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Synthesis and conformational aspects of 20- and 40-membered macrocyclic mono and dinuclear uranyl complexes incorporating salen and (*R*)-BINOL units

Maria E. Amato, Francesco P. Ballistreri, Andrea Pappalardo, Domenico Sciotto, Gaetano A. Tomaselli* and Rosa Maria Toscano

Dipartimento Scienze Chimiche, University of Catania, Viale A. Doria 6, 95125 Catania, Italy

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Abstract—20- and 40-membered macrocyclic mono and dinuclear uranyl complexes **11–13** incorporating salen and (*R*)-BINOL units have been designed and synthesized starting from 4-*tert*-butylphenol in eight steps. NMR measurements (COSY, NOESY/EXSY) indicate that such complexes in solution are involved in conformational equilibria, which for the 20-membered derivatives are observable already at room temperature (k_1=300 s^{-1} at 300 K) and which are probably related to a flipping motion of salicylaldehyde units. T-ROESY experiments suggest that in solution, the dinuclear complexes do not assume structures wrapped around the metal ions.

1. Introduction

The design and synthesis of chiral macrocycles acting as enantioselective receptors are of great interest in the field of enzyme mimicking enantioselective catalysis[1] as well as in those of chiral resolution[2] and chiral sensing.[3] Recently particular attention has been devoted to neutral ditopic receptors able to simultaneously bind chiral ammonium cations and their counter anions.[4–13] In this paper we describe the synthesis of some chiral macrocyclic ligands incorporating both a salen unit containing a chiral diimine bridge and the (*R*)-BINOL unit. The salen framework, due to the presence of two stereogenic carbon atoms in the diimine bridge, generates a chiral pocket which can coordinate a metal cation, say the uranyl cation (via imine nitrogen and phenolic oxygen atoms), which represents a Lewis acidic site able to bind the counter anion of an ion pair as guest.[14] On the other hand, the (*R*)-BINOL unit can provide π electron rich regions able to develop CH–π interactions thus facilitating the recognition of the pertinent counter cation.

2. Synthetic scheme

The synthesis of the key intermediate **7** from 4-*tert*-butylphenol is illustrated in Scheme 1. Treatment of **1** with CH_2O and base gave the known 2,6-bis(hydroxymethyl)-4-*tert*-butylphenol (**2**) (70%), which upon selective oxidation (MnO_2) was converted into 2-hydroxy-3-hydroxymethyl-5-*tert*-butylbenzaldehyde (**3**) (62%). Allylation of **3** with allyl bromide and K_2CO_3 in dry MeCN produced the 2-allyloxy derivative **4** (88%), which underwent reaction with $SOCl_2$ in CH_2Cl_2 to afford chloromethyl compound **5** (65%). Subsequent alkylation of (*R*)-BINOL with **5** and K_2CO_3 in refluxing MeCN to give bis-ether **6** (78%), followed by Pd-catalyzed dealkylation, afforded the desired bis-salicylaldehyde derivative **7** in 71% yield.

Reaction of bis-aldehyde **7** with (1*R*,2*R*)-1,2-diphenylethylenediamine (Scheme 2) in refluxing EtOH under high dilution conditions gave a mixture of 1:1 (20-membered) and 2:2 (40-membered) macrocycles **8** and **9**, which were isolated by flash chromatography in 13% and 75% yields, respectively.

Likewise, reaction of bis-aldehyde **7** with (1*R*)-*trans*-1,2-cyclohexanediamine in refluxing EtOH gave the 40-membered macrocycle **10** as the main product (96% isolated yield) and hardly isolable quantities of the 20-membered macrocycle.

3. NMR spectra of macrocycles 8, 9 and 10

The ^1H NMR spectra of compounds **8**, **9** and **10** were recorded both in $CDCl_3$ and $(CD_3)_2CO$. In $CDCl_3$ the spectra consist of similar and relatively simple patterns of resonances showing only one set of signals for each pair of

* Corresponding author. Tel.: +39 095338836; fax: +39 095580138; e-mail: gtomaselli@unict.it

