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Synthesis and characterization of Ni(II) and Cu(II) complexes of 6-(β-(3,4-dimethoxyphenylethyl))cyclam (L_1) and 6-(β-(3,4-dihydroxyphenylethyl))cyclam (H_2L_2) (cyclam = 1,4,8,11-tetraazacyclotetradecane). X-ray crystal structures of $[Cu(L_1)Br_2]$ and $[Cu(H_2(BrL_2))Br]Br\cdot H_2O$ and metal ion templated formation of multinuclear macrocyclic complexes

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Abstract

The synthesis of 6-(β-(3,4-dimethoxyphenyl)ethyl)cyclam (L_1) and the corresponding Ni(II) and Cu(II) complexes is described. Demethylation of the complexes of L_1 was carried out with BBr_3 and the corresponding Ni(II) and Cu(II) complexes of H_2L_2 (H_2L_2 = 6-(β-(3,4-dihydroxyphenyl)ethyl)cyclam) have been isolated and characterized. Reaction of $[Cu(L_1)Br_2]$ with Br_2 resulted in bromination of the phenyl group, to yield $[Cu(BrL_1)Br_2]$. Demethylation of $[Cu(BrL_1)Br_2]$ yielded the corresponding bromo-catechol appended macrocyclic complex $[Cu(H_2(BrL_2))]Br_2$, where $H_2(BrL_2)$ = 6-(β-(6-bromo-3,4-dihydroxyphenyl)-ethyl)cyclam. The crystal structures of $[Cu(L_1)Br_2]$ and $[Cu(H_2(BrL_2))Br]Br\cdot H_2O$ have been determined. In both complexes, the Cu(II) ion is within the macrocyclic cavity with an average Cu–N distance of (2.01 Å). In $[Cu(L_1)Br_2]$, the Cu(II) is pseudo-octahedral, with Cu–Br(1) = 2.9996(3) and Cu– Br(2) = 2.925(3) Å whereas in $[Cu(H_2(BrL_2))Br]Br\cdot H_2O$, the Cu(II) is square pyramidal with a Cu–Br distance of 2.904(2) Å. Reaction of $[M(H_2L_2)]^{2+}$ ($M = Ni^{2+}$ and Cu^{2+}) ions with Fe(III) in basic aqueous media led to the formation of the tetranuclear species $[Fe(M(L_2)Br_2)_3]^{3-}$, which has been monitored by UV–Vis and EPR spectroscopy.

Keywords: Crystal structures; Copper complexes; Substituted cyclams; Self-assembly; Multinuclear complexes

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1. Introduction

The design and syntheses of new ligands with various functionalities is a key factor in the advancement of the coordination chemistry [1]. In particular, such strategies have been useful in modifying: (i) binding constants [2] for use in selective metal extraction and as therapeutic agents [3], (ii) the reactivity of metal centers with regard to biomimetic [4–6] and catalytic functions [7,8] and recently, (iii) in the self-assembly and formation of supramolecular structures [9–12] and in materials chemistry [13]. Among bifunctional ligands, those with a macrocyclic ring and a chelating pendant arm are unique in that they offer facile routes to heteronuclear supramolecular structures through self-assembly [14]. Specifically, such processes can be assisted by metal ion templates which may be different from the metal ion present in the macrocycle [15]. Since the reactivity of metal centers is controlled by their coordination environments, such ligands offer a versatile approach to building unique supramolecular structures of rich chemistry and application [16].

As a result of the relative ease of functionalization of the secondary nitrogens in cyclam [17], the majority of the ligands derived from cyclam have either chelating moieties such as 2,2′-bipy [18,19] or mostly monoden-

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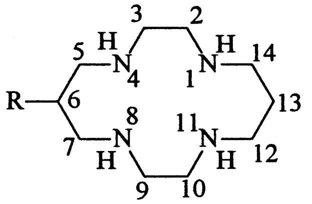
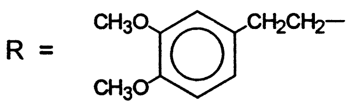
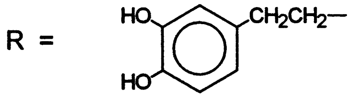
tate pendant arms such as aminoethyl or hydroxyethyl groups on one of the nitrogens [20]. Bridging of the nitrogens with suitable agents have also been described [21]. A variety of pendant arms with groups such as phenol, pyridyl and other heterocyclic rings substituted at the C(5) position of cyclam have been prepared and studied by Kimura [22,23]. In all these cases, owing to their proximity and orientation, these monodentate substituents invariably coordinate to the metal center in the macrocyclic cavity. Tabushi's cyclization method offers a general route to C(6)-substituted cyclams [24,25][1]. However, other methods have also been described for specific substituents [26,27].



R = H = Cyclam



for L_1



for H_2L_2

In the ligands L_1 and H_2L_2, described here, we have introduced a 3,4-disubstituted phenylethyl unit into the C(6) position of cyclam. The 3,4-disubstitution in the phenyl group and the ethylene bridge connecting this group to the 6-position in cyclam, orients the catecholate oxygens in L_2 for exodentate chelation and hence, makes them available for template assisted self-assembly of cyclam units on a suitable metal ion such as Fe(III), Ga(III) and Al(III). We report here the syntheses of Cu(II) and Ni(II) complexes of L_1 and H_2L_2 and preliminary data on a spectroscopic investigation of the formation of multinuclear species on Fe(III).

2. Experimental

2.1. Materials

Reagents purchased from Aldrich Chemical Co., and 1,4,8,11-tetraazaundecane (97%) purchased from Acros Chemical Co., were used without further purification. Non-aqueous solvents and electrolytes were purified by standard methods [28].

