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# Chelate Complexes of the Pyrid-2-yl Analogue of Tetracyclone

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**Abstract.** The tetradentate ligand 2,3,4,5-tetra(pyrid-2-yl)cyclopent-2,4-dien-1-one (**3**) was prepared and used for the synthesis of the dinuclear chelates [μ-(**3**)($MX_2$)$_2$] ($MX_2$ = $BeCl_2$, $ZnCl_2$, $ZnBr_2$, $HgCl_2$, $HgBr_2$); the closely related $BeCl_2$ chelate of the bidentate ligand 2,5-diphenyl-3,4-di(pyrid-2-yl)cyclopent-2,4-dien-1-one (**1**) was also prepared. The structures of these compounds were determined by X-ray crystallography and compared to those of the corresponding unchelated analogues [(py)$_2$$MX_2$] (py = pyridine). Aggregation to polymeric chains by chloro-bridging was observed for [μ-(**3**)($HgCl_2$)$_2$] in the crystal.

**Keywords:** Beryllium; Chelate ligands; Crystal structures; Mercury; Zinc

## Introduction

We recently started to investigate the coordination chemistry of pyridyl-substituted tetracyclone analogues and have already reported results obtained with the bidentate N,N-ligands 2,5-diphenyl-3,4-di(pyrid-2-yl)cyclopenta-2,4-dien-1-one (**1**) [1, 2] and 2,5-diphenyl-3,4-di(pyrid-3-yl)cyclopenta-2,4-dien-1-one (**2**) [3]. The former compound was shown to form chelates with metal dihalides $MX_2$, whereas the latter species, which contains two pyrid-3-yl substituents, turned out to act as a bridging ligand, giving rise to helically chiral coordination polymers. We have now extended our study to the tetradentate ligand 2,3,4,5-tetra-(pyrid-2-yl)cyclopent-2,4-dien-1-one (**3**) and here report on first results obtained with this compound.

## Results and Discussion

The synthesis of **3** involves dehydration of the readily available precursor 4-hydroxy-2,3,4,5-tetra(pyrid-2-yl)cyclopent-2-en-1-one [4]. While generation of **3** from this compound has been reported to be feasible in boiling ethylene glycol (ca. 200 °C), there are conflicting reports concerning the possibility of isolating the product from the resulting reaction mixture [4, 5]. Isolation of **3** failed in our hands. We consequently developed a different dehydration protocol, which utilises solid phase conditions, viz. heating of a 1:10 mixture of the precursor and silica gel to ca. 200 °C in an inert atmosphere. This method had previously been applied to the small-scale synthesis of **1** [6]. Isolation of **3** was easily achieved by Soxhlet extraction of the dark red solid obtained after the heating process. If the dehydration procedure was carried out in air, 1,3,4,5-tetra(pyrid-2-yl)-6-oxa-bicyclo[3.1.0]hex-2-en-1-one (**4**) was obtained as a second product in substantial amounts. Its formation is very likely due to oxidation of **3** with oxygen, since a closely related product (viz. the tetraphenyl analogue) can be obtained from tetracyclone under very similar conditions [7]. The separation of **3** and **4** is extremely tedious, because their chromatographic behaviour is very similar and they tend to form mixed crystals.

The structures of **3** (Figure 1) and **4** (Figure 2) have been investigated by single-crystal X-ray diffraction. In the case of **4**, a mixed crystal containing ca. 5 % of **3** had to be used, which necessarily compromises the quality of the structure determination. Consequently, a detailed discussion of bond parameters is not meaningful for **4**. The bond parameters of **3** compare well with those of closely related compounds such as, for example, **1** [1].

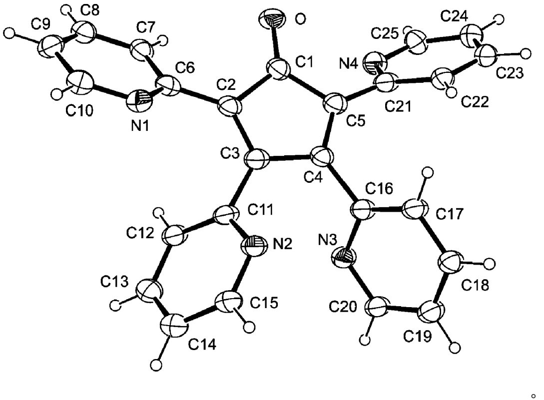

**Fig. 1** Molecular structure of **3**. Selected bond lengths/Å and angles/°:

C(1)−O 1.224(5), C(1)−C(2) 1.513(7), C(1)−C(5) 1.514(7), C(2)−C(3) 1.373(6), C(2)−C(6) 1.461(7), C(3)−C(4) 1.496(7), C(4)−C(5) 1.361(6); C(6)−C(2)−C(3) 130.0(4), C(2)−C(3)−C(11) 126.1(5), C(4)−C(3)−C(11) 123.5(4), C(3)−C(4)−C(16) 121.7(4), C(5)−C(4)−C(16) 127.3(5), C(4)−C(5)−C(21) 133.3(4).

