487(65)			
4	984		491(18)	542(10)		361(100)
5	–	484(14)			356(30)	390(30)
6	–		512(50)			
7	954	428(89)	478(36)			352(74)
8	1038	470(100)				
9	995	448(53)				366(85)

* Positive ion FAB mass spectral data.



In our latest studies on these macrocyclic compounds, the crystal structure of a dinuclear manganese(II) complex of the pendant-arm macrocycle (H_2L^7) resulting from the cyclocondensation of sodium 2,6-diformyl-4-methylphenolate with *N*-(2-methylenepridine)-2-aminoethyl, *N′*, *N*"-bis(2-aminoethyl)amine has been determined by X-ray diffraction [23]. The structural data indicate that the coordination situation about the metal atom is similar to that we have suggested for the copper complexes. The coordination polyhedron of each metal atom is a considerably distorted octahedron. The nitrogen atoms of the secondary amine and the pyridine group on the side arm in addition to those donor species from the ring are coordinated to the metal, while the tertiary amine does not form a bond with the metal.

One of our purposes to design these reactions is trying to obtain their trinuclear complexes by holding the third metal atom through the pendant functional arms above the macrocycle, hopefully to model certain metalloenzymes containing trimetal centers. Contrary to our anticipation, dinuclear metal complexes have been obtained, where the pendant-arm has been coordinated to the metal atom on the ring without exception, this is presumably resulted from the strong chelating effect of the arm attached to the macrocycle.

3.3. MAGNETIC AND ELECTROCHEMICAL PROPERTIES OF THE COMPLEXES

The magnetic moments of each Cu^{2+} ion in complexes **1**–**9** at room temperature lie in the normal range for a free Cu^{2+} ion, reflecting a very weak magnetic exchange between the two copper ions in each compound at 'high' temperature. But it is impossible to be aware whether ferromagnetic or anti-ferromagnetic interactions function in the molecule without magnetic data at low temperature. The corresponding data together with the electrochemical data of all complexes are presented in Table IV.

The electrochemical properties of complexes **1**–**9** have been studied by means of cyclic voltammetry. The cyclic voltammogram of complex **6** is shown in Figure 2. The data indicate that the cyclic voltammograms of all complexes have a reversible couple at +0.38–+0.54 V (*vs.* SCE) and an irreversible couple at −0.48–−0.72 V,

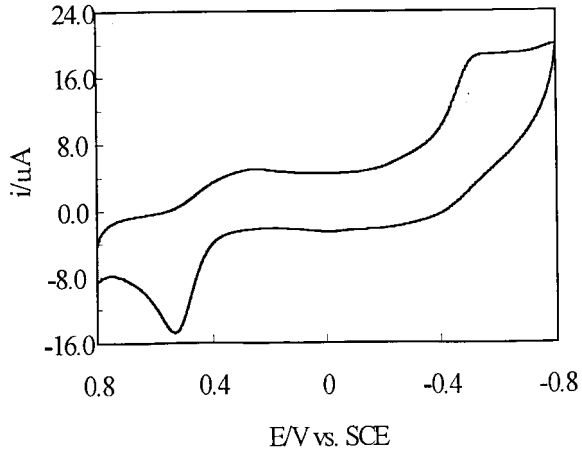


Figure 2. Cyclic voltammogram of complex **6** (ca. 1.0×10^{-3} mol dm^{-3}) in DMF at the scan rate of mV/S. Supporting electrolyte: 0.1 mol dm^{-3} TEAP.

Table IV. Magnetic moments (B.M.) and electrochemical data* (values in V *vs.* SCE) for complexes **1**–**9**

Complex	T (K)	μ_{eff}	$E^{1/2}$ 1[Cu(II)Cu(II)/Cu(II)Cu(I)]	$E^{1/2}$ 2[Cu(II)Cu(I)/Cu(I)Cu(I)]
1	285	2.08	0.43(rev)	−0.48(irr)
2	285	1.89	0.38(rev)	−0.72(irr)
3	274	1.80	0.51(rev)	−0.62(irr)
4	285	2.04	0.54(rev)	−0.58(irr)
5	273	2.12	0.41(rev)	−0.48(irr)
6	285	2.14	0.40(rev)	−0.50(irr)
7	273	1.93	0.36(rev)	−0.51(irr)
8	273	2.14	0.48(rev)	−0.68(irr)
9	273	2.06	0.45(rev)	−0.63(irr)

* rev.= chemically reversible, irr.= irreversible.

which are assigned to the following stepwise reduction processes, $Cu^{II}Cu^{II} \rightarrow Cu^{II}Cu^{I}$ and $Cu^{II}Cu^{I} \rightarrow Cu^{I}Cu^{I}$, respectively [24]. The irreversibility of the second wave is indicative of the instability of the copper(I) oxidation state at the N_4O_2 or N_3O_3 sites.

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