Research Article

Molecular Architectures Derived from Metal Ions and the Flexible 3,3′-Bipyridine Ligand: Unexpected Dimer with Hg(II)

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The flexible ditopic ligand 3,3′-bipyridine (3,3′-bpy) has been reacted with a series of transition metal species (Ag⁺, Hg²⁺, cis-a₂M²⁺ (a₂ = NH₃ or a₂ = en; M = Pt, Pd), trans-a₂Pt²⁺ (a = NH₃)) in an attempt to produce discrete cyclic constructs. While Ag⁺ gave a polymeric structure {[Ag(3,3′-bpy)](ClO₄)·H₂O}ₙ (1), with all other metal entities cyclic structures were formed. Interestingly, Hg(CH₃COO)₂ produced a dinuclear complex [Hg(3,3′-bpy)(CH₃COO)₂]·3H₂O (2), in which the two 3,3′-bpy ligands adopt a cis-orientation of the coordinating pyridyl entities. With cis-(NH₃)²Pt²⁺, a cyclic complex 4 was isolated in crystalline form which, according to HRMS, is a trimer. With trans-(NH₃)²Pt²⁺, different species are formed according to ¹H NMR spectroscopy, the nature of which was not established.

1. Introduction

The “molecular library” concept has proven highly efficient in designing discrete supramolecular metal complexes by combining di- or multitopic metal entities with rigid di- or multitopic ligands [1, 2]. It is less straightforward if ligands are flexible and can adopt, in principle, different rotamer states. In its simplest form, this is the case when two N-heterocyclic ligands are connected via a C–C bond. Examples are, among others, 2,2′-bipyridine (2,2′-bpy), 3,3′-bipyridine (3,3′-bpy) and, 2,2′-bipyrazine (2,2′-bpz) (Scheme 1). While 2,2′-bpy, in the overwhelming number of structures, acts as a chelating ligand with the two ring N atoms in a cis-orientation, there are also rare cases of 2,2′-bpy adopting a bridging mode, hence being in a transconfiguration or half-way between cis and trans-[3]. It depends on the conformation of the ligand and the geometry of the metal, what kind of construct/s is/are formed. With 2,2′-bpz, we have studied this question in more detail and have characterized a number of discrete molecular entities, which include a flat triangular structure, 3D triangular entities of different shapes (prism, vase), as well as a tetranuclear open box [4, 5]. In all these cases the N4/N4′ positions are involved in metal coordination, occasionally complemented by addition of metal chelation via N1/N1′, and influenced by counter anions.

In principle, 3,3′-bipyridine (3,3′-bpy) metal complexes should be able to reveal analogous topologies as 2,2′-bpz, with the advantage of higher basicities of the N donor atoms (Figure 1). There are several reports in the literature on polymeric structures containing cis- [6] and in particular trans-arranged 3,3′-bpy ligands [7], yet none with a discrete molecular metallacycle. The only related examples are those of trinuclear cycles containing three cis-a₂M³⁺ units (a₂ = diamine; M = Pd or Pt) and three 4,7-phenanthroline ligands, which can be considered rigid analogous of 3,3′-bpy ligands with the two pyridine entities fixed in a cis-orientation [8, 9]. Our interest in discrete cationic metallacycles stems, among others, from their potential of interacting noncovalently with DNA [10] or particular DNA secondary structures such as DNA quadruplexes [11], as well as their ability to act as hosts for anions [12, 13]. In the present study, we have employed different transition metal ions and metal entities which previously have been shown by others and ourselves to produce discrete cyclic complexes, namely Ag(I), Hg(II), enPd(II), cis-(NH₃)²Pt(II) as well as trans-a₂Pt(II) (a = NH₃) [14–16].
Scheme 1: cis- and trans-orientation of pyridine and pyrazine rings in 2,2'-bpy, 3,3'-bpy, and 2,2'-bpz.