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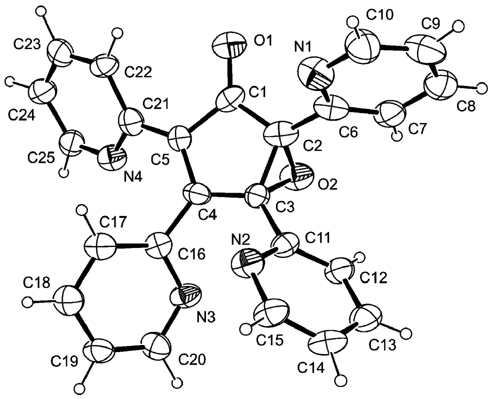

**Fig. 2** Molecular structure of **4**. Selected bond lengths/Å and angles/°:

C(1)−O(1) 1.227(9), C(1)−C(2) 1.49(1), C(1)−C(5) 1.50(1), C(2)−C(3) 1.50(1), C(2)−O(2) 1.474(9), C(3)−C(4) 1.41(1), C(3)−O(2) 1.487(9), C(4)−C(5) 1.39(1); C(2)−O(2)−C(3) 61.0(5), C(3)−C(2)−C(6) 128.2(8), C(2)−C(3)−C(11) 112.2(7), C(4)−C(3)−C(11) 124.9(8), C(3)−C(4)−C(16) 123.1(8), C(5)−C(4)−C(16) 124.0(9), C(4)−C(5)−C(21) 124.3(7).

The reaction of the tetradentate ligand **3** with metal dihalides $MX_2$ in a 1:2 ratio afforded the expected dinuclear chelates [μ-(**3**)($MX_2$)$_2$] ($MX_2$ = $BeCl_2$, $ZnCl_2$, $ZnBr_2$, $HgCl_2$, $HgBr_2$). In addition, the beryllium chelate [(**1**)$BeCl_2$] has been prepared for comparison. These complexes are fairly soluble in polar solvents like dichloromethane. Metal coordination is evidenced by a characteristic low-field shift of ca. 0.5 ppm of the $^1$H NMR signals of the pyridyl α-H atoms with respect to the uncoordinated ligand.

**Table 1** Pertinent structural parameters for the chelates [(**1**)$MX_2$] and [μ-(**3**)($MX_2$)$_2$] as well as for the unchelated analogues [(py)$_2MX_2$]

| | M−N/Å | M−X/Å | N−M−N/° | X−M−X/° | |
|---|---|---|---|---|---|
| [(py)$_2$BeCl$_2$] | 1.76/1.78 | 1.99/1.99 | 101.8 | 114.6 | [8a] |
| (4 individual molecules) | 1.76/1.76 | 1.99/2.00 | 103.3 | 113.4 | |
| | 1.74/1.76 | 2.00/2.01 | 105.1 | 114.7 | |
| | 1.76/1.77 | 2.00/2.00 | 106.7 | 115.1 | |
| [(**1**)BeCl$_2$] | 1.77/1.77 | 1.99/1.92 | 101.0 | 112.3 | this work |
| [μ-(**3**)(BeCl$_2$)$_2$] | 1.76/1.75 | 2.00/1.99 | 102.8/101.8 | 110.6/112.0 | this work |
| [(py)$_2$ZnCl$_2$] | 2.05/2.05 | 2.21/2.23 | 106.3 | 120.9 | [8b] |
| [(**1**)ZnCl$_2$] | 2.07/2.05 | 2.21/2.22 | 95.4 | 122.2 | [1] |
| [μ-(**3**)(ZnCl$_2$)$_2$] | 2.05/2.07 | 2.21/2.23 | 95.2 | 119.8 | this work |
| [(py)$_2$ZnBr$_2$] | 2.04/2.04 | 2.35/2.37 | 107.2 | 120.9 | [8c] |
| [μ-(**3**)(ZnBr$_2$)$_2$] | 2.05/2.08 | 2.35/2.36 | 95.2 | 119.8 | this work |
| [(py)$_2$HgCl$_2$]$_n$ | 2.27/2.27 | 2.75/2.77 | 180 | 90.2/180 | [8d] |
| [(**1**)HgCl$_2$] | 2.43/2.41 | 2.36/2.36 | 78.3 | 144.2 | [1] |
| [μ-(**3**)(HgCl$_2$)$_2$] | 2.47/2.34 | 2.38/2.38 | 77.8 | 138.2 | this work |
| [(py)$_2$HgBr$_2$] | 2.38/2.39 | 2.48/2.48 | 90.7 | 141.2 | [8d] |
| [(**1**)HgBr$_2$] | 2.40/2.41 | 2.48/2.49 | 79.1 | 137.3 | [1] |
| [μ-(**3**)(HgBr$_2$)$_2$] | 2.41/2.36 | 2.48/2.51 | 80.8 | 134.5 | this work |

The structures of all complexes have been investigated by single-crystal X-ray diffraction (Figures 3 − 8). Pertinent structural parameters for the dinuclear complexes are collected in Table 1, together with corresponding values for the closely related mononuclear chelates [(**1**)$MX_2$] [1] and the unchelated analogues [(py)$_2MX_2$].