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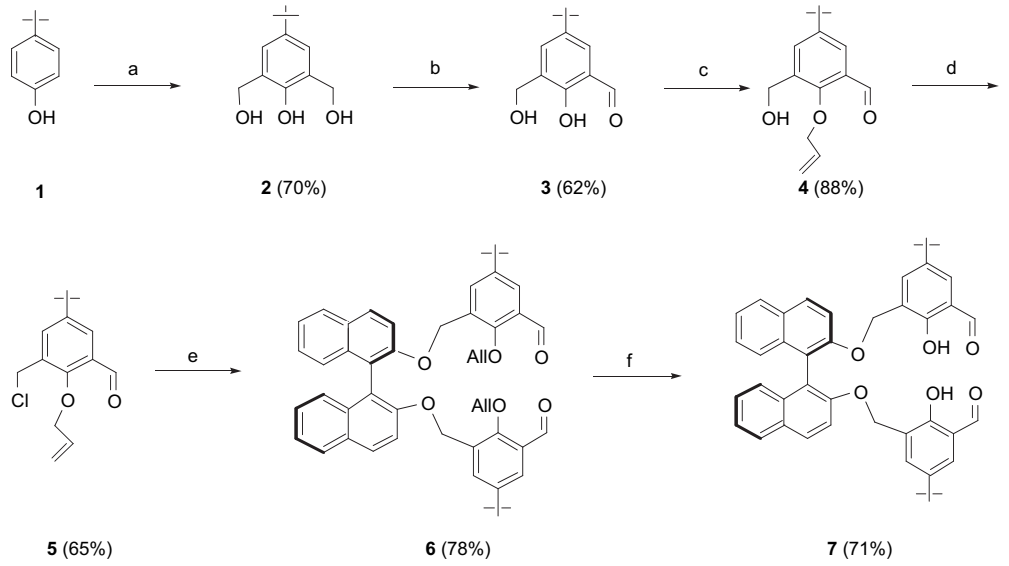
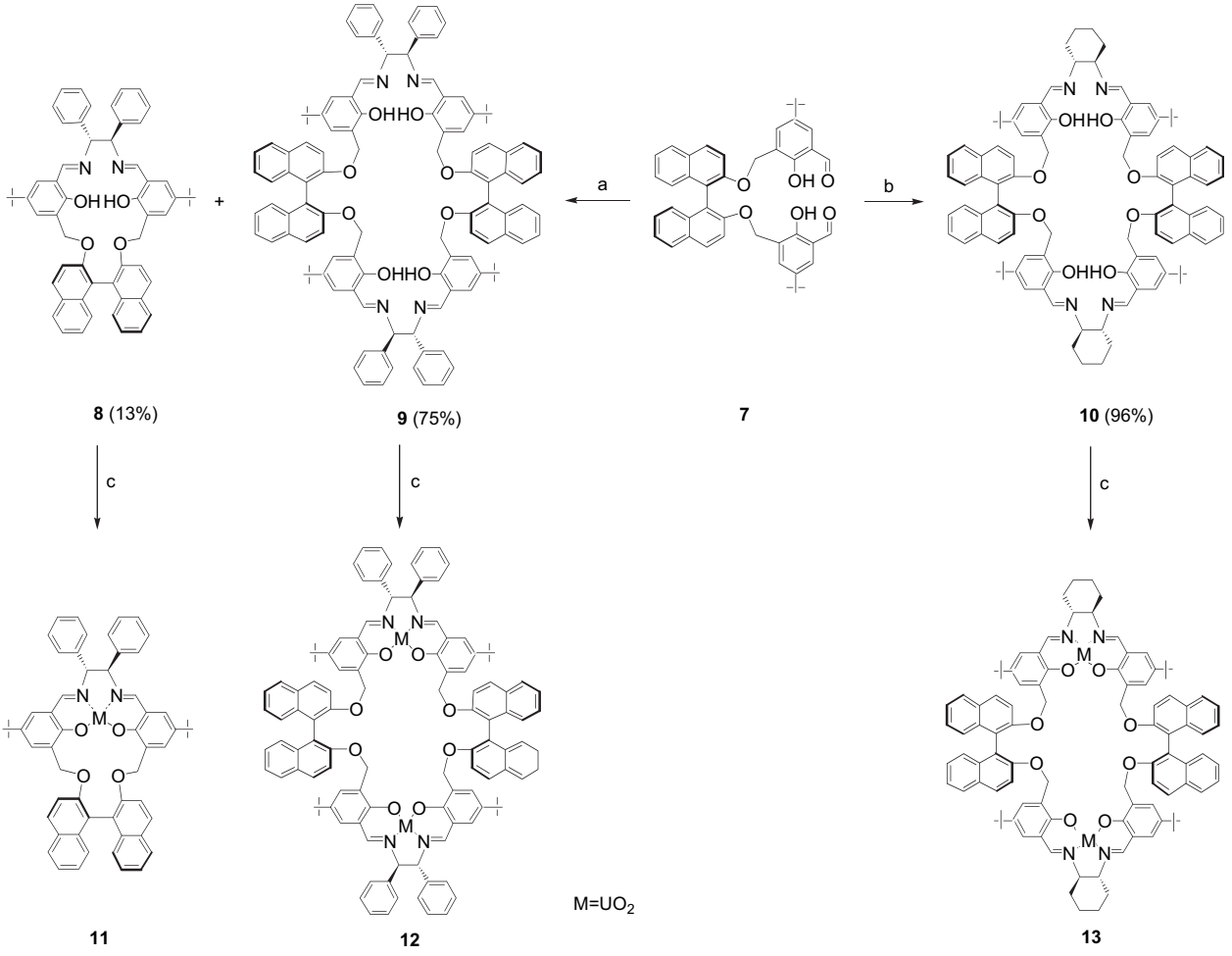


Scheme 1. *Reagents and conditions*: (a) NaOH, CH_2O, 7 d, rt; (b) MnO_2, $CHCl_3$, 8 h, rt; (c) $CH_2{=}CHCH_2Br$, K_2CO_3, CH_3CN, reflux 1.5 h; (d) $SOCl_2$, CH_2Cl_2, 2 h; (e) (*R*)-2,2′-dihydroxy-1,1′-binaphthalene, K_2CO_3, CH_3CN, reflux 15 h; (f) $Pd(OAc)_2$, PPh_3, Et_3N, HCO_2H, 80% EtOH, reflux 45 min.



Scheme 2. *Reagents and conditions*: (a) (1*R*,2*R*)-1,2-diphenylethylenediamine, EtOH, reflux, 1 d; (b) (1*R*)-*trans*-1,2-cyclohexanediamine, EtOH, reflux, 1 d; (c) $UO_2(AcO)_2{\cdot}2H_2O$, MeOH, 12 h, rt.

identical but not chemically equivalent groups. The presence of the imine CH═N proton (at 8.38 ppm for **8**, 8.32 ppm for **9** and 8.19 ppm for **10**) and the contemporary disappearance of the signal at 10.4 ppm of the aldehydic proton of **7** support the imine formation. The low field singlets (δ 12.83 ppm for compound **8**, 13.27 ppm for **9** and 13.30 ppm for **10**) indicate that the phenolic hydroxyls are strongly hydrogen bonded to the imine nitrogens.[15] Interestingly the two

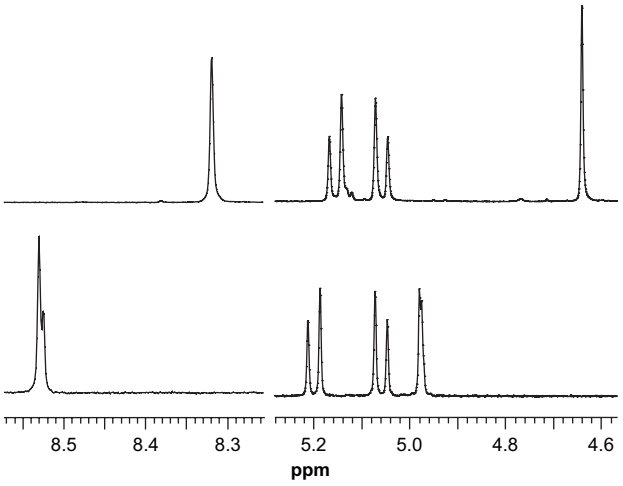


Figure 1. Selected ^{1}H NMR spectral regions (500 MHz) of **9** in $CDCl_3$ (top) and in $(CD_3)_2CO$ (bottom) displaying the splitting of imine, diimine bridge and methylene proton signals in $(CD_3)_2CO$ at 300 K.