*2.2. Preparation of 1,2-dimethoxy-4-(β-tosyloxyethyl)-benzene (**1**)*

To 20 g (0.109 mol) of 3,4-dimethoxy phenylethanol dissolved in 250 ml of CH_2Cl_2, was added 20.76 g (0.109 mol) of *p*-toluene sulfonylchloride under stirring. The resulting clear solution was cooled in an ice bath and 15 ml (0.118 mol) of Et_3N was dropped in slowly over a period of 30 min, while maintaining the temperature below 10°C. This mixture was stored in a refrigerator for 16 h. Most of the precipitated $[Et_3NH]Cl$ was filtered off under suction. The filtrate was concentrated in a rotary evaporator and the resulting oil was dissolved in dry CH_3COCH_3 and filtered to remove traces of $[Et_3NH]Cl$. The filtrate was concentrated and traces of solvents were removed under vacuum. A clear pale yellow liquid was obtained. Yield: 32 g (97% based on the alcohol). ^1H NMR ($CDCl_3$, ppm): 2.40 (s, 3H, CH_3), 2.80 (t, 2H, Ph–CH_2–), 3.79, 3.81 (s, 6H, –OCH_3), 4.19 (t, 2H, CH_2–OTs), 6.62 (m, 3H, Ar), 7.41 (d of d, 4H, tosyl group). ^{13}C NMR: 21.5 (CH_3–Ar) 34.5 ($PhCH_2$), 70.8 (CH_2OTs), 55.7 and 55.8 (OCH_3), 111.2, 111.9, 120.8, 121.0, 126.0, 127.7, 129.7, 144.7, 147.9 and 148.8 (aromatics). FAB MS: Calc. for $C_{17}H_{20}SO_5$, 336.10. Found, 336.10%.

*2.3. Preparation of 1,2-dimethoxy-4-(β-iodoethyl)-benzene (**2**)*

To a solution of 12.0 g (0.08 mol) of anhydrous NaI in 100 ml of CH_3COCH_3, a solution of 22.7 g (74.5 mmol) of **1** in 100 ml of CH_3COCH_3 was added. An immediate reaction occurred with the precipitation of sodium tosylate. The mixture was refluxed for 1 h to ensure the completion of the reaction. The precipitated sodium tosylate was filtered off under suction and the filtrate was concentrated to remove acetone. The resulting oil was dissolved in CH_2Cl_2, washed several times with a solution of $Na_2S_2O_3$ until faint yellow in color, filtered, dried over anhydrous sodium sulfate and filtered. The filtrate was concentrated and traces of solvents were removed under vacuum to form a pale yellow oil. Yield: 15.72 g (91% based on the tosylate). ^1H NMR ($CDCl_3$, ppm): 2.10 (t, 2H, Ph–CH_2), 3.30 (t, 2H, CH_2–I), 3.79, 3.81 (s, 6H, OCH_3), 6.75 (m, 3H, aromatic). ^{13}C NMR: 6.45 (CH_2–I), 39.9 (Ph–CH_2), 55.8 (OCH_3), 112.4, 112.9, 121.6, 133.3, 147.8, 148.1 (aromatic). FAB MS. Calc. for $C_{10}H_{13}O_2I$: 291.99. Found: 291.9% [M^+].

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[1] 6-(β-(2,3-Dimethoxyphenyl)ethyl cyclam and 6-dipy substituted cyclams have been prepared.

2.4. Preparation of (β-(3,4-dimethoxyphenyl)ethyl)-dimethylmalonate (3)

In a 500-ml three-necked flask equipped with a N_2 inlet and a condenser, 1.70 g (0.068 mol) of 97% NaH was suspended in 150 ml of dry $CH_3OCH_2CH_2OCH_3$ and stirred with a magnetic stirrer. Neat dimethyl malonate, 9.0 g (0.0687 mol) was dropped in slowly, brisk effervescence occurred due to liberation of hydrogen and a clear solution formed. This solution was heated to 60–65°C and 20.2 g (0.068 mol) of **2** in 50 ml of $CH_3OCH_2CH_2OCH_3$ was added dropwise over a period of 5 h. The reaction mixture was maintained at this temperature for a further period of 20 h, after which it was cooled and concentrated to dryness. The residue was suspended in 200 ml of water and extracted with 2×75 ml of CH_2Cl_2. The combined extracts were washed successively with 50 ml of 0.1 M HCl and 2×50 ml of water and dried over anhydrous Na_2SO_4. The bulk of the solvent was removed in a rotary evaporator and final traces under vacuum to obtain a very pale yellow oil. Yield: 19.4 g (97% based on the iodide). ^{1}H NMR ($CDCl_3$, ppm): 2.52 (t, 2H, CH_2–CH), 2.64 (t, 2H, $PhCH_2$), 3.68 (s, 6H, OCH_3), 4.05, 4.15 (s, 6H, $C(O)OCH_3$), 6.65 (m, 3H, aromatic). ^{13}C NMR: 30.6 ($PhCH_2$) 32.8 (CH_2–CH), 50.7 (CH), 52.5 ($C(O)OCH_3$), 55.7, 55.8 (OCH_3), 111.2, 111.7, 120.4, 137.0, 147.4, 148.8 (aromatic), 169.7 (C=O). MS (CH_4 CI): Calc. for $C_{15}H_{20}O_6$: 296.12. Found: 297 [$M+1$, 65%], 325 [$M+29$, 5%] and 337 [$M+41$, 5%], 165 [dimethoxyphenylethyl, 100%].

2.5. Preparation of 6-(β-(3,4-dimethoxyphenyl)ethyl)-5,7-dioxo-1,4,8,11-tetraazacyclotetradecane (4)

To a solution of 7.4 g (0.025 mol) of **3** dissolved in 500 ml of freshly distilled anhydrous ethanol, a solution of 4.0 g (0.025 mol) of 1,4,8,11-tetraazaundecane (2,3,2-tet) was added and stirred using a magnetic stirrer. A dry N_2 atmosphere was maintained and the mixture was refluxed gently (85–90°C) for 7 days. Ethanol was removed in a rotary evaporator and the resulting oil was further evacuated under vacuum at 60°C to remove traces of ethanol and other volatile impurities. A sticky solid (9.80 g) was obtained. This solid was dried under vacuum and used for reduction without further purification. A small quantity of this impure lactam was purified as follows. A total of 2.00 g of the crude product in 50 ml of water was diluted with 350 ml of acetone to yield 1.1 g of pure **4** as a white precipitate, which was filtered off and dried under vacuum. It was highly hygroscopic. Yield: 55% based on **3**. M.p.: > 210°C. ^{1}H NMR ($CDCl_3$, ppm): 1.5 (m, 2H, C–CH_2–C), 2.06 (d of d, 2H, $PhCH_2$), 3.04 (d of d, 2H, Ph–C–CH_2), 2.40 and 2.57 (m, 12H, CH_2–N), 3.70 and 3.73 (s, 6H, –OCH_3), 3.46 (d of t, 1H, C(O)–CH–C(O)), 6.60 (m, 3H, aromatic). ^{13}C NMR: 33.1 ($PhCH_2$) 38.9 ($PhCCH_2$), 28.5 (C–CH_2–C), 48.9, 50.5 (NH–C) and 54.3 (C(O)–C–C(O), cyclam ring carbons), 55.7 and 55.8 (OCH_3), 111.0, 111.7, 120.2, 133.7, 147.1 and 148.6 (aromatic carbons), 170.8 (C=O). FAB MS (negative ion). Calc. for $C_{20}H_{32}N_4O_4$: 392.24. Observed: 391.2 $[M-H]^-$.