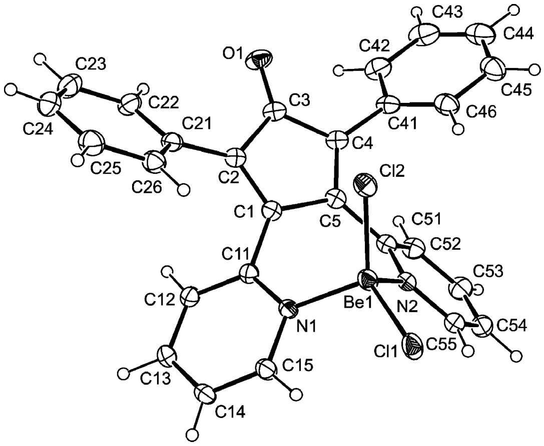

**Fig. 3** Molecular structure of [(**1**)$BeCl_2$]. Selected bond lengths/Å and angles/°:

C(3)−O(1) 1.216(2), C(1)−C(2) 1.352(2), C(2)−C(3) 1.500(2), C(3)−C(4) 1.503(2), C(4)−C(5) 1.348(2), C(1)−C(5) 1.514(2), C(1)−C(11) 1.475(2), C(11)−N(1) 1.361(2), C(5)−C(51) 1.472(2), C(51)−N(2) 1.362(2), Be(1)−N(1) 1.766(2), Be(1)−N(2) 1.767(2), Be(1)−Cl(1) 1.986(2), Be(1)−Cl(2) 1.919(2); Be(1)−N(1)−C(11) 122.2(1), Be(1)−N(2)−C(51) 121.3(1), N(1)−C(11)−C(1) 118.6(1), N(2)−C(51)−C(5) 119.7(2), C(11)−C(1)−C(5) 125.3(1), C(1)−C(5)−C(51) 126.1(1), C(2)−C(3)−C(4) 107.0(1), N(1)−Be(1)−N(2) 101.0(1), Cl(1)−Be(1)−Cl(2) 112.3(1).

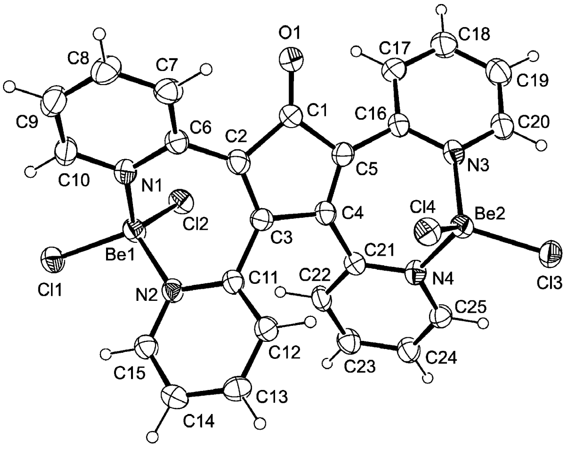

**Fig. 4** Molecular structure of [μ-(**3**)($BeCl_2$)$_2$]. Selected bond lengths/Å and angles/°:

C(1)−O(1) 1.206(8), C(1)−C(2) 1.510(9), C(2)−C(3) 1.353(9), C(3)−C(4) 1.498(8), C(4)−C(5) 1.326(9), C(1)−C(5) 1.514(9), C(2)−C(6) 1.440(9), C(6)−N(1) 1.379(8), C(3)−C(11) 1.478(9), C(11)−N(2) 136.9(7), Be(1)−N(1) 1.76(1), Be(1)−N(2) 1.75(1), Be(1)−Cl(1) 1.997(8), Be(1)−Cl(2) 1.989(8); Be(1)−N(1)−C(6) 123.0(5), Be(1)−N(2)−C(11) 120.0(5), N(1)−C(6)−C(2) 116.7(5), C(6)−C(2)−C(3) 132.2(6), C(2)−C(3)−C(11) 127.1(5), C(3)−C(11)−N(2) 117.9(5), C(2)−C(1)−C(5) 106.0(5), N(1)−Be(1)−N(2) 102.8(5), Cl(1)−Be(1)−Cl(2) 110.6(4).

It is instructive to compare the structures of the chelates with those of unchelated analogues of the type [(py)$_2MX_2$] (py = pyridine). These complexes are monomeric and exhibit pseudotetrahedral metal coordination, the exception being the chloro-bridged coordination polymer [(py)$_2HgCl_2$]$_n$, which contains hexacoordinate metal atoms bearing two py ligands in *trans* orientation [8]. We pause to note that such

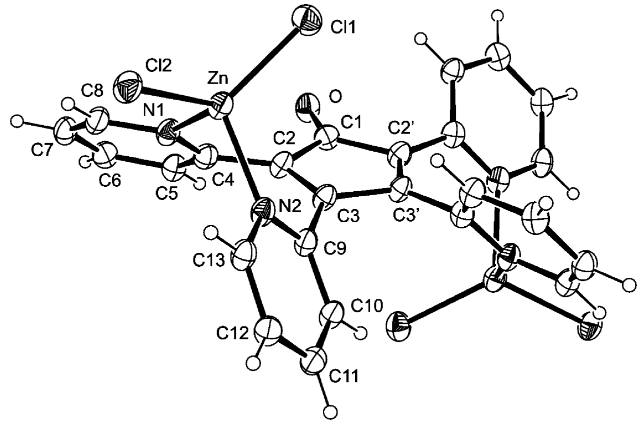

**Fig. 5** Molecular structure of [μ-(**3**)($ZnCl_2$)$_2$]. Selected bond lengths/Å and angles/°:

C(1)−O 1.220(6), C(1)−C(2) 1.500(5), C(2)−C(3) 1.351(5), C(3)−C(3′) 1.515(7); C(3)−C(2)−C(4) 132.5(4), C(2)−C(3)−C(9) 129.0(3), C(3′)−C(3)−C(9) 121.3(2).