diastereotopic methylene protons ArOCH_2BINOL of macrocycle **8** resonate as an AB system centred at δ 4.67 ppm ($\Delta\delta$ 0.54 ppm, J_{AB}=12.0 Hz), while for 40-membered macrocycles **9** and **10** the $\Delta\delta$ difference is reduced to ca. 0.09 ppm (J_{AB}=12.8 Hz) and to ca. 0.10 ppm (J_{AB}=14.6 Hz), respectively, which might indicate that in these compounds partial rotation about the Ar*O*–*C*H$_2$ bond occurs and it is less hindered in **9** and **10** than in the smaller and more strained macrocycle **8**.

By way of contrast, in $(CD_3)_2CO$ for compound **9** splitting of the signals of the imine as well as of the methyne protons of diimine bridge is observed (Fig. 1). This observation might be consistent with a dynamic interconversion process on the NMR time-scale among different diastereomeric conformations. Indeed, calculations performed by Macromodel program[16] pointed out the existence of a large number of conformers having comparable energy indicative of a great flexibility of macrocycle **9** (Fig. 2). For compound **10**

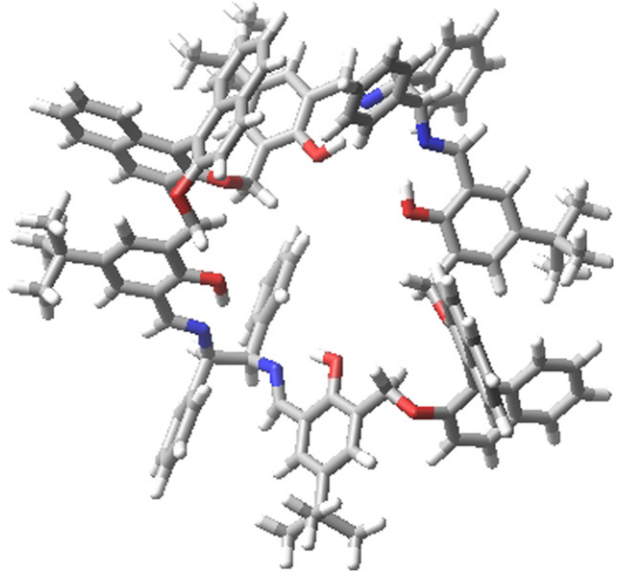


Figure 2. Computed optimized structure of macrocycle **9**.

diimine bridge proton signals, which resonate at 3.23 ppm, appear as an unresolved multiplet due to the scalar coupling with the adjacent cyclohexyl ring methylene protons even in $(CD_3)_2CO$.

4. Uranyl complexes 11, 12 and 13

Macrocycles **8**, **9** and **10** were employed as ligands to bind the uranyl cation to yield the corresponding mono and dinuclear complexes **11**, **12** and **13** (Scheme 2). The structural characterization of all new complexes was carried out by FAB$^+$ and by NMR spectroscopies (see Section 6). The ^{1}H NMR spectrum of **11** in $CDCl_3$ solution when compared with that of the corresponding free ligand **8** shows broadening of all the resonances, the absence of the phenolic OH signal and a significant downfield shift for several resonances in agreement with the presence of a coordinated uranyl cation. We have previously observed by X-ray measurements of very strictly correlated complexes[17] a pentagonal bipyramidal coordination geometry for uranyl(VI) ion with two axial oxo groups and with the fifth equatorial site occupied by an adventitious water molecule. This site is also available for complexation with anionic monodentate ligands X^- and its presence therefore makes the complex a potential receptor for Q^+X^- onium salts (Q^+=quaternary ammonium ion).

The aromatic region of the spectrum is fairly crowded preventing detailed analysis. However, for conformational analysis purposes the resonances arising from CH=N azomethine, diimine bridge and methylene protons are quite diagnostic. In fact the splitting of these signals, observed for complex **11** and which was not present in the free ligand **8**, supports the presence of a conformational equilibrium, which at room temperature is already slow on the NMR time-scale, in agreement with a larger degree of rigidity of this complex. In order to get an insight into the conformational behaviour of compound **11**, phase-sensitive NOESY/EXSY spectra at 300 K of **11** have also been acquired (Fig. 3).

The 2D map suggests that an exchange process is occurring on the NMR time-scale involving the ArCH_2OAr methylene protons as well as the two imine and diimine bridge protons. A rate constant, k, of ca. 300 s^{-1} at 300 K can be estimated assuming that the exchange process follows first order kinetics.[18] The process (Fig. 4) might envisage the flipping motion of the salicylaldehyde framework observed for uranyl salophen complexes, which inverts the curvature of the salophen ligand.[13–15,19]

This observation seems to indicate that coordination of the uranyl(VI) cation, owing to its large ionic radius, causes conformational stiffening, i.e., rigidity and then restricted rotation, and therefore slows down the rate of the conformational equilibrium with respect to that of the free ligand.