Figure 1: Feasible discrete (I–IV) and polymeric (V, VI) structures of 3,3'-bpy metal complexes, and novel dinuclear complex (VII) observed in the HgII complex 2.
2. Experimental

2.1. Synthesis Procedures. AgClO₄ and Hg(CH₃COO)₂ were of commercial origin. 3,3′-bpy [17], PdCl₂(en) [18], cis-PtCl₂(NH₃)₂ [19], and trans-PtCl₂(NH₃)₂ [20] were prepared according to known literature procedures.

\[ [\text{Ag}(3,3′-\text{bpy})]_2(\text{ClO}_4^-)·2\text{H}_2\text{O}]_n \] (1). To a solution of 3,3′-bpy (15.6 mg, 0.1 mmol) in water (3 mL), an aqueous solution (2 mL) of AgClO₄ (20.7 mg, 0.1 mmol) was added. The white precipitate which formed immediately was centrifuged off and recrystallized from water (4 mL, 40 °C). Colorless crystals were obtained after 2 d at room temperature. Yield: 37.1 mg (74%). Anal. Calcd (%) for C₁₂H₁₈N₆O₇Pd: C, 30.8; H, 4.0; N, 18.0. Found: C, 31.4; H, 2.6; N, 7.5.

\[ \text{Hg}(3,3′-\text{bpy})(\text{CH}_3\text{COO})_2·2\text{H}_2\text{O} \] (2). An aqueous solution (4 mL) of 3,3′-bpy (31.2 mg, 0.2 mmol) and Hg(CH₃COO)₂ (31.9 mg, 0.1 mmol) was stirred at room temperature for 12 h. The solution is filtered and kept at room temperature. After 3 d, colorless crystals were obtained. Yield: 61 mg (66%). Anal. Calcd (%) for C₁₀H₁₀AgClN₂O₅: C, 17.3; H, 2.6; N, 7.9. Found: C, 17.5; H, 2.3; N, 8.1.

\[ [{\text{Pd}}(en)(3,3′-\text{bpy})]_2(\text{NO}_3^-)·2\text{H}_2\text{O}]_n \] (3). An aqueous suspension (15 mL) of PdCl₂(en) (47.4 mg, 0.2 mmol) and AgNO₃ (68 mg, 0.4 mmol) was stirred in dark for 12 h. The resultant AgCl precipitate was filtered off and 3,3′-bpy (31.2 mg, 0.2 mmol) was added to the filtrate. The solution was stirred at 40 °C for 1 day and then concentrated to a volume of 4 mL by rotary evaporator. The solution was filtered and kept at room temperature. After 4 d, light yellow powder was recovered. Yield: 250 µL/min, (iii) injection volume 5 µL, (iv) scan of wavelength range from 200 to 600 nm. The parameters for MS were as follows: (i) ionisation mode ESI (electrospray ionization), (ii) source voltage 3.8 kV, Capillary voltage 41 V, Capillary temperature 275 °C, tube lens voltage 140 V, (iii) scanned mass range 150 m/z to 2000 m/z with resolution set to 60000. Analysis was done by flow injection (without any column).

2.5. Determination of pKₐ Values. The pKₐ values of 3,3′-bipy ligand were determined by evaluating the changes in chemical shifts of bipyridine protons at different pH values. pD values were measured by use of a glass electrode and addition of 0.4 units to the uncorrected pH meter reading (pH*). The graphs (chemical shifts versus pH) were evaluated with a nonlinear least-squares fit according to Newton-Gauss method [24] and the acidity constants (calculated for D₂O) were converted to values valid for H₂O [25].

3. Results and Discussion

1H NMR Spectra of 3,3′-Bipyridine. Figure 2 displays a typical 1H NMR spectrum of the free ligand at pD 6.8. The individual resonances show the expected coupling patterns [17]. In the D₂O spectrum, all resonances show splitting due to long-range coupling. For example, the H2 signal is split into a doublet due to coupling with H4 (1.5 Hz) and additionally displays coupling with H5 (0.7 Hz). Upon protonation, all resonances are downfield shifted, with H6 affected most. pKₐ values for [3,3′-bpyH]⁺ and [3,3′-bpyH₂]²⁺, as determined by pD dependent ¹H NMR spectroscopy, are 4.58 ± 0.1 and 2.71 ± 0.1 (values converted to H₂O), respectively. These values compare with 4.3 and ca. 0.3 for 2,2′-bpy, and 0.45 and ~1.35 for 2,2′-bpy, and reflect the higher basicity of 3,3′-bpy as compared to two other ligands.
complexes as a consequence of fast exchange. Only averaged signals of the free ligand and the various Ag reveal resonances due to individual species, but rather gives a polymeric structure rather than a discrete cyclic structure as we had hoped for. The silver atom (Ag1) shows interaction [27, 28] with a neighbor silver atom (Ag0.03 ppm (H4), 0.05 ppm (H6), and 0.04 ppm (H5).