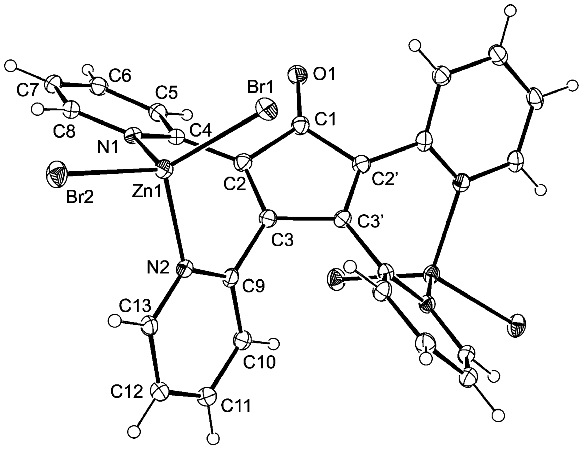

**Fig. 6** Molecular structure of [μ-(**3**)($ZnBr_2$)$_2$]. Selected bond lengths/Å and angles/°:

C(1)−O 1.215(5), C(1)−C(2) 1.506(4), C(2)−C(3) 1.349(4), C(3)−C(3′) 1.504(7); C(3)−C(2)−C(4) 133.1(3), C(2)−C(3)−C(9) 128.3(3), C(3′)−C(3)−C(9) 121.5(2).

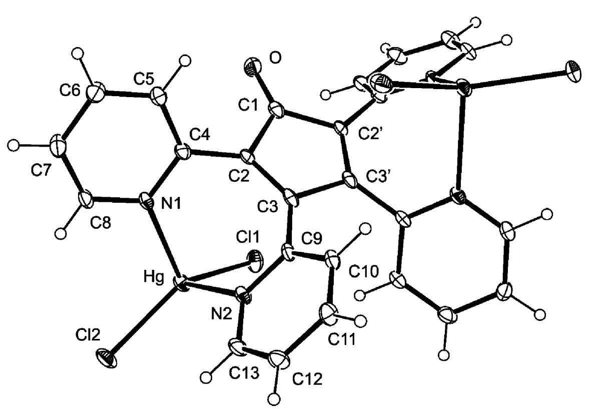

**Fig. 7** Molecular structure of [μ-(**3**)($HgCl_2$)$_2$]. Selected bond lengths/Å and angles/°:

C(1)−O 1.21(1), C(1)−C(2) 1.509(8), C(2)−C(3) 1.344(9), C(3)−C(3′) 1.53(1); C(3)−C(2)−C(4) 131.0(6), C(2)−C(3)−C(9) 129.4(3), C(3′)−C(3)−C(9) 121.1(4).

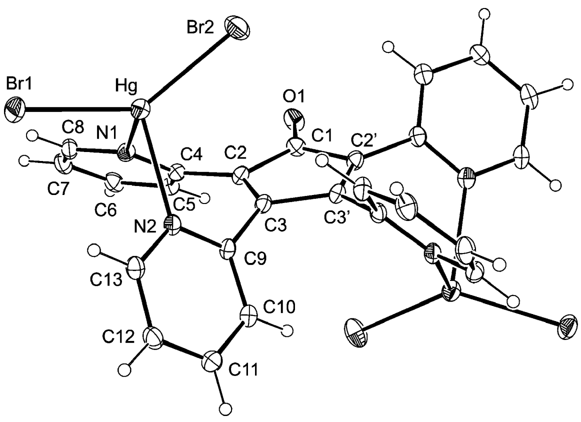

**Fig. 8** Molecular structure of [μ-(**3**)($HgBr_2$)$_2$]. Selected bond lengths/Å and angles/°:

C(1)−O 1.202(7), C(1)−C(2) 1.509(5), C(2)−C(3) 1.340(5), C(3)−C(3′) 1.518(8); C(3)−C(2)−C(4) 131.9(4), C(2)−C(3)−C(9) 128.7(4), C(3′)−C(3)−C(9) 121.2(2).

a *trans* orientation is impossible for the chelating N atoms of ligands **1** and **3**. With the exception of the special case of $MX_2$ = $HgCl_2$, M−N and M−X bond lengths are very similar for the respective unchelated complexes [(py)$_2$$MX_2$] and the corresponding chelates of **1** and **3**. Considering the bond angles at the metal atom, only marginal differences are observed for the three beryllium complexes. For metals with larger radius than Be the N−M−N angles become considerably more acute in the chelates, while the X−M−X angles are affected only slightly. For example, for $MX_2$ = $ZnCl_2$ the N−M−N angle is 106.3° in the unchelated complex, whereas it is only 95.4° and 95.2° in [(**1**)$ZnCl_2$] and [μ-(**3**)($ZnCl_2$)$_2$], respectively. This is due to the rigid ligand framework of **1** and **3**. The pronounced ligand-induced decrease in the N−Zn−N angles does not lead to a concomitant increase of the X−Zn−X angle, which is ca. 120° for all zinc complexes discussed here. It has been noted that a further decrease of this angle is prevented by repulsive interactions between the two X ligands [8b]. In the four mercury chelates, the N−M−N angle is particularly small, ranging from 77.8° to 80.8°. This is due to the larger size of the coordinated metal atom, which leads to much longer M−N bonds (ca. 2.1 Å for M = Zn versus ca. 2.4 Å for M = Hg).

In our consideration of the unchelated complexes of the type [(py)$_2$$MX_2$], M = $HgCl_2$ turned out to be rather peculiar. Interestingly, $MX_2$ = $HgCl_2$ also represents a special case in the context of the chelates investigated in this study. While [(**1**)$HgCl_2$] exhibits two very similar Hg−N bond lengths (2.41 and 2.43 Å), the dinuclear [μ-(**3**)($HgCl_2$)$_2$] has a short (2.34 Å) and a long Hg−N bond (2.47 Å). Closer inspection of the crystal packing reveals that the molecular units of [μ-(**3**)($HgCl_2$)$_2$] are aggregated through Hg···Cl contacts in such a way that the coordination environment of the Hg atom can be considered as a 4 + 1 type (Figure 9).