NMR spectra of dinuclear uranyl complexes **12** and **13** were also obtained in $(CD_3)_2CO$. The methylene protons resonate as an AB system at 5.56–5.79 ppm (J_{AB}=ca. 15.2 Hz) and at 5.45–5.57 ppm (J_{AB}=ca. 14.2 Hz) in **12** and **13**, respectively. The imine and the diimine proton signals which in

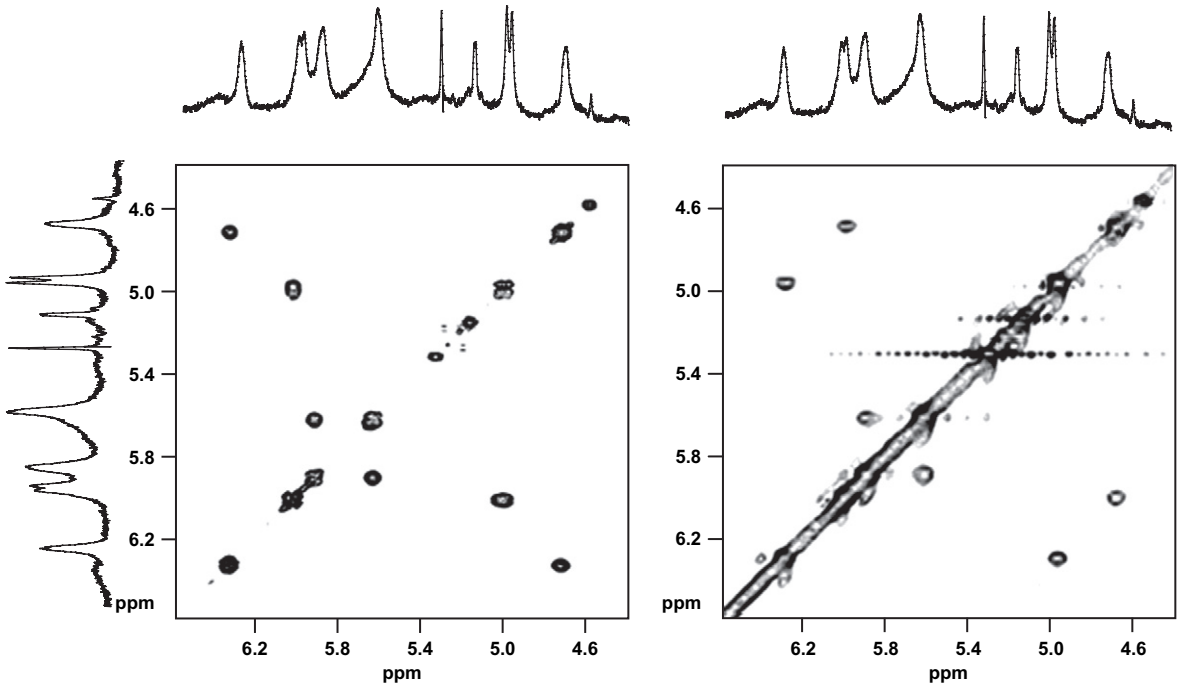


Figure 3. Selected spectral regions (500 MHz, $CDCl_3$) of 2D-COSY (left) and EXSY (right) spectra of complex **11** at 300 K (mixing time=50 ms).

$(CD_3)_2CO$ appeared doubled in the spectrum of free ligand **9** are both narrow singlets now in the spectrum of corresponding uranyl complex **12**. The obvious interpretation of these at first sight contrasting findings is the possibility that chemical shift differences between doubled signals, already observed in the corresponding free ligand **9** and which were assumed to indicate the presence of a conformational equilibrium, in the case of complex **12** are too small to be measured at room temperature. In order to check such a hypothesis we ran the ^1H NMR spectrum of **12** at variable temperatures in the range 300–183 K (Fig. 5). As the temperature is gradually lowered the proton NMR resonances of **12** showed a general progressive small downfield shift, with the exception of the *tert*-butyl group signal, which on the contrary was shifted slightly upfield. The signals of methylene, imine and diimine bridge protons start to collapse at 228 K and when the temperature reaches 183 K at least two forms are present in slow exchange. From the Eyring equation, a $\Delta G^{\ddagger}=$ 11.9 kcal mol^{-1} value at $T_c=228$ K can be calculated for the activation barrier of the interconversion equilibrium. The aromatic portion and the *tert*-butyl group signals were also significantly affected. Unfortunately, it was difficult to determine the number of conformers in equilibrium and to assign the resonances in order to establish their conformational structures because of the ambiguous line shape evolution and the extensive broadening.

Finally, the T-ROESY maps of **12** and **13**, which show cross-peaks corresponding to the almost unbroken pattern of neighbouring protons already present in the spectra of free ligands **9** and **10**, indicate that no extra dipolar contacts could be detected and suggest that these dinuclear

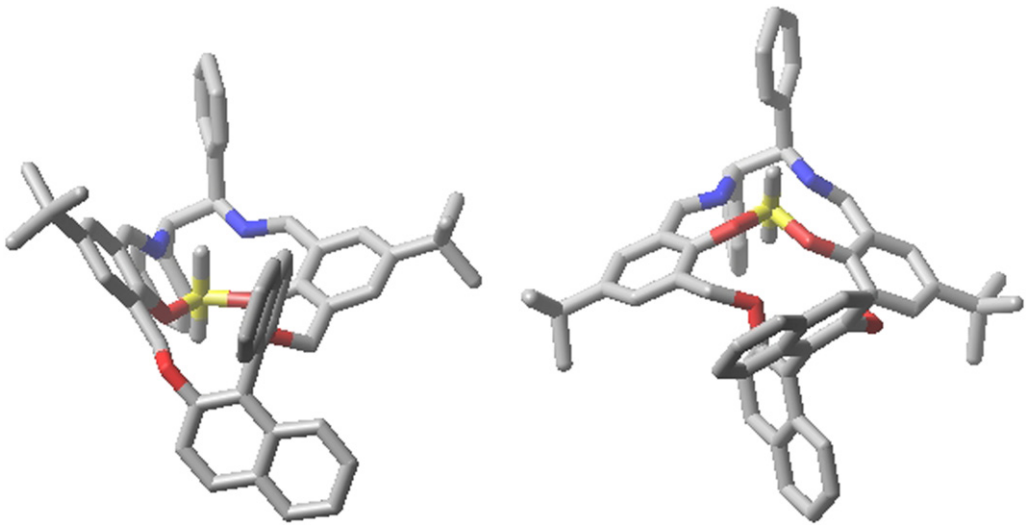


Figure 4. Computer calculated structures of conformers involved in the flipping motion of **11**.