2.6. Preparation of 6-(β-(3,4-dimethoxyphenylethyl))-1,4,8,11-tetraazacyclotetradecane (L_1)

To a suspension of 15.7 g (55% pure, 0.022 mol) of crude **4** in 100 ml of $CH_3OCH_2CH_2OCH_3$, 500 ml of 1.0 M BH_3·THF was added under a N_2 atmosphere. The mixture was stirred manually with a spatula and the crisp white solid that formed was crushed carefully to form a good suspension. This suspension was stirred with a magnetic stirrer and refluxed in a N_2 atmosphere for 16–20 h. The mixture was occasionally cooled and the white solids sticking to the sides and the bottom of the flask were released with a spatula to maintain a good suspension. The reaction mixture was cooled and excess borane was decomposed by dropwise addition of 10% HCl under vigorous stirring. The organic solvents were removed in a rotary evaporator, the resulting aqueous solution was made strongly acidic (6 M HCl) and refluxed for 30 min. The mixture was cooled and filtered to remove any insoluble material. The filtrate was made strongly basic (pH 12) with 30% NaOH solution and the free ligand was extracted with $CHCl_3$ in a continuous extractor for 12 h. The $CHCl_3$ extract was dried over anhydrous Na_2SO_4 and concentrated to dryness. The resulting oily impure ligand (15.1 g) was dissolved in methanol and acidified with concentrated HCl until a clear solution was formed. This solution was concentrated to dryness and the resulting light brown oil was digested with 100 ml of anhydrous ethanol and the ethanol was decanted off. This process was repeated four or more times until the brown oil was transformed to a light creme colored solid which was then filtered under suction. This highly hygroscopic solid weighed 5.56 g. Yield: 46% based on 55% pure lactam. *Anal.* Calc. for $C_{20}H_{38}N_4O_2 \cdot 4HCl \cdot 2H_2O$: C, 43.96; H, 8.12; N, 10.25. Found: C, 43.53; H, 7.92; N, 10.72%. ^{1}H NMR (D_2O, ppm): 1.76 (2H, m, C–CH_2–C), 2.11 (3H, m, CH_2–CH–), 2.58 (2H, t, $ArCH_2$–), 3.20 and 3.38 (8H each, m, NH–CH_2–), 3.64 and 3.66 (3H, s, CH_3O–), 6.76–6.82 (3H, m, Ar). ^{13}C NMR: 22.7 (C–CH_2–C), 33.7, 35.5 (Ph–CH_2–CH_2–), 43.3 (–CH–), 44.1, 44.4, 45.0 and 49.3 (CH_2– NH), 57.5 (CH_3O–), 112.1, 112.4, 121.0, 134.1, 146.6 and 148.1 (aromatic carbons). MS: Calc. for $[(C_{20}H_{36}N_4O_2)H]^+$, 365.28. Observed 365.0. HRMS: Calc. for $[(C_{20}H_{36}N_4O_2)H]^+$, 365.2916. Observed 365.2918.

2.6.1. [Cu(L_1)Br_2]

To a solution of 6.73 g of $CuBr_2$ (0.03 mol) in 200 ml of H_2O, a solution of 10.07 g of the crude ligand dissolved in 130 ml of EtOH was added under stirring. A dark blue color developed instantaneously. The mixture was refluxed for 16 h and concentrated to dryness. The resulting solid was dissolved in 200 ml of H_2O and filtered to remove any insoluble materials. The clear filtrate was acidified with 10 ml of 48% HBr and extracted with $CHCl_3$ in a continuous extractor. The $CHCl_3$ extract was dried over anhydrous Na_2SO_4 and concentrated to dryness to yield 4.0 g of a crisp dark pink solid. Yield: 24.7% based on crude ligand. MS (ES): *m/e* Calc. for $C_{20}H_{36}N_4O_2CuBr$ [*M* − Br]: 506.14. Found: 505.9. A peak for the dimeric species $[(C_{20}H_{36}N_4O_2CuBr)\cdots Br\cdots(C_{20}H_{36}N_4O_2CuBr)]^+$ at 1095 was also observed. HRMS: Calc. for $[C_{20}H_{36}N_4O_2CuBr]^+$, 506.1319. Observed 506.1314.

2.6.2. [Cu(BrL_1)]Br_2

To a solution of 100 mg (17.0×10^{-5} mol) of [Cu(L_1)]Br_2 in 20 ml of $CHCl_3$, 5 ml of a 1% solution of Br_2 in $CHCl_3$ was added and the mixture was stirred for 2 h under nitrogen. Excess Br_2 and the solvent was removed and the resulting solids were carried over for demethylation. Yield: 100 mg (89% based on [Cu(L_1)]Br_2) *Anal.* Calc. for $C_{20}H_{35}N_4O_2CuBr_3$: C, 36.03; H, 5.29; N, 8.40; Cu, 9.53. Found: C, 36.75; H, 5.57; N, 8.42; Cu, 9.68%. MS (ES): Calc. for $[C_{20}H_{35}N_4O_2CuBr_2]$, 586.88. Observed 586.2.

2.6.3. [Ni(L_1)Br_2]

To 0.60 g (2.40 mmol) of $Ni(OAc)_2\cdot4H_2O$ dissolved in 100 ml of 50% aqueous ethanol, a solution of 1.00 g (1.83 mmol) of $L_1\cdot4HCl\cdot2H_2O$ in 50 ml of H_2O was added and the solution was heated in an oil bath at 60–65°C for 6 h. The solution pH was adjusted to 7.0 by dropwise addition of 1.0 M NaOH solution and ethanol was removed under vacuum. The resulting aqueous solution was made acidic with 10 ml HBr and extracted with $CHCl_3$ in a continuous extractor for 8 h. The resulting pale yellow solution was dried over anhydrous Na_2SO_4 and concentrated to dryness to give a pale pink solid. Yield: 0.22 g (83% based on pure $L_1\cdot4HCl\cdot2H_2O$). ^{1}H NMR (D_2O): 1.04 (1H, m, H(6)), 1.23 (2H, m, H(13)), 1.59 (2H, m, H(α)), 1.81 (H, m, H(13a)), 2.40 (2H, m, H(9,14)), 2.50 (2H, m, H(β)), 2.59 (2H, m, H(9,14)), 3.13 (4H, m, H(5,7)), 3.64, 3.73 (6H, s, –OCH_3), 6.86 (3H, m, aromatic). HRMS: Calc. for $[C_{20}H_{36}N_4O_2NiBr]^{2+}$, 501.1375. Observed 501.1372.