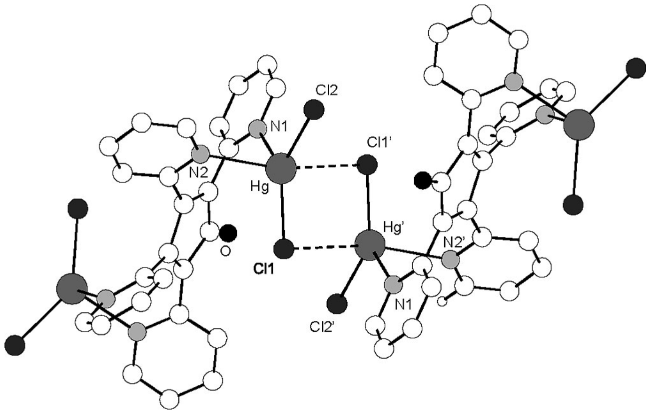

**Fig. 9** Aggregation of [μ-(**3**)($HgCl_2$)$_2$] by chloro-bridging in the crystal. Selected bond angles/°:

Cl(1)−Hg−Cl(1′) 88.43(6), Cl(1)−Hg−N(2) 102.2(1), N(1)−Hg−N(2) 77.8(2), N(1)−Hg−Cl(2) 102.3(1), Cl(2)−Hg−Cl(1′) 88.12(6), N(1)−Hg−Cl(1) 116.9(1), Cl(1′)−Hg−N(2) 152.9(4), Cl(1)−Hg−Cl(2) 138.24(7).

The Hg···Cl distance is ca. 3.15 Å, which is shorter than the sum of the estimated van der Waals radii. This contact could largely result from crystal packing forces [9], but may also be due to a long intermolecular bond. Such intermolecular contacts are quite common in inorganic chemistry, a well-known example being $ReOCl_4$, which forms centrosymmetric chloro-bridged dimers in the solid state with particularly long M···Cl distances of 3.55 Å [10]. In the coordination chemistry of mercury, a weak intermolecular bond has been reported, for example, for $[NEt_4]_2[Hg_2PtCl_8]$, whose anion is aggregated in the solid state to form polymeric zig-zag chains of $[Hg_2PtCl_8]_n^{2n-}$ [11]. The intermolecular Hg···Cl distances of 3.15 Å are very similar to the distance present in [μ-(**3**)($HgCl_2$)$_2$]. If the Hg atom in this complex is considered to be pentacoordinate, its coordination polyhedron is best described as distorted trigonal bipyramidal, which renders nitrogen atom N(1) equatorial and N(2) axial. Not surprisingly, the equatorial Hg−N(1) distance is considerably smaller than the axial Hg−N(2) distance (2.34 Å versus 2.47 Å, vide supra).

We note that two isomers are possible for mononuclear chelates of **3**, depending on whether the metal atom is chelated by the pyridyl units in position 2 and 3 or 3 and 4. However, attempts to obtain mononuclear complexes of **3** by using one equivalent of the respective metal dihalide invariably afforded the isolation of the corresponding dinuclear [μ-(**3**)($MX_2$)$_2$]. It is as yet unclear whether this is due to the comparatively low solubility of the dinuclear species or rather to cooperative metal binding, similar to allosteric effects observed in functional proteins. Studies concerning the complexation equilibria in solution will be performed in due course.

## Experimental Part

4-Hydroxy-2,3,4,5-tetra(pyrid-2-yl)cyclopent-2-en-1-one was prepared according to the published procedure [4]. $BeCl_2$ was prepared from the elements using a quartz tube and subsequent sublimation in vacuo [12]. All other materials were procured from commercial sources and used as received. NMR spectra were recorded at 300 K with a Varian Unity INOVA 500 spectrometer (500.13 MHz for $^1H$, ext. TMS). Elemental analyses were performed by the Microanalytical Laboratory of the University of Kassel.

### 2,3,4,5-Tetra(pyrid-2-yl)cyclopent-2,4-dien-1-one (3):

A mixture of 4-hydroxy-2,3,4,5-tetra(pyrid-2-yl)cyclopent-2-en-1-one (849 mg, 2.0 mmol) and silica gel (ca. 8.5 g, previously dried in vacuo at ca. 250 °C) was heated to ca. 200 °C under a stream of $N_2$. After 0.5 h the dark red mixture was allowed to cool to room temperature and was subsequently subjected to Soxhlet extraction with diethyl ether (ca. 400 mL). Crystallization afforded the product (621 mg, 78 %) as a red, crystalline solid. If the reaction was carried out in air, mixtures of **3** and 1,3,4,5-tetra(pyrid-2-yl)-6-oxa-bicyclo[3.1.0]hex-3-en-1one (**4**) with varying ratios of the two compounds were obtained in similar overall yield.

**$^1$H NMR** ($CDCl_3$): $\delta$ = 7.03 (m, 2 H), 7.12 (m, 2 H), 7.36 (m, 2 H), 7.41 (m, 2 H), 7.50 (m, 2 H), 7.59 (m, 2 H), 8.27 (m, 2 H), 8.45 (m, 2 H). **$^{13}$C{$^1$H} NMR** ($CDCl_3$): $\delta$ = 122.4, 122.5, 125.3, 125.4, 126.1, 135.2, 135.7, 148.5, 149.4, 150.0, 152.8, 156.3, 199.5.

### [μ-(3)($MX_2$)$_2$] (M = Zn, Hg; X = Cl, Br) (general procedure)

**3** (39 mg, 0.1 mmol) was dissolved in ethanol (10 mL). $MX_2$ (0.2 mmol) was added. The mixture was stirred at 65 °C for 14 h and was subsequently allowed to cool to room temperature. The product was isolated by filtration, washed with small amounts of diethyl ether and *n*-hexane and dried in vacuo.