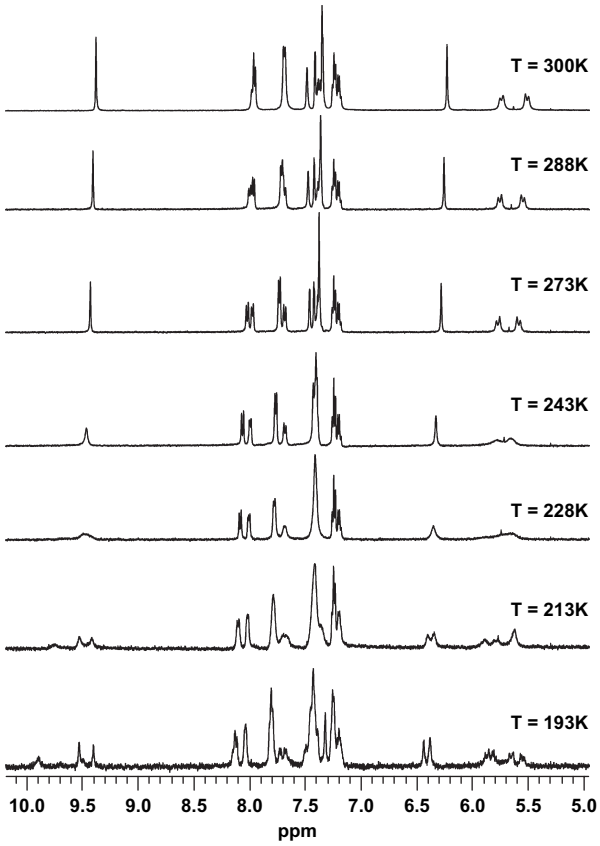


Figure 5. Variable temperature ^{1}H NMR spectrum of dinuclear complex **12** (500 MHz, $(CD_3)_2CO$) at relevant temperatures.

complexes do not, in solution, assume structures wrapped around the metal ions.

5. Conclusions

We have synthesized new mono and dinuclear uranyl chiral macrocyclic salen complexes and have determined their structures in solution by NMR measurements. Our findings point out that, as expected, the 20-membered mononuclear complex displays a larger degree of rigidity than the 40-membered dinuclear complexes. However, all three complexes are involved in conformational equilibria which are observable already at room temperature for the 20-membered complex. Even if it is not possible to define the number of conformers and their detailed structures involved in these equilibria, it appears reasonable to assume that all conformers might be associated with the occurrence of a flipping motion of the salicylaldehyde framework similar to that already observed for uranyl salophen complexes. Therefore, these complexes seem to have the requisites to work as potential neutral ditopic enantioselective receptors.

6. Experimental

6.1. General

Melting points were determined on a Kofler hot stage apparatus and are uncorrected. The NMR experiments were carried out at 27 °C on a Varian UNITY Inova 500 MHz spectrometer (^{1}H NMR at 499.88 MHz, ^{13}C NMR at 125.7 MHz in $CDCl_3$) equipped with pulse field gradient module (*Z* axis) and a tunable 5 mm Varian inverse detection probe (ID-PFG). The chemical shifts (ppm) were referenced to TMS. IR spectra were obtained with a Perkin–Elmer 1340 spectrophotometer. ESI mass spectra were obtained by employing an ES-MS Thermo-Finnigan LCQ-DECA spectrometer equipped with an ion trap analyzer. FAB(+) mass spectra were obtained on an MS 50 spectrometer using 3-nitrobenzyl-alcohol as a matrix. All chemicals were of reagent grade and were used without further purification.

6.1.1. 2,6-Bis-hydroxymethyl-4-*tert*-butylphenol (2). This compound was prepared by a slight modification of a literature procedure.[20] To a solution of NaOH (10.0 g, 0.25 mol) in H_2O (90 mL) was added 4-*tert*-butylphenol (**1**) (37.5 g, 0.25 mol), the suspension was slightly heated to give a clear solution. The solution was cooled to 0 °C and 37% formaldehyde (37.6 mL, 0.5 mol) was added dropwise under mechanical stirring. The mixture was stirred at room temperature for seven days. To complete the precipitation, NaCl (42.5 g) was added and the precipitate was filtered off and suspended in 500 mL of H_2O. The suspension was cooled and 5% aq HCl was added. The resulting white suspension was extracted four times with CH_2Cl_2 and the combined organic phases were dried (Na_2SO_4). The crude product was column chromatographed [SiO_2, eluent AcOEt/petroleum ether 40–60 °C (gradient 3:1 to 5:1)] to afford **2** (36.5 g, 70%) as a white solid. Mp 74–75 °C.[20] ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.29 (s, 9H), 4.82 (s, 4H), 7.10 (s, 2H).

6.1.2. 2-Hydroxy-3-hydroxymethyl-5-*tert*-butylbenzaldehyde (3). By adopting a literature procedure for similar compounds,[21] a mixture of **2** (10.5 g, 50 mmol) and MnO_2 (43.5 g, 500 mmol) in $CHCl_3$ (ca. 30 mL/g of phenol) was stirred at room temperature for 6–8 h. After filtration, the solid was subjected to Soxhlet extraction with $CHCl_3$ overnight. The removal of chloroform on a rotary evaporator gave a residue, which was column chromatographed (SiO_2, eluent petroleum ether/AcOEt 20:1 to 10:1, v/v) to give small amounts (5–6%) of 2,6-diformyl-4-*tert*-butylphenol followed by the desired mono-aldehyde **3** (6.5 g, 62%); yellow oil, which solidifies on standing. Mp 87–88 °C (86–87 °C).[22] ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.34 (s, 9H), 4.78 (s, 2H), 7.49, 7.63 (d, J=2.4 Hz, 1H each), 9.92 (s, 1H), 11.23 (s, 1H). ESI-MS: *m*/*z* 209 $[MH]^+$. Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.23; H, 7.69. Found: C, 69.58; H, 7.72.