2.6.4. [Cu(H_2L_2)Br]Br

To 100 mg (0.17 mmol) of [Cu(L_1)Br_2] dissolved in 10 ml of CH_2Cl_2, 0.3 ml (1.19 mmol) of neat BBr_3 was added at room temperature. During addition of BBr_3, the mixture was stirred vigorously and an oxygen free N_2 atmosphere was maintained. The pink solution of [Cu(L_1)Br_2] turned reddish immediately and remained cloudy throughout the reaction. After 4 h, the solvent and excess BBr_3 were removed under vacuum to give a dark red fuming solid. Anhydrous methanol (15 ml) was added and the solution was refluxed for 30 min and filtered to remove any insoluble materials. The filtrate was concentrated to dryness under vacuum to yield 50 mg of a red–violet hygroscopic solid. Yield: 53% based on [Cu(L_1)Br_2]. HRMS: Calc. for $[Cu(L_1)Br_2]^+$, 478.1006. Observed 478.0999.

2.6.5. [Cu(H_2(BrL_2))Br]Br·H_2O

[Cu(BrL_1)Br_2] (100 mg (0.15 mmol)) was used and the reaction was carried out exactly as described above for [Cu(L_2)Br]Br. The violet solid obtained was recrystallized from 80% aqueous methanol. Yield: 77 mg (80% based on [Cu(BrL_1)Br_2]. *Anal.* Calc. for $C_{18}H_{33}N_4O_3CuBr_3$: C, 32.92; H, 5.06; N, 8.53. Found: C, 33.68; H, 5.07; N, 8.52%. MS (ES): Calc. for $[C_{18}H_{33}N_4O_3CuBr_2]^+$, 558.04. Observed 558.0.

2.6.6. [Ni(H_2L_2)]Br_2

Demethylation was carried out exactly as described in the above cases except 100 mg (0.17 mmol) of [Ni(L_1)Br_2] was used. Soon after the addition of BBr_3, the reaction mixture turned brownish and cloudy. The dark solid obtained from the reaction mixture upon dissolution in methanol gave a yellowish–brown solution. As a dry solid, the complex was very dark in color and was also found to be very hygroscopic. Yield: 80 mg (85% based on [Ni(L_1)Br_2]). HRMS: Calc. for $[C_{18}H_{32}N_4O_2NiBr]^+$, 473.1062. Observed 473.1074.

2.6.7. $[(Me_4N^+)_3][Fe(M(L_2)Br_2)_3]$ ($M = Cu^{2+}$ or Ni^{2+})

To a mixture of 10 ml of 8.0×10^{-4} M [M(H_2L_2)Br_2] and 0.53 ml of 5×10^{-3} M $[Fe(OH_2)_6](ClO_4)_3$ or $[Fe(NO_3)_3]\cdot9H_2O$ in aqueous MeOH (8:2 MeOH:H_2O), was added aliquots of 5 μl of 0.1 M $[Me_4N][OH]\cdot5H_2O$ in water with stirring under a N_2 atmosphere. The formation of the Fe–catecholate complex was monitored by UV–Vis spectroscopy at 500 nm for Ni and at 525 nm for the Cu complex, respectively, until the maximum absorption values were reached. The resulting dark purplish–red solutions were stable for only about 10 min after which they tended to precipitate out. The individual solutions were diluted with 25 ml of absolute EtOH and stirred at this point for a further period of 15 min. The resulting dark purple solids were removed by centrifugation, washed with 10 ml aliquots of EtOH and Et_2O and dried under vacuum. Yield: 4–5 mg (77–96%). See Tables 4 and 5 for UV–Vis and EPR spectroscopic characterizations.

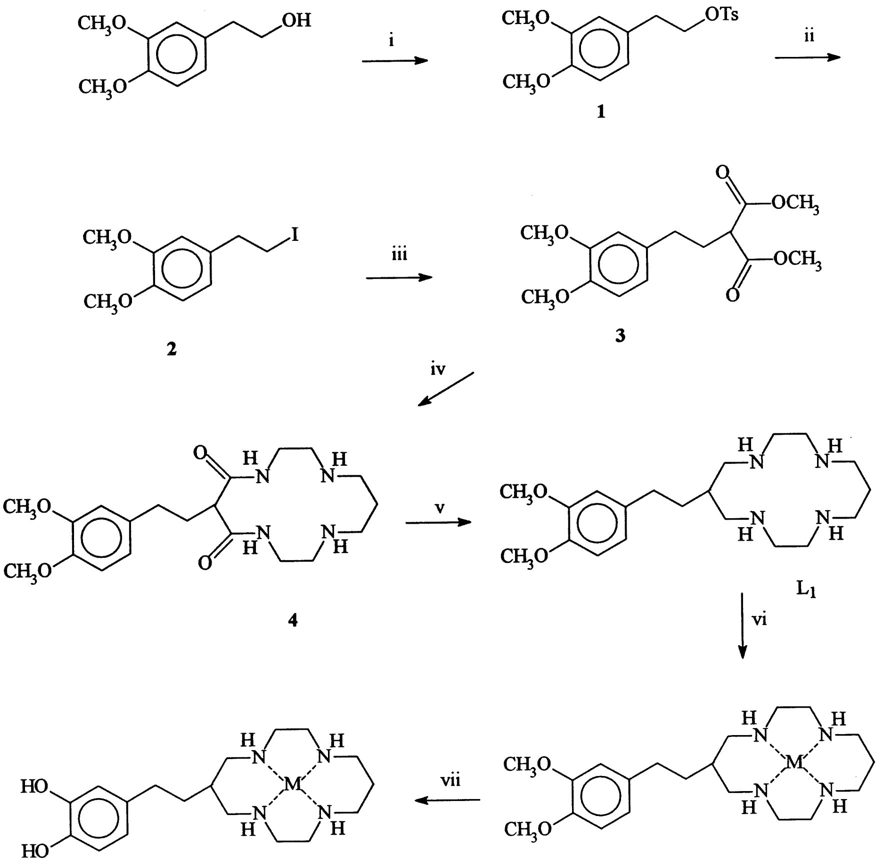
2.7. Crystallographic data collection and structure solution