1H NMR resonances of 3, 3′-bpy in D2O display a moderate sensitivity on concentration, which is consistent with intermolecular stacking. For example, when going from 0.0125 M to 0.125 M, upfield shifts are 0.06 ppm (H2), 0.06 ppm (H4), 0.06 ppm (H2), 0.09 ppm (H6), and 0.13 ppm (H5).

Ag⁺ and Hg²⁺ Coordination. Addition of Ag⁺ ions to an aqueous solution of 3, 3′-bpy in D2O expectedly does not reveal resonances due to individual species, but rather gives only averaged signals of the free ligand and the various Ag complexes as a consequence of fast exchange.

A similar situation applies to mixtures of 3, 3′-bpy and Hg(II) acetate. The spectrum of the dinuclear Hg(II) complex 2 has its 1H resonances (δ, ppm; D2O, pD 5.2) at 8.97, 8.73, 8.44, and 7.88 as well as 2.02 (acetate). No coupling of any of the 3, 3′-bpy resonances with the ¹⁹⁹Hg isotope is observed as in a previously reported case [26], and a comparison of the shifts of 2 with those of the free ligand at the same pD (downfields shifts of H2, 0.06 ppm; H4, 0.06 ppm; H6, 0.09 ppm; H5, 0.13 ppm) does not permit any conclusions regarding the bonding situation in solution. The Δρmax and Δρmin (e Å⁻³) values are given in Table 1.

Table 1: Crystallographic data for compounds [[Ag(3, 3′-bpy)](ClO₄) · H₂O]ₙ (1) and [Hg(3, 3′-bpy)(CH₂COO)₂]₂ · 3H₂O (2).

|               | 1                          | 2                          |
|---------------|----------------------------|-----------------------------|
| Formula       | C₁₀H₁₆Ag₁Cl₁N₂O₅           | C₂₈H₃₄Hg₂N₄O₁₁             |
| Formula weight (g mol⁻¹) | 381.52                    | 1003.77                    |
| Crystal color and habit | colorless prisms           | colorless prisms           |
| Crystal size (mm) | 0.20 × 0.20 × 0.10         | 0.15 × 0.10 × 0.05         |
| Crystal system | monoclinic                 | triclinic                  |
| Space group   | P2₁/c                      | P-1                        |
| a (Å)         | 9.7606(10)                 | 8.5635(5)                  |
| b (Å)         | 7.3145(8)                  | 9.2069(6)                  |
| c (Å)         | 19.572(2)                  | 11.3262(6)                 |
| α (°)         | 90                         | 74.746(5)                  |
| β (°)         | 119.148(9)                 | 84.183(4)                  |
| γ (°)         | 90                         | 63.221(6)                  |
| V (Å³)        | 1220.4(2)                  | 769.21(8)                  |
| Z             | 4                          | 1                          |
| Dₐdol. (g cm⁻³) | 2.077                      | 2.167                      |
| F (000)       | 752                        | 478                        |
| μ (mm⁻¹)      | 1.888                      | 10.034                     |
| No. reflections collected | 2333                     | 3572                       |
| No. reflections observed | 1557                     | 2969                       |
| Rint         | 0.0317                     | 0.0359                     |
| No. parameters refined | 172                      | 208                        |
| R [I > 2σ(I)] | 0.0331                     | 0.0270                     |
| wR (all reflections) | 0.0572                     | 0.0453                     |
| Goodness-of-fit (GOF) | 1.041                   | 0.911                      |
| Δρmax and Δρmin (e Å⁻³) | 0.941 and –0.517   | 1.078 and –1.283  |