6.1.3. 2-Allyloxy-3-hydroxymethyl-5-*tert*-butylbenzaldehyde (4). A stirred mixture of **3** (5.20 g, 25 mmol), allyl bromide (6.05 g, 50 mmol) and anhydrous K_2CO_3 (3.45 g, 25 mmol) in dry MeCN (150 mL) was refluxed for 1.5 h. After evaporation of the solvent, the residue was partitioned between 0.1 M HCl and CH_2Cl_2. The organic layer was washed with water, dried over anhydrous Na_2SO_4 and concentrated. The oily residue was purified by column chromatography (SiO_2, eluent petroleum ether/AcOEt 5:1, v/v) to give **4** (5.45 g, 88%) as a pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.34 (s, ^{t}Bu, 9H), 2.13 (t, J=5.9 Hz, CH_2OH, 1H), 4.53 (dt, J=5.7, 1.3 Hz, $OCH_2CH{=}CH_2$, 2H), 4.78 (d, J=5.9 Hz, CH_2OH, 2H), 5.33 (ddd, J=10.3, 2.6,

1.5 Hz, $OCH_2CH{=}CH_aH_b$, 1H), 5.44 (ddd, J=17.1, 2.9, 1.5 Hz, $OCH_2CH{=}CH_aH_b$, 1H), 6.11 (m, $OCH_2CH{=}CH_2$, 1H), 7.71, 7.82 (d, J=2.6 Hz, ArH, 1H each), 10.34 (s, CHO, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 31.2, 34.6, 60.7, 78.1, 118.9, 125.1, 128.7, 132.6, 132.8, 134.5, 147.8, 190.2. ESI-MS: m/z 249 $[MH]^+$. Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.59; H, 8.06. Found: C, 72.86; H, 8.01.

6.1.4. 2-Allyloxy-3-chloromethyl-5-*tert*-butylbenzaldehyde (5). To a chilled solution of **4** (4.25 g, 17.1 mmol) in CH_2Cl_2 (150 mL) was added dropwise under stirring a solution of $SOCl_2$ (5.1 g, 43.2 mmol) in CH_2Cl_2 (50 mL). The mixture was allowed to stir for 2 h. After removal of most of the solvent, toluene (20 mL) was added and the mixture was concentrated to dryness. The oily residue was partitioned between brine and CH_2Cl_2 (3×15 mL), dried (Na_2SO_4) and concentrated. The crude product was column chromatographed (SiO_2, eluent petroleum ether/AcOEt 10:1, v/v) to afford **5** (2.95 g, 65%) as a light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.34 (s, ^{t}Bu, 9H), 4.59 (dt, J=5.9, 1.3 Hz, $OCH_2CH{=}CH_2$, 2H), 4.69 (s, CH_2Cl, 2H), 5.35 (ddd, J=10.4, 2.6, 1.3 Hz, $OCH_2CH{=}CH_aH_b$, 1H), 5.47 (ddd, J=17.1, 3.0, 1.5 Hz, $OCH_2CH{=}CH_aH_b$, 1H), 6.13 (m, $OCH_2CH{=}CH_2$, 1H), 7.71, 7.86 (d, J=2.6 Hz, ArH, 1H each), 10.34 (s, CHO, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 31.1, 34.6, 40.4, 78.4, 118.9, 126.2, 129.1, 131.7, 132.5, 134.4, 148.1, 157.9, 189.8. ESI-MS: m/z 267 $[MH]^+$. Anal. Calcd for $C_{15}H_{19}ClO_2$: C, 67.67; H, 7.14. Found: C, 67.97; H, 7.10.

6.1.5. (*R*)-2,2′-Bis(2-allyloxy-3-formyl-5-*tert*-butyl-benzyloxy)-1,1′-binaphthalene (6). A stirred mixture of (*R*)-2,2′-dihydroxy-1,1′-binaphthalene (1.17 g, 4.1 mmol), **5** (2.4 g, 9 mmol) and anhydrous K_2CO_3 (3.24 g, 23.5 mmol) in dry MeCN (150 mL) was refluxed for 15 h under N_2. Usual workup followed by column chromatography (SiO_2, eluent petroleum ether/AcOEt 7:1, v/v) afforded bis-aldehyde **6** (2.4 g, 78%) as a thick colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.02 (s, ^{t}Bu, 18H), 4.13–4.22 (m, $OCH_2CH{=}CH_2$, 4H), 5.09 and 5.14 (ABq, J=12.2 Hz, binaph–OCH_2, 4H), 5.23 (dd, J=10.4, 0.9 Hz, $OCH_2CH{=}CH_aH_b$, 2H), 5.29 (dd, J=17.1, 1.2 Hz, $OCH_2CH{=}CH_aH_b$, 2H), 5.89–5.97 (m, $OCH_2CH{=}CH_2$, 2H), 7.13 (d, J=2.4 Hz, ArH, 2H), 7.14 (d, J=8.2 Hz, 8,8′-binaphH, 2H), 7.19 (dt, J=7.5, 1.1 Hz, 7,7′(6,6′)-binaphH, 2H), 7.33 (dt, J=7.5, 1.1 Hz, 6,6′(7,7′)-binaphH, 2H), 7.54 (d, J=8.8 Hz, 3,3′-binaphH, 2H), 7.66 (d, J=2.4 Hz, ArH, 2H), 7.88 (d, J=8.2 Hz, 5,5′-binaphH, 2H), 8.00 (d, J=8.8 Hz, 4,4′-binaphH, 2H), 10.22 (s, CHO, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 31.2, 34.6, 66.2, 77.9, 115.8, 118.7, 121.0, 124.2, 124.7, 125.3, 125.5, 126.8, 128.3, 128.6, 129.9, 131.4, 132.9, 134.3, 147.7, 153.9, 157.4, 190.3. FAB(+) MS: m/z 747 $[MH]^+$, 770 $[MNa]^+$. Anal. Calcd for $C_{50}H_{50}O_6$: C, 80.43; H, 6.70. Found: C, 80.32; H, 6.75.