Dark purple single crystals suitable for X-ray crystallography were obtained by slow diffusion of ether into a chloroform solution in the case of $[Cu(L_1)Br_2]$ and from a solution of aqueous methanol (80%) in the case of $[Cu(BrL_2)]Br_2{\cdot}H_2O$. Experimental factors common to data collection for both crystals are as follows: a Siemens SMART/CCD diffractometer equipped with an LT-II low temperature device was used to collect diffraction data at 193(2) K using graphite-monochromated X-radiation of $\lambda = 0.71073$ Å and ω–2θ methods. An index range of $-10 \leq h \leq 10$, $-14 \leq k \leq 13$, $-14 \leq l \leq 18$ for $[Cu(L_1)Br_2]$ and $-19 \leq h \leq 22$, $-14 \leq k \leq 15$, $-16 \leq l \leq 16$ for $[Cu(BrL_2)]Br_2{\cdot}H_2O$ was used. Corrections for absorption were made using the SADABS program. SHELXTL [29] was used for structure solutions and refinements were based on F^2. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed in calculated positions and refined isotropically on the basis of corresponding C atoms [$U(H) = 1.2\ U_{eq}$ (C)]. Pertinent crystallographic information is given in Table 1.

Microanalyses were performed by Canadian Microanalytical Services Ltd., Delta, B.C., Canada. HRMS was used for identification of samples that were hygroscopic. Mass spectra were obtained either on a Finnigan 3200 GCMS using chemical ionization methods or on a Kratos Concept Model 2H mass spectrometer by FAB (negative or positive ion mode) and electro-spray (ES) techniques. In all cases, the theoretical isotopic distributions of relevant peaks were calculated and were found to agree with the experimentally observed spectra. All the m/e values observed by HRMS were within ± 5 ppm of calculated values. UV–Vis spectra were recorded on a Cary 17 dual beam spectrophotometer. EPR spectra were recorded in an X-band Varian ES-6 spectrometer at liquid N_2 temperatures in solvents as indicated in the text. EPR spectra of Fe(III) catecholate species were obtained by preparing a uniform mixture with MgO and by cooling this matrix in liquid N_2 temperatures. Diphenyl picryl hydrazide (DPPH, $g = 2.0037$) was used as an external standard. A three-electrode cell configuration was used in electrochemical experiments. Platinum electrodes were used as working electrodes. Redox potentials in aqueous media were measured against a saturated calomel electrode (SCE), (0.244 V versus NHE) and an Ag/Ag^+ electrode [30] was used for measurements in non-aqueous media. The Fc/Fc^+ couple was used either as an external or an internal standard. Cyclic voltammetry experiments were performed using a Princeton Applied Research Galvanostat/Potentiostat model 273 instrument interfaced to an IBM PC. The Coreware version 2 and Corrview, version 1.5 software packages for Windows (Scribners Associates, Inc.) were used to collect and process cyclic voltammetry data. Reversibility of cyclic voltammograms were confirmed as described elsewhere [31].

Table 1
Crystal data and structure parameters

Compound	$[Cu(L_1)Br]Br{\cdot}H_2O$	$[Cu(H_2(BrL_2))Br_2]$
Empirical formula	$C_{20}H_{36}Br_2CuN_4O_2$	$C_{18}H_{25}Br_3CuN_4O_3$
Formula weight	587.89	648.69
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
Unit cell dimensions		
a (Å)	8.4572(7)	17.054(2)
b (Å)	11.2250(10)	11.7801(11)
c (Å)	13.9768(12)	12.6049(12)
α (°)	97.864(2)	90.00
β (°)	97.087(2)	108.790(2)
γ (°)	108.727(2)	90.00
V (Å^3)	1224.8(2)	2397.4(4)
Z	2	4
D_{calc} (Mg m^{-3})	1.594	1.797
Absorption coefficient (mm^{-1})	4.176	5.936
$F(000)$	598	1276
θ Range (°)	1.49–25.00	2.14–25.00
Crystal size (mm)	$0.5 \times 0.3 \times 0.2$	$0.05 \times 0.05 \times 0.02$
Reflections collected	6064	11 233
Unique	4031 [$R_{int} = 0.0449$]	4136 [$R_{int} = 0.1279$]
Data/restraints/parameters	3745/0/262	4136/0/263
Goodness-of-fit on F^2	0.939	0.965
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0785$, $wR_2 = 0.1880$	$R_1 = 0.0832$, $wR_2 = 0.1576$
Largest difference peak and hole (e Å^{-3})	1.450, -1.778	0.737, -0.869



Scheme 1. Reaction conditions: (i) TsCl–Et_3N–CH_2Cl_2; (ii) NaI–acetone; (iii) NaH–$CH_2(COOMe)_2$–$MeOCH_2CH_2OMe$; (iv) 2,3,2-tet–EtOH reflux 7 days; (v) THF–BH_3 reflux 24 h; (vi) M^{2+} (M = Ni or Cu)–HBr extraction; (vii) BBr_3–$CHCl_3$–RT.