**$MX_2$ = $ZnCl_2$:** red microcrystalline solid (62 mg, 95 %). An analytical sample was obtained by recrystallization from dichloromethane. Elemental analysis: $C_{26}H_{16}N_4Cl_4OZn_2 \cdot CH_2Cl_2$ (745.92): C 41.63 (calcd. 41.87), H 2.85 (2.43), N 6.95 (7.51) %.

**$^1$H NMR** ($CDCl_3$): $\delta$ = 7.54 (m, 2 H), 7.68 (m, 6 H), 7.75 (m, 2 H), 8.09 (m, 2 H), 9.12 (m, 2 H), 9.17 (m, 2 H).

**$MX_2$ = $ZnBr_2$:** dark orange microcrystalline solid (80 mg, 95 %). Elemental analysis: $C_{26}H_{16}N_4Br_4OZn_2$ (838.79): C 35.02 (calcd. 35.80), H 2.27 (1.92), N 6.02 (6.68) %.

**$^1$H NMR** ($CDCl_3$): $\delta$ = 7.55 (m, 4 H), 7.66 (m, 4 H), 7.73 (m, 2 H), 8.08 (m, 2 H), 9.23 (m, 4 H).

**$MX_2$ = $HgCl_2$:** orange microcrystalline solid (81 mg, 87 %). An analytical sample was obtained by recrystallization from dichloromethane. Elemental analysis: $C_{26}H_{16}N_4Cl_4Hg_2O \cdot 2CH_2Cl_2$ (1101.30): C 29.34 (calcd. 29.45), H 1.82 (1.83), N 4.76 (5.09) %.

**$^1$H NMR** ($CDCl_3$): $\delta$ = 7.29 (m, 2 H), 7.38 (m, 2 H), 7.50 (m, 4 H), 7.56 (m, 2 H), 7.89 (m, 2 H), 8.80 (m, 4 H). **$^{13}$C{$^1$H} NMR** ($CDCl_3$): $\delta$ = 124.9, 125.3, 125.4, 127.7, 127.9, 138.3, 138.6, 148.0, 148.4, 148.8, 150.2, 155.4, 200.4.

**$MX_2$ = $HgBr_2$:** orange microcrystalline solid (72 mg, 65 %). Elemental analysis: $C_{26}H_{16}N_4Br_4Hg_2O$ (1109.23): C 26.73 (calcd. 27.07), H 1.82 (1.45), N 4.20 (5.05) %.

**$^1$H NMR** ($CDCl_3$): $\delta$ = 7.21 (m, 2 H), 7.38 (m, 2 H), 7.50 (m, 4 H), 7.55 (m, 2 H), 7.89 (m, 2 H), 8.81 (m, 2 H), 8.85 (m, 2 H). **$^{13}$C{$^1$H} NMR** ($CDCl_3$): $\delta$ = 125.1, 125.5, 125.6, 128.1, 128.4, 138.5, 138.9, 148.3, 148.7, 149.1, 150.4, 155.4, 199.5.

[(**1**)BeCl$_2$]: **1** (2,5-diphenyl-3,4-di(pyrid-2-yl)cyclopent-2,4,dien-1-one [1]) (970 mg, 2.50 mmol) was suspended in 15 mL CH$_2$Cl$_2$, and 2.50 mmol BeCl$_2$ was added. The mixture was stirred at 20 °C for 3 days, during which the colour slowly changed form orange-red to dark red. After filtration from 200 mg microcrystalline product, the volume of the filtrate was reduced to 13 mL using a stream of dry nitrogen. Well shaped moisture sensitive red single crystals, which are suitable for X-ray crystallography, could be isolated after standing the solution at 20 °C for 14 h. Evacuation of the solution to dryness leads to 860 mg crystal powder (88 %).

**IR spectrum**/cm$^{-1}$ (nujol mull, CsBr plates): 1715 (vst) νC=O, 686 (st) $\nu_{as}$BeN$_2$, 590 (st) $\nu_s$BeN$_2$, 561 (vst) $\nu_{as}$BeCl$_2$, 504 (m) $\nu_s$BeCl$_2$.

[μ-(**3**)(BeCl$_2$)$_2$]: The synthesis is analogous to [(**1**)BeCl$_2$], using 267 mg of **3** (0.69 mmol), 5 mL CH$_2$Cl$_2$, 1.38 mmol BeCl$_2$. Red moisture sensitive single crystals of [μ-(**3**)(BeCl$_2$)$_2$]$\cdot$3CH$_2$Cl$_2$ could be isolated by filtration. Evacuation leads to the solvent-free microcrystalline product (300 mg, 79 %).

**IR spectrum**/cm$^{-1}$ (nujol mull, AgCl plates): 1611 (st) νC=O, 619 (m, br) νBeN, 556 (m) $\nu_{as}$BeCl$_2$, 531 (m) $\nu_s$BeCl$_2$.