6.1.6. (*R*)-2,2′-Bis(2-hydroxy-3-formyl-5-*tert*-butyl-benzyloxy)-1,1′-binaphthalene (7). A stirred mixture of **6** (2.35 g, 3.1 mmol), $Pd(OAc)_2$ (47 mg, 0.2 mmol), PPh_3 (255 mg, 1.1 mmol), Et_3N (7.85 g, 77.5 mmol) and HCO_2H (3.58 g, 77.5 mmol) in 80% EtOH was refluxed for 45 min. After removal of the solvent, the residue was partitioned between CH_2Cl_2 and 0.1 M HCl. The organic layer was dried (Na_2SO_4) and concentrated. The crude product was purified by column chromatography (SiO_2, eluent petroleum ether/AcOEt 7:1, v/v) to afford **7** (1.5 g, 71%). Mp 210–212 °C (CH_2Cl_2/EtOH). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.94 (s, ^{t}Bu, 18H), 5.11 and 5.14 (ABq, J=13.0 Hz, OCH_2, 4H), 7.01 (d, J=2.3 Hz, ArH, 2H), 7.20–7.25 (m, 6,6′(7,7′),8,8′-binaphH and ArH, 6H), 7.32 (ddd, J=8.1, 6.1, 1.8 Hz, 7,7′(6,6′)-binaphH, 2H), 7.58 (d, J=9.0 Hz, 3,3′-binaphH, 2H), 7.87 (d, J=8.1 Hz, 5,5′-binaphH, 2H), 7.99 (d, J=9.0 Hz, 4,4′-binaphH, 2H), 9.74 (s, CHO, 2H), 10.99 (s, OH, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 30.9, 33.8, 64.8, 115.0, 119.1, 120.2, 123.7, 125.3, 125.5, 126.5, 128.0, 128.1, 129.5, 129.6, 132.6, 134.1, 142.5, 153.8, 156.0, 196.8. IR (KBr) ν_{max}: 3037, 2954, 1651, 1260, 1210, 1050, 810 cm^{-1}. FAB(+) MS: m/z 667 $[MH]^+$. Anal. Calcd for $C_{44}H_{42}O_6$: C, 79.28; H, 6.31. Found: C, 79.60; H, 6.27.

6.1.7. Macrocycles 8 and 9. Solutions of **7** (0.2 g, 0.3 mmol) and (1*R*,2*R*)-1,2-diphenylethylendiamine (0.064 g, 0.3 mmol) in abs EtOH (50 mL) were dropped separately but synchronously from two dropping funnels into boiling abs EtOH (50 mL) under rapid stirring. The reaction mixture was refluxed for an additional 15 h, and cooled. After removal of the solvent, the crude product was subjected to flash chromatography (SiO_2, eluent petroleum ether/AcOEt 20:1, v/v) to afford macrocycles **8** (R_f=0.28, petroleum ether/AcOEt 15:1; 32 mg, 13%) and **9** (R_f=0.05, petroleum ether/AcOEt 15:1; 190 mg, 75%).

Compound **8**: mp 186–188 °C (CH_2Cl_2/EtOH). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.92 (s, ^{t}Bu, 18H), 4.40 and 4.94 (AB, J=12.0 Hz, O–CH_2, 4H), 4.71 (s, CH–N, 2H), 6.77 and 7.06 (AB, J=2.2 Hz, ArH, 4H), 7.12–7.14, (m, binaphH, 4H), 7.24–7.38 (m, ArH and binaphH, 14H), 7.88 (d, J=8.1 Hz, 5,5′-binaphH, 2H), 7.90 (d, J=9.0 Hz, 4,4′-binaphH, 2H), 8.38 (s, CH=N, 2H), 12.83 (s, OH, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 31.1, 33.7, 65.8, 81.1, 116.0, 117.3, 120.7, 123.5, 124.4, 125.6, 126.2, 126.7, 127.5, 127.6, 127.8, 127.9, 128.5, 129.5, 134.0, 140.4, 140.9, 155.10, 155.14, 165.5. FAB(+) MS: m/z 843 $[MH]^+$. Anal. Calcd for $C_{58}H_{54}N_2O_4$: C, 82.66; H, 6.41; N, 3.33. Found: C, 82.93; H, 6.36; N, 3.34.

Compound **9**: mp 272–274 °C (CH_2Cl_2/EtOH). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.79 (s, ^{t}Bu, 36H), 4.64 (s, CH–N, 4H), 5.06 and 5.15 (AB, J=12.8 Hz, O–CH_2, 8H), 6.66 and 6.87 (ABq, J=2.4 Hz, ArH, 8H), 7.04–7.26, (m, ArH and (6,6′),(7,7′),(8,8′)-binaphH, 32H), 7.61 (d, J=9.0 Hz, 3,3′-binaphH, 4H), 7.83 (d, J=8.1 Hz, 5,5′-binaphH, 4H), 7.98 (d, J=9.0 Hz, 4,4′-binaphH, 4H), 8.32 (s, CH=N, 4H), 13.27 (s, OH, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 31.0, 33.6, 65.1, 80.2, 114.5, 116.8, 120.0, 123.4, 124.3, 125.3, 126.32, 126.35, 127.5, 127.7, 127.8, 127.9, 128.3, 129.3, 134.1, 139.7, 141.0, 153.9, 154.9, 166.7. ^{1}H NMR (500 MHz, CD_3COCD_3): δ 0.83 (s, ^{t}Bu, 36H), 4.97 (br s, CH–N, 4H), 5.06 and 5.21 (AB, J=12.8 Hz, O–CH_2, 8H), 6.77 and 7.02 (m, ArH, 8H), 7.01–7.32 (m, ArH and (6,6′),(7,7′),(8,8′)-binaphH, 32H), 7.71 (d, J=9.3 Hz, 3,3′-binaphH, 4H), 7.94 (d, J=8.1 Hz, 5,5′-binaphH, 4H), 8.12 (d, J=9.0 Hz, 4,4′-binaphH, 4H), 8.53 (br s, CH=N, 4H), 13.29 (s, OH, 4H). IR (KBr) ν_{max}: 3447, 2953, 1623, 1594, 1456, 1269, 1220, 885, 810 cm^{-1}. FAB(+) MS: m/z 1685

$[MH]^+$. Anal. Calcd for $C_{116}H_{108}N_4O_8$: C, 82.66; H, 6.41; N, 3.33. Found: C, 82.49; H, 6.46; N, 3.31.