3. Results and discussion

3.1. Syntheses of ligands and complexes

The preparation of ligands and complexes is outlined in Scheme 1. The ligand, L_1 was synthesized based on an extension of the method of Tabushi et al. [24]. The synthesis of the iodide **2** was best achieved via the tosylate under very mild conditions. The precursor ester **3** was prepared from a reaction of the carbanion of the dimethyl malonate ester with **2**. Conventional methods such as refluxing with K_2CO_3 in THF gave very poor yields with side products arising from β-elimination. The method described here with NaH as the base and $CH_3OCH_2CH_2OCH_3$ as the solvent gave excellent yields. Syntheses of **1** to **3** proceeded without any side products and the crude products from these reactions were found to be very pure and were used without further purification. The cyclization method was not efficient and was the critical step that controlled the overall yield of the complexes. Even under high dilution conditions, the yields of L_1 were only 30–35% and the products were often contaminated with unreacted 2,3,2-tet and β-elimination products (3,4-dimethoxystyrene and corresponding polymeric products) arising from **3**. The cyclic lactam **4** was difficult to purify and hence, the bulk product was taken to the reduction step without further purification. Only a small quantity was purified for characterization purposes. The high stability of macrocyclic complexes in acidic media [32] was exploited to extract the complexes, $[M(L_1)Br_2]$ (M = Ni(II) and Cu(II)) into chloroform, free of acid unstable complexes. Solid cyclam complexes of the type, $[M(cyclam)X_2]$ (M = Cu(II) or Ni(II) and X = Cl^-Br^-) are neutral and soluble in $CHCl_3$, but are not easily extracted into $CHCl_3$ from aqueous media [33]. However, due to axial coordination, the complexes of L_1 described here are neutral and also, the presence of 3,4-dimethoxyphenylethyl moiety renders these complexes more lipophilic, which facilitated their extraction into $CHCl_3$. The purity of complexes thus obtained were checked by chromatography on a Sephadex CM C-25 cation exchange resin using 0.3 M NaCl as eluant. The complexes of L_1 described here are solids, but are difficult to purify by crystallization. However, the bromo derivatives were easily crystallized. The complexes of H_2L_2 are relatively stable in oxygen and were also difficult to crystallize. Due to their hygroscopic nature, they tend to form oily layers which solidified to amorphous solids upon drying in vacuo. Hence, these

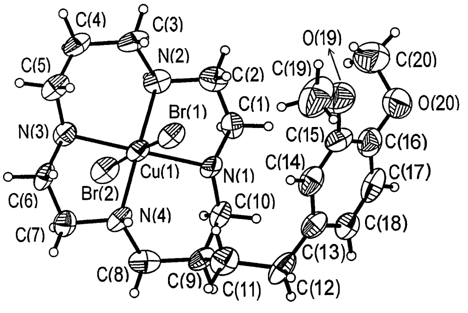


Fig. 1. ORTEP diagram of $[Cu(L_1)Br_2]$ (30% ellipsoid).

complexes were best analyzed by high resolution mass spectroscopy using the ES technique.

3.2. Structure of $[Cu(L_1)Br_2]$

An ORTEP diagram of $[Cu(L_1)Br_2]$ is shown in Fig. 1. Although, a bromide bridged dimeric species, $[(C_{20}H_{36}N_4O_2CuBr)\cdots Br\cdots(C_{20}H_{36}N_4O_2CuBr)]^+$ was observed in the mass spectrum, the crystal contained only the discrete molecules of the neutral dibromo complex. The Cu(II) ion sits well within the macrocyclic cavity and in the plane defined by the four nitrogen donors. An average Cu–N distance of 2.026 Å observed in this compound is typical of such distances observed in various Cu(II) complexes of cyclam derivatives [34,35]. With two bromide ions occupying the axial sites, the coordination geometry around the Cu(II) ion is pseudo octahedral. The Cu–Br(1) distance is slightly longer (2.9941 Å) than the Cu–Br(2) distance (2.9251 Å). Other structural parameters of the cyclam ring are very similar to those observed in similar complexes [36–38]. As expected, the O–C(Ar) distances, C(15)–O(19) and C(16)–O(20) (1.334 and 1.359 Å) are distinctly shorter than the O–CH_3 distances, O(19)–C(19) and O(20)–C(20) (1.432 and 1.450 Å). The ethylene bridge connecting the cyclam ring and the aromatic ring adopts a *cisoid* conformation. Important bond distances and angles are listed in Tables 2 and 3.

Table 2
Important bond distances (Å) and bond angles (°) for $[Cu(L_1)Br]Br\cdot H_2O$

Cu(1)–N(4)	2.004(7)	N(4)–Cu(1)–N(1)	94.5(3)
Cu(1)–N(1)	2.023(7)	N(4)–Cu(1)–N(3)	86.2(3)
Cu(1)–N(3)	2.024(7)	N(1)–Cu(1)–N(3)	178.4(3)
Cu(1)–N(2)	2.029(7)	N(4)–Cu(1)–N(2)	177.9(3)
Cu(1)–Br(2)	2.9251(16)	N(1)–Cu(1)–N(2)	85.5(3)
Cu(1)–Br(1)	2.9941(16)	N(3)–Cu(1)–N(2)	93.8(3)
N(1)–C(10)	1.462(11)	N(4)–Cu(1)–Br(2)	90.7(2)
N(1)–C(1)	1.485(10)	N(1)–Cu(1)–Br(2)	93.4(2)
N(2)–C(3)	1.462(11)	N(3)–Cu(1)–Br(2)	85.2(2)
N(2)–C(2)	1.490(12)	N(2)–Cu(1)–Br(2)	91.4(2)
N(3)–C(5)	1.471(12)	N(4)–Cu(1)–Br(1)	86.8(2)
N(3)–C(6)	1.499(11)	N(1)–Cu(1)–Br(1)	86.4(2)
N(4)–C(7)	1.470(11)	N(3)–Cu(1)–Br(1)	95.1(2)
N(4)–C(8)	1.503(12)	N(2)–Cu(1)–Br(1)	91.1(2)
		Br(2)–Cu(1)–Br(1)	177.48(5)

Table 3
Important bond distances (Å) and bond angles (°) for $[Cu(BrL_2)Br_2]$

Cu(1)–N(2)	2.008(9)	N(2)–Cu(1)–N(4)	175.4(4)
Cu(1)–N(4)	2.008(8)	N(2)–Cu(1)–N(1)	86.3(4)
Cu(1)–N(1)	2.010(9)	N(4)–Cu(1)–N(1)	92.6(4)
Cu(1)–N(3)	2.039(9)	N(2)–Cu(1)–N(3)	95.0(4)
Cu(1)–Br(2) # 1	2.904(2)	N(4)–Cu(1)–N(3)	86.1(4)
Br(2)–Cu(1) # 1	2.904(2)	N(1)–Cu(1)–N(3)	177.8(4)
Br(3)–C(18)	1.912(14)	N(2)–Cu(1)–Br(2) # 1	89.2(3)
O(1)–C(16)	1.38(2)	N(4)–Cu(1)–Br(2) # 1	95.3(3)
O(2)–C(15)	1.36(2)	N(1)–Cu(1)–Br(2) # 1	92.4(3)
N(1)–C(2)	1.458(14)	N(3)–Cu(1)–Br(2) # 1	89.5(3)
N(1)–C(3)	1.467(13)		
N(2)–C(4)	1.474(14)		
N(2)–C(5)	1.479(14)		
N(3)–C(7)	1.48(2)		
N(3)–C(8)	1.485(14)		
N(4)–C(9)	1.485(13)		
N(4)–C(10)	1.509(13)		

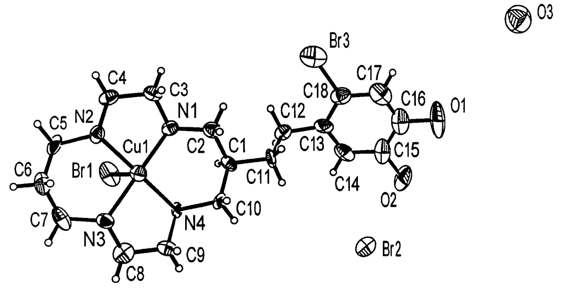


Fig. 2. ORTEP diagram of $[Cu(BrL_2)Br]Br\cdot H_2O$ (30% ellipsoid).