## *X-ray crystallography*

Single crystals were obtained by crystallization from dichloromethane. Stoichiometric solvent inclusion was observed in most cases. For each data collection a single crystal was mounted on a glass fibre and all geometric and intensity data were taken from this sample. Data collection using MoKα radiation ($\lambda$ = 0.71073 Å) was made on a Stoe IPDS2 diffractometer equipped with a 2-circle goniometer and an area detector. Absorption correction was done by integration using X-red [13]. The data sets were corrected for Lorentz and polarisation effects. The structures were solved by direct methods (SHELXS97) and refined using alternating cycles of least squares refinements against $F^2$ (SHELXL97) [14]; SIR-92 was used for structure solution in case of the Be complexes [15]. All non H atoms were found in difference Fourier maps and were refined with anisotropic displacement parameters. H atoms were placed in constrained positions according to the riding model with the 1.2 fold isotropic displacement parameters. Pertinent crystallographic data are collected in Tables 2 and 3. Graphical representations were made using ORTEP-3 win [16].

Supplementary Material. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplemental publication CCDC-669383 for [(**1**)BeCl$_2$], CCDC-669384 for [μ-(**3**)(BeCl$_2$)$_2$], CCDC-670276 for **3**, CCDC-670277 for **4**, CCDC-670278 for [μ-(**3**)(ZnCl$_2$)$_2$], CCDC-670279 for [μ-(**3**)(ZnBr$_2$)$_2$], CCDC-670280 for [μ-(**3**)(HgCl$_2$)$_2$], and CCDC-670281 for [μ-(**3**)(HgBr$_2$)$_2$]. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK (Fax: int.code+(1223)336-033; e-mail for enquiry: fileserv@ccdc.cam.ac.uk).

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**Table 2** Crystal data and structure refinement for **3**, **4**, [(**1**)BeCl$_2$], and [μ-(**3**)(BeCl$_2$)$_2$]$\cdot$3CH$_2$Cl$_2$

| Compound | **3** | **4** | [(**1**)BeCl$_2$] | [μ-(**3**)(BeCl$_2$)$_2$]$\cdot$3CH$_2$Cl$_2$ |
|---|---|---|---|---|
| Empirical formula | $C_{25}H_{16}N_4O$ | $C_{25}H_{16}N_4O_2$ | $C_{27}H_{18}BeCl_2N_2O$ | $C_{28}H_{22}Be_2Cl_{10}N_4O$ |
| Formula weight | 388.42 | 404.42 | 466.37 | 803.05 |
| Temperature / K | 133(2) | 133(2) | 173(2) | 193(2) |
| Crystal system | monoclinic | monoclinic | monoclinic | monoclinic |
| Space group | $P\ 2_1/c$ | $P\ 2_1/a$ | $Cc$ | $P\ 2_1/c$ |
| Lattice parameters | $a$ = 18.894(4) | $a$ = 11.348(3) | $a$ = 13.668(1) | $a$ = 12.136(1) |
| length / Å | $b$ = 8.576(1) | $b$ = 9.066(3) | $b$ = 11.440(1) | $b$ = 13.926(2) |
| | $c$ = 11.997(3) | $c$ = 19.698(5) | $c$ = 14.667(1) | $c$ = 20.684(2) |
| angle / ° | $\beta$ = 99.16(2) | $\beta$ = 101.35(2) | $\beta$ = 92.35(1) | $\beta$ = 90.97(1) |
| Cell volume / Å$^3$ | 1919.0(7) | 1986.8(9) | 2291.4(3) | 3495.2(7) |
| $Z$ | 4 | 4 | 4 | 4 |
| $d_{calc.}$ / gcm$^{-3}$ | 1.344 | 1.352 | 1.352 | 1.526 |
| $\mu$ / mm$^{-1}$ | 0.085 | 0.089 | 0.306 | 0.828 |
| $F$(000) | 808 | 840 | 960 | 1616 |
| $\theta$ range / ° | 2.61 to 25.0 | 2.11 to 25.0 | 2.32 to 26.09 | 1.68 to 26.16 |
| Index ranges | $-16 \rightarrow h \rightarrow 22$ | $-13 \rightarrow h \rightarrow 13$ | $-16 \rightarrow h \rightarrow 16$ | $-15 \rightarrow h \rightarrow 14$ |
| | $-10 \rightarrow k \rightarrow 10$ | $-10 \rightarrow k \rightarrow 10$ | $-14 \rightarrow k \rightarrow 14$ | $-17 \rightarrow k \rightarrow 17$ |
| | $-11 \rightarrow l \rightarrow 14$ | $-23 \rightarrow l \rightarrow 23$ | $-18 \rightarrow l \rightarrow 18$ | $-25 \rightarrow l \rightarrow 25$ |
| Refls. collected | 6176 | 11777 | 15675 | 26276 |
| Independent refls. | 3176 [$R_{int}$ = 0.1378] | 3415 [$R_{int}$ = 0.3060] | 4469 [$R_{int}$ = 0.0449] | 6745 [$R_{int}$ = 0.1304] |
| Refls. observed | 1401 | 725 | 4053 | 3578 |
| $T_{min}$ / $T_{max}$ | – | – | 0.47 / 1.0 | 0.77 / 1.0 |
| Data / restraints / parameters | 3176 / 0 / 271 | 3415 / 0 / 280 | 4469 / 0 / 370 | 6745 / 0 / 426 |
| GOF on $F^2$ | 0.812 | 0.609 | 0.971 | 0.980 |
| Final $R$ indices | $R1$ = 0.0720 | $R1$ = 0.0750 | $R1$ = 0.0257 | $R1$ = 0.0946 |
| [$I > 2\sigma(I)$] | $wR2$ = 0.1643 | $wR2$ = 0.1740 | $wR2$ = 0.0573 | $wR2$ = 0.2524 |
| $R$ indices | $R1$ = 0.1462 | $R1$ = 0.2621 | $R1$ = 0.0303 | $R1$ = 0.1440 |
| (all data) | $wR2$ = 0.1886 | $wR2$ = 0.2483 | $wR2$ = 0.0584 | $wR2$ = 0.2821 |
| Extinction coeff. | – | – | – | 0.006(2) |
| Largest diff. peak and hole / eÅ$^{-3}$ | 0.242 and −0.239 | 0.228 and −0.210 | 0.145 and −0.176 | 0.642 and −0.591 |