6.1.8. Macrocycle 10. Solutions of **7** (0.2 g, 0.3 mmol) and (1*R*)-*trans*-1,2-cyclohexanediamine (0.035 g, 0.3 mmol) in abs EtOH (50 mL) were dropped separately but synchronously from two dropping funnels into boiling abs EtOH (50 mL) under rapid stirring. The reaction mixture was refluxed for an additional 15 h, and cooled. After removal of the solvent, the crude product was dissolved in CH_2Cl_2, filtered on Celite and concentrated to afford after crystallization macrocycle **10** (0.21 g, 96%). Mp 250–252 °C (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.79 (s, ^{t}Bu, 36H), 1.38–1.44 (m, *CH*$_2$–CH$_2$–CH–N, 8H), 1.76–1.82 (m, CH$_2$–*CH*$_2$–CH–N, 8H), 3.20–3.26 (m, CH–N, 4H), 5.05 and 5.15 (AB, J=14.6 Hz, O–CH$_2$, 8H), 6.62 and 6.83 (ABq, J=2.0 Hz, ArH, 8H), 7.13–7.26, ((6,6′),(7,7′),(8,8′)-binaphH, 12H), 7.61 (d, J=8.5 Hz, 3,3′-binaphH, 4H), 7.82 (d, J=8.0 Hz, 5,5′-binaphH, 4H), 7.97 (d, J=9.0 Hz, 4,4′-binaphH, 4H), 8.19 (s, CH═N, 4H), 13.30 (s, OH, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 24.0, 31.0, 33.6, 34.0, 65.3, 73.0, 114.8, 117.0, 120.3, 123.4, 124.6, 125.4, 126.32, 126.36, 127.5, 127.9, 128.0, 128.1, 128.4, 129.5, 134.0, 139.5, 141.0, 154.0, 154.9, 165.8. ^{1}H NMR (500 MHz, CD_3COCD_3): δ 0.79 (s, ^{t}Bu, 36H), 1.46–1.54 (m, *CH*$_2$–CH$_2$–CH–N, 8H), 1.76–1.91 (m, CH$_2$–*CH*$_2$–CH–N, 8H), 3.33–3.40 (m, CH–N, 4H), 4.98 and 5.17 (AB, J=12.8 Hz, O–CH$_2$, 8H), 6.73–6.97 (m, ArH, 8H), 7.10–7.33 (m, (6,6′),(7,7′),(8,8′)-binaphH, 12H), 7.74 (d, J=8.5 Hz, 3,3′-binaphH, 4H), 7.94 (d, J=8.0 Hz, 5,5′-binaphH, 4H), 8.12 (d, J=9.0 Hz, 4,4′-binaphH, 4H), 8.35 (s, CH═N, 4H), 13.25 (s, OH, 4H). IR (KBr) ν_{max}: 3446, 2963, 1679, 1634, 1549, 1429, 1360, 1269, 862 cm^{-1}. FAB(+) MS: *m*/*z* 1489 $[MH]^+$. Anal. Calcd for $C_{100}H_{104}N_4O_8$: C, 80.65; H, 6.99; N, 3.76. Found: C, 80.96; H, 7.03; N, 3.74.

6.1.9. UO_2 complexes 11–13. $(AcO)_2UO_2\cdot 2H_2O$ (5.94 mg, 0.014 mmol) was added as a solid to stirred solution of the ligand **8**, **9** or **10** (0.012 mmol) in MeOH (5 mL). The mixture was allowed to stir overnight at room temperature and was monitored by TLC (eluent: 5% EtOH in CH_2Cl_2). The solvent was removed on a rotary evaporator under vacuum and the residue was dissolved in CH_2Cl_2, filtered and concentrated to produce the pertinent uranyl complexes in nearly quantitative yields.

Compound **11**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.95 (s, ^{t}Bu, 18H), 4.71 (d, J=10.0 Hz, O–CH$_2$, 2H), 5.01 (d, J=10.0 Hz, O–CH$_2$, 2H), 5.61 (s, CH–N, 2H), 5.92 (s, CH–N, 2H), 6.02 (d, J=10.0 Hz, O–CH$_2$, 2H), 6.31 (d, J=10.0 Hz, O–CH$_2$, 2H), 6.89–8.25 (m, ArH and binaphH, 26H), 8.72 (s, CH═N, 2H), 8.95 (s, CH═N, 2H). Anal. Calcd for $C_{58}H_{52}N_2O_6U\cdot H_2O$: C, 61.70; H, 4.79; N, 2.48. Found: C, 61.48; H, 4.82; N, 2.46.

Compound **12**: ^{1}H NMR (500 MHz, CD_3COCD_3): δ 1.12 (s, ^{t}Bu, 36H), 5.56 and 5.79 (AB, J=15.2 Hz, O–CH$_2$, 8H), 6.24 (s, CH–N, 4H), 7.12–8.02 (m, ArH and binaphH, 52H), 9.38 (s, CH═N, 4H). Anal. Calcd for $C_{116}H_{104}N_4O_{12}U_2\cdot 2H_2O$: C, 61.70; H, 4.79; N, 2.48. Found: C, 61.95; H, 4.81; N, 2.47.

Compound **13**: (500 MHz, CD_3COCD_3): δ 1.14 (s, ^{t}Bu, 36H), 1.62–1.98 (m, C*H*$_2$–CH$_2$–CH–N, 8H), 2.11–2.59 (m, CH$_2$–C*H*$_2$–CH–N, 8H), 4.11 (m, CH–N, 4H), 5.45 and 5.57 (AB, J=14.2 Hz, O–CH$_2$, 8H), 7.02–8.06 (m, ArH and binaphH, 32H), 9.48 (s, CH═N, 4H). Anal. Calcd for $C_{100}H_{100}N_4O_{12}U_2\cdot 2H_2O$: C, 58.25; H, 5.05; N, 2.72. Found: C, 58.06; H, 5.08; N, 2.71.

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