3.3. Structure of $[Cu(H_2(BrL_2))Br]Br\cdot H_2O$

An ORTEP view of the molecule is shown in Fig. 2. As in the previous structure, many of the features pertaining to the macrocycle are very similar except the coordination geometry around the Cu(II) ion. Unlike in $[Cu(L_1)Br_2]$, the Cu(II) is square pyramidal and with the coordinated bromide (Cu–Br(1)) at 2.904(2) Å. The other bromide ion and the water molecule do not show any interaction at all with the metal center. The bulky bromine at C18 appears to exert an influence on the conformation of the ethylene bridge linking the aromatic ring to the cyclam. Unlike in $[Cu(L_1)Br_2]$, this bridge adopts a *transoid* conformation pushing the aromatic group away from the macrocycle.

3.4. UV–Vis spectroscopy

The UV–Vis spectroscopic data for the complexes are listed in Table 4. The complexes of L_1 and L_2 exhibit features characteristic of cyclam complexes [39,40] along with the aromatic absorption bands in the ultra-violet region. In $CHCl_3$, the bands at 500 nm ($\varepsilon = 30\ M^{-1}cm^{-1}$) for $[Ni(L_1)Br_2]$ and at 530 nm ($\varepsilon = 57\ M^{-1}cm^{-1}$) for $[Cu(L_1)Br_2]$ indicate that the bromide ions are coordinated axially and hence the metal centers adopt pseudo octahedral geometry. However, in aqueous medium, a mixture of octahedral and square planar species was present. In particular, this is clearly evident from the ^1H NMR spectrum of the $[Ni(L_1)]^{2+}$ species which showed predominantly sharp lines corresponding to the diamagnetic square planar species [41]. The aromatic substituents were not expected to interact with the metal centers in the cyclam cavity. Such interactions would be obvious, particularly, in the case of $[Ni(H_2L_2)]^{2+}$, where deprotonation of the catecholate rings with bases could be expected to produce a dramatic change in the spectroscopic features. However, no such change was observed. In the case of $[Cu(H_2L_2)]^{2+}$, there was also no change observed under anaerobic conditions. However, it is well known that in basic medium, Cu(II) is known to catalyze the aerial oxidation of phenolic groups [42] and in the case of $[Cu(H_2L_2)]^{2+}$, a brown insoluble product was observed. However, this has not been fully investigated at present and will be the subject of a future report.

3.5. Electrochemistry

Cyclic voltammograms of complexes of L_1 were studied both in $CHCl_3$ and in aqueous media, and those of L_2 in aqueous methanolic medium. Under the conditions employed, the Cu(II) complexes of both L_1 (in $CHCl_3$ and in H_2O) and H_2L_2 (in aqueous MeOH) did not show any characteristic redox activity. $[Ni(L_1)Br_2]$ in $CHCl_3$ did show a redox wave for the $Ni^{2+/3+}$ couple. At 10 mV s^{-1} this wave was very sharp with $E_{p,a}$ at 0.780 mV and $E_{p,c}$ at 0.900 mV suggestive of a strong tendency of the redox active species to be adsorbed on the electrode surface (supplementary figure 1). This could be due to formation of bromo-bridged species of the type $[\cdots Br[(L_1)Ni^{III}]\cdots Br\cdots\ [Ni^{III}(L_1)]\text{-}Br\cdots]_n^{3n+}$, which the d^7 Ni(III) ion could enhance in $CHCl_3$. This might be compared with the tendency of $[Cu(L_1)Br_2]$ to form a dimeric species as observed in mass spectroscopic experiments. At higher scan rates (100–1000 mV s^{-1}), particularly when these waves tend to broaden, the formation of this polymeric species may be very slow. However, in aqueous medium no such phenomenon was observed and only a quasi-reversible (supplementary figure 2) wave was observed ($E_{1/2} = 0.98$ V; $\Delta E_p = 135$ mV; 100 mV s^{-1}). The reversibility improved considerably in acidic medium and also in the presence of chloride. However, there was no dramatic lowering of the redox potential as has been observed in the cyclam complexes [43]. The $[Ni(H_2L_2)]^{2+}$ cation also showed a scan-rate dependent irreversible wave ($E_{p,a} = 1.19$ V; $E_{p,a} = 0.839$ V; $\Delta E_p = 351$ mV; 10–1000 mV s^{-1}; supplementary figure 3). The Ni(III) species of both L_1 and H_2L_2 were reasonably stable when prepared chemically (vide infra). As might be expected, the Ni(III) complex of L_1 was indefinitely stable compared with that of H_2L_2 which decomposed over time owing to internal oxidation of the catecholate groups.

3.6. EPR spectroscopy

The EPR spectra of the Cu(II) (in 1:1 EtOH–DMF glass) and Ni(III) species (in aqueous medium) were recorded with no distinct differences observed between the complexes of L_1 and H_2L_2. The Cu(II) and Ni(III) spectra closely resembled those of the Ni(III) and Cu(II) complexes of cyclam [39,44] with *g* features as listed in Table 5. The Ni(III) species were prepared in aqueous medium with $K_2S_2O_8$ as the oxidant. The Ni(III) species of L_1 was indefinitely stable compared with a lifetime of about 1 h at room temperature for the complex of L_2 (3×10^{-4} M). There was no evidence for any steric contribution from the aromatic substituents. Both Ni(III) species formed *trans*-dichloro species as clearly demonstrated by the hyperfine interactions. There is no evidence that coordination of the phenolic groups to the Ni(III) center with a subsequent dissociation of protons.