**Table 3** Crystal data and structure refinement for [$\mu$-(**3**)($ZnCl_2$)$_2$], [$\mu$-(**3**)($ZnBr_2$)$_2$], [$\mu$-(**3**)($HgCl_2$)$_2$], and [$\mu$-(**3**)($HgBr_2$)$_2$]

| Compound | [$\mu$-(**3**)($ZnCl_2$)$_2$]$\cdot 2CH_2Cl_2$ | [$\mu$-(**3**)($ZnBr_2$)$_2$]$\cdot CH_2Cl_2$ | [$\mu$-(**3**)($HgCl_2$)$_2$]$\cdot 2CH_2Cl_2$ | [$\mu$-(**3**)($HgBr_2$)$_2$]$\cdot CH_2Cl_2$ |
|---|---|---|---|---|
| Empirical formula | $C_{26}H_{18}Cl_6N_4OZn_2$ | $C_{26}H_{18}Br_4Cl_2N_4OZn_2$ | $C_{27}H_{20}Cl_8Hg_2N_4O$ | $C_{26}H_{18}Br_4Cl_2Hg_2N_4O$ |
| Formula weight | 745.88 | 923.72 | 1101.25 | 1194.16 |
| Temperature / K | 133(2) | 133(2) | 133(2) | 133(2) |
| Crystal system | monoclinic | monoclinic | monoclinic | monoclinic |
| Space group | *C* 2/*c* | *C* 2/*c* | *C* 2/*c* | *C* 2/*c* |
| Lattice parameters | $a$ = 7.3223(9) | $a$ = 7.489(1) | $a$ = 21.761(2) | $a$ = 7.8651(6) |
| length / Å | $b$ = 24.520(2) | $b$ = 24.246(4) | $b$ = 13.7508(9) | $b$ = 23.490(2) |
|  | $c$ = 16.364(2) | $c$ = 16.692(3) | $c$ = 14.464(1) | $c$ = 16.813(1) |
| angle / ° | $\beta$ = 98.174(9) | $\beta$ = 96.23(1) | $\beta$ = 129.417(5) | $\beta$ = 94.604(6) |
| Cell volume / Å$^3$ | 2908.1(5) | 3013.0(8) | 3343.6(5) | 3096.1(4) |
| $Z$ | 4 | 4 | 4 | 4 |
| $d_{calc.}$ / gcm$^{-3}$ | 1.704 | 2.036 | 2.188 | 2.562 |
| $\mu$ / mm$^{-1}$ | 2.230 | 7.102 | 9.841 | 15.268 |
| $F$(000) | 1488 | 1776 | 2056 | 2176 |
| $\theta$ range / ° | 1.66 to 25.00 | 1.68 to 25.0 | 1.91 to 25.50 | 1.73 to 25.0 |
| Index ranges | $-8 \rightarrow h \rightarrow 8$ | $-8 \rightarrow h \rightarrow 7$ | $-26 \rightarrow h \rightarrow 26$ | $-9 \rightarrow h \rightarrow 9$ |
|  | $-28 \rightarrow k \rightarrow 28$ | $-28 \rightarrow k \rightarrow 28$ | $-16 \rightarrow k \rightarrow 16$ | $-27 \rightarrow k \rightarrow 27$ |
|  | $-19 \rightarrow l \rightarrow 19$ | $-19 \rightarrow l \rightarrow 16$ | $-17 \rightarrow l \rightarrow 17$ | $-19 \rightarrow l \rightarrow 19$ |
| Refls. collected | 9379 | 5890 | 11219 | 9796 |
| Independent refls. | 2573 [$R_{int}$ = 0.1251] | 2439 [$R_{int}$ = 0.0370] | 3114 [$R_{int}$ = 0.0790] | 2715 [$R_{int}$ = 0.0855] |
| Refls. observed | 2000 | 1997 | 2580 | 2389 |
| $T_{min}$ / $T_{max}$ | 0.8767 and 0.9334 | 0.2408 and 0.4437 | 0.2646 and 0.6653 | 0.0189 and 0.2089 |
| Data / restraints / parameters | 2573 / 0 / 178 | 2439 / 0 / 179 | 3114 / 0 / 192 | 2715 / 0 / 179 |
| GOF on $F^2$ | 0.932 | 0.950 | 1.010 | 1.005 |
| Final $R$ indices | $R1$ = 0.0431 | $R1$ = 0.0255 | $R1$ = 0.0402 | $R1$ = 0.0229 |
| [$I > 2\sigma(I)$] | $wR2$ = 0.1061 | $wR2$ = 0.0578 | $wR2$ = 0.0963 | $wR2$ = 0.0497 |
| $R$ indices | $R1$ = 0.0542 | $R1$ = 0.0351 | $R1$ = 0.0463 | $R1$ = 0.0278 |
| (all data) | $wR2$ = 0.1097 | $wR2$ = 0.0610 | $wR2$ = 0.0978 | $wR2$ = 0.0510 |
| Extinction coeff. | − | 0.00 | 0.00064(7) | 0.00030(2) |
| Largest diff. peak and hole / eÅ$^{-3}$ | 0.579 and −0.694 | 0.627 and −0.366 | 3.077 and −4.173 | 1.102 and −1.126 |

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