GOF = [Σw(Fo² – Fc²)]² / [ΣwFo]²; R = Σ|Fo| – |Fc| / Σ|Fo|; wR = [Σw(Fo² – Fc²)²]/Σw(Fo²)²]¹/².
in 1, in 2 the 3,3'-bpy ligands adopt a cis-conformation of the two pyridyl rings, with a twist angle of 30.4(2)°, and act as bridges between two mercury centers. The coordination geometry of the Hg ion (Table 3) is distorted tetrahedral, enclosing two 3,3'-bpy entities (Hg1-N1a, 2.274(3) Å; Hg1-N1b, 2.263(3) Å), and two chelating/semichelating acetates (Hg1-O11, 2.490(3) Å; Hg1-O12, 2.392(3) Å; and Hg1-O21, 2.286(3) Å; Hg1-O22, 2.762(3) Å). Selected distances and angles around mercury are listed in Table 3. Both 3,3'-bpy ligands and their bonded mercury atoms are almost coplanar with a tendency towards a boat conformation (distance from Hg1 to the plane defined by N1a, N1b, N1a, N1b' is 0.58 Å).

The disposition of the acetate ligands is worthy to be discussed in more detail. Both ligands form a dihedral angle of 79.23(16)° with each other. The ligand containing O11,O12 is roughly coplanar with the pyridyl rings (7.27(27)°, 23.28(23)°), whereas the ligand A2 (with O21,O22) is roughly perpendicular (78.33(15), 72.81(14)°). Both are asymmetrically coordinated to Hg1, displaying significant longer bond distances of those oxygen atoms involved in hydrogen bonding: O1w· · ·O11, 2.802(5) Å (Hg1-O11, 2.490(3) Å versus Hg1-O12, 2.392(3) Å) and O1w· · ·O22, 2.757(4) Å (Hg1-O21, 2.286(3) Å versus Hg1-O22, 2.762(3) Å). Further hydrogen bonding includes a twofold O1w· · ·O2w (2.785(10) Å) connection. Besides hydrogen bonding, the crystal packing includes π−π-and anion−π-interactions. N1a-pyridyl rings are pairwise π−π stacked (3.5 Å), and both rings are involved in an additional anion−π-interaction with O11 (O11· · · centroid, 3.47 Å). Considering the latter, the formation of staggered rows is observed, in which each molecule displays four anion−π-interactions with neighbor molecules. Rows are interconnected by π−π-stacking and hydrogen bonding.

**Complexes with enPd**II** and cis-((N)H)2Pt**II**. Reactions of 3,3'-bpy with [Pd(en)(H2O)2](NO3)2 and cis-[(Pt(NH3)2(H2O)2](NO3)2 (1 : 1 ratio) give products of 1 : 1 stoichiometry [[Pd(en)(3,3'-bpy)](NO3)2]n (3) and cis-[(Pt(NH3)2)(3,3'-bpy)](PF6)2]n (4) which, according to 1H NMR spectroscopy, are pure materials. Only single sets of 3,3'-bpy resonances are observed in both compounds, indicating that both compounds must be cyclic. Chemical shifts (δ, ppm; D2O, TMA as internal reference) are as follows: 3, 9.15, 8.84, 8.27, 7.69 ppm (3,3'-bpy) and 2.98 (en); 4, 8.99, 8.95, 8.23, 7.67 (3,3'-bpy). When TSP was used...
Figure 3: (a) Detail of the coordination sphere of the silver atom in 1. (b) Polymeric motif between Ag1 and 3,3′-bpy bridging ligands in 1.