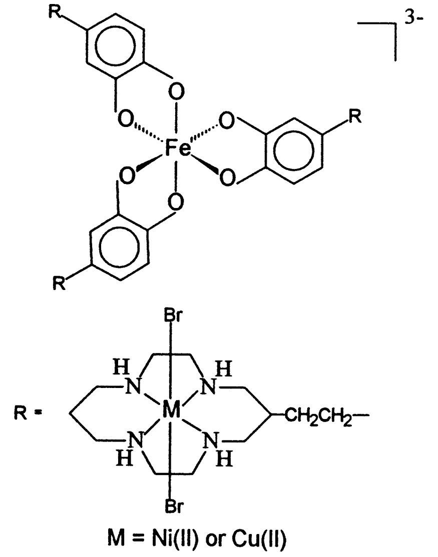
Table 4
UV–Vis spectroscopic data for complexes

Compound	Solvent	λ (nm) (ε (M^{-1} cm^{-1}))
$[Cu(L_1)Br_2]$	$CHCl_3$	530(57), 285 sh (5980), 279(6700), 240(9500)
$[Ni(L_1)Br_2]$	$CHCl_3$	500 br sh(30), 350(183), 287(4200), 273(6070)
$[Cu(L_2)]Br_2$	8:2 CH_3OH–H_2O (v/v)	487(132), 278(6770), 225 sh(12 410)
$[Ni(L_2)]Br_2$	8:2 CH_3OH–H_2O (v/v)	455(88), 350(320), 281(240), 220 sh(13 600)
$[Fe(Ni(L_2))_3]^{3+}$	8:2 CH_3OH–H_2O (v/v)	500(4045), 359 sh(5270), 295(18 500)
$[Fe(Cu(L_2))_3]^{3+}$	8:2 CH_3OH–H_2O (v/v)	525(5060), 360(32 450), 260(34 350)

Table 5
EPR spectroscopic data (see Section 2 for conditions)

Complex	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$
$[Cu(L_1)Br_2]$	2.143	2.048	200G
$[Cu(L_2)Br_2]$	2.143	2.048	200G
$[Ni(L_1)Cl_2]^+$	2.022	2.176	27.5G
$[Ni(L_2)Cl_2]^+$	2.022	2.174	27.5G
$[Fe(Cu(L_2))_3]^{3+}$	4.367, 4.118 and 3.805 (2.067 for Cu(II))		
$[Fe(Ni(L_2))_3]^{3+}$	4.396, 4.144 and 3.828		

3.7. Formation of template-assisted multinuclear species on Fe(III)



The formation of species of the type $[Fe(M(L_2)Br_2)_3]^{3-}$ (M = Cu(II) and Ni(II)) were both studied by UV–Vis spectroscopy (see Table 4). Spectrophotometric titration of a solution of $[Fe(OH_2)_6](ClO_4)_3$ or $[Fe(NO_3)_3]\cdot 9H_2O$ with solutions of $[M(H_2L_2)Br_2]^{2+}$ in aqueous methanol (8:2 MeOH–H_2O) in the presence of a base (at least 6 equivalents of a strong base such as $[Me_4N][OH]\cdot H_2O$) produced intense violet–blue species in solution. However, these species are only meta-stable in solution and are very easily precipitated (within 10 min from 1×10^3 M solutions) out of aqueous solutions in which they were prepared. They are also sparingly soluble in most solvents. The UV–Vis spectroscopic data, recorded before such precipitation, are presented in Table 4. The intense bands observed at 500 nm ($\varepsilon = 4045$ M^{-1} cm^{-1}) for the $[Fe(Ni(L_2)Br_2)_3]^{3-}$ and at 525 nm ($\varepsilon = 5060$ M^{-1} cm^{-1}) for the $[Fe(Cu(L_2)Br_2)_3]^{3-}$ complex anions are characteristic of the $[Fe(catecholate)]^{3-}$ chromophore [45,46]. EPR spectra of $[Fe(Ni(L_2)Br_2)_3]^{3-}$ and $Fe(Cu(L_2)Br_2)_3]^{3-}$ were obtained in a MgO matrix and they both showed three distinguishable features with g-values in the range of 3.8–4.4 (see Table 5) suggesting the presence of an $[FeO_6]^{3-}$ chromophore and with $S = 5/2$ for the Fe(III) [45]. The environment around $[FeO_6]^{3-}$ may not be homogeneous suggesting the orientation of the cyclam units may vary independently. Considering the structure of the ligands, one would not expect any direct interaction between the Fe(III) and the metal ions in the cyclam units. However, the EPR spectrum of $Fe(Cu(L_2)Br_2)_3]^{3-}$ was somewhat sharper compared with that of $Fe(Ni(L_2)Br_2)_3]^{3-}$. Also, a broad signal around $g = 2.067$ for the Cu(II) ion was observed in the case of $Fe(Cu(L_2)Br_2)_3]^{3-}$. The coordination geometry of the Ni(II) center may vary depending on the counter ions present in solution. Also, depending upon the pH used in the preparation of the $Fe(M(L_2)Br_2)_3]^{3-}$ species, the conformation of the cyclam rings may differ. The influence of such factors on the spectroscopic parameters is under further investigation.

4. Conclusions

The synthesis and characterization of the Ni(II) and Cu(II) complexes of L_1 and H_2L_2 are described. The structures of the Cu(II) complexes, $[Cu(L_1)Br_2]$ and $[Cu(H_2(BrL_2))Br]Br\cdot H_2O$ are reported. As has been shown here, the catecholate groups in the complexes of L_2^{2-} are exodentate in nature and available for chelating suitable metal ions such as Fe(III). A detailed investigation of the formation of multinuclear species, their structure and properties are under detailed investigation.

5. Supplementary material

Crystallographic information in CIF format for the two structures, $[Cu(L_1)Br_2]$ and $[Cu(H_2(BrL_2))Br]Br\cdot H_2O$ are available from the Cambridge Crystallographic Data Center (CCDC deposit nos. 134871 and 134872). Copies of this material may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www:http//www.ccdc.cam.ac.uk). Figures (S1–S5) of cyclic voltammograms of $[Ni(L_1)Br_2]$ and $[Ni(H_2L_2)]Br_2$ and UV–Vis spectra for the formation of multinuclear complexes on Fe(III) template are available as hard copies. Ordering information is given on any masthead page.

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