Table 3: Selected bond distances (Å) and angles (°) for compound 2.

| Bond/Angle | Distance/Angle |
|------------|---------------|
| Hg1-N1a    | 2.274(3)      |
| N1a-Hg1-N1b| 114.74(11)    |
| N1b-Hg1-O11| 88.58(11)     |
| Hg1-O11    | 2.490(3)      |
| N1a-Hg1-O12| 140.71(12)    |
| Hg1-O12    | 2.392(3)      |
| N1a-Hg1-O12| 103.25(12)    |
| Hg1-O21    | 2.762(3)      |
| N1b-Hg1-O12| 89.72(12)     |

The high resolution MS of a sample of 4 was carried out and confirmed a triangular structure (see (II) or (IV) in Figure 1). The mass spectrum displayed peaks due to [M–(PF6)]⁺: 1880.08114 (calcd. 1880.07904), (M–(PF6)2)²⁺: 867.55844 (calcd. 867.55828), and [M–(PF6)₄]⁴⁺: 361.29666 (calcd. 361.29621). The HRMS spectrum of [M–(PF6)₄]⁴⁺ is given in Figure 6 and compared with the simulated spectrum.

Reaction with trans-[Pt(NH₃)₂(D₂O)₂]²⁺. Reaction of 3,3′-bpy with trans-[Pt(NH₃)₂(D₂O)₂](NO₃)₂ was carried out with different ratios between 3,3′-bpy and the Pt species (10 : 1, 2 : 1, 1 : 1, 1 : 10) on the ¹H NMR scale in D₂O. Without exception, the spectra displayed time-dependent changes, but within 2-3 d at 50°C, constant spectra were obtained. Even then, however, resonances due to multiple products were present. In the case of a large excess of ligand over Pt (10 : 1), the spectrum reveals the presence of a major species attributed to trans-[Pt(NH₃)₂(3,3′-bpy)₂]²⁺ and excess 3,3′-bpy (Figure 7). The resonances of the free 3,3′-bpy (L) were unambiguously identified by adding solid 3,3′-bpy to the NMR sample. The two sets of pyridine resonances of the coordinated 3,3′-bpy ligands of the 1 : 2 complex are assigned on the basis of their relative intensities. What strikes is that the H2 and H4 resonances of the free ligand are very much broadened (cf. Figure 2(a)) and that H2, H4, and H6 are upfield shifted by ca. 0.2, 0.08, and 0.14 ppm, respectively. As these shifts cannot be interpreted with a pH effect, we propose that the presence of the 1 : 2-Pt complex has an effect on the rotamer equilibrium of the ligands.
free ligand. Consistent with this proposal, the two resonances closest to the C3–C3 bond, hence H2 and H4, become quite broad. Stacking interactions between free and coordinated 3, 3′-bpy could possibly account for this feature.

The $^1$H NMR spectrum of a 1:1 mixture of trans-[Pt(NH$_3$)$_2$(D$_2$O)$_2$]$^{2+}$ and 3, 3′-bpy displays four H2 (H2′) singlets of different relative intensities at lowest field, and at least for the H6 (H6′) resonances also four components can be differentiated. Free 3, 3′-bpy is not detectable. It is obvious that the self-assembly process of trans-(NH$_3$)$_2$Pt$^{	ext{II}}$ and 3, 3′-bpy does not lead to a preferred single product, unlike in the case of enPd$^{	ext{II}}$ and cis-(NH$_3$)$_2$Pt$^{\text{II}}$.

4. Summary

The flexible ditopic ligand 3, 3′-bipyridine forms with Hg(CH$_3$COO)$_2$ and cis-[Pt(NH$_3$)$_2$(H$_2$O)$_2$](PF$_6$)$_2$ discrete di- and trinuclear cycles 2 and 4, respectively. The solid state structure of the Hg(II) complex 2 is unique in that it represents the smallest possible entity of any cyclic complex. It appears that the opening of the N1a-Hg-N1b angle to ca. 115° allows the dinuclear to be formed. A similar structure, with the two 3, 3′-bpy ligands approximately coplanar, is not to be expected for cis-a$_2$Pt$^{\text{II}}$ with its 90° bonding angle. Consequently, 4 is a cyclic trinuclear compound. On the NMR time scale, 2 is kinetically labile in aqueous solution, but 4 is inert. We plan to further study 4 with regard to its host-guest chemistry and its noncovalent interaction with DNA.
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