Novel Dinuclear Palladium(II) Complexes with the Chelating Ligand Bis(1-methylimidazol-2-yl) Ketone (bmik) and Pyridine-2-thiolate, Pyrimidine-2-thiolate, and 1-Methylimidazole-2-thiolate as Bridging Secondary Ligands

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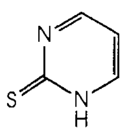
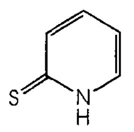
Three novel dinuclear palladium(II) complexes with the chelating ligand bis(1-methylimidazol-2-yl) ketone (bmik) as well as pyridine-2-thiolate (pyt), pyrimidine-2-thiolate (pymt), and 1-methylimidazole-2-thiolate (meimt) as bridging secondary ligands were prepared by reactions of diaqua[bis(1-methylimidazol-2-yl) ketone]palladium(II) nitrate with the ligands in aqueous solution. The thiolates bridge the two metal atoms in the μ-*N*,*S* mode. The structures of the following compounds were analyzed by single crystal X-ray diffraction: Bis(μ-pyridine-2-thiolato-*N*,*S*)-bis{[bis(1-methylimidazol-2-yl) ketone]palladium(II)}nitrate $[Pd_2(bmik)_2(pyt)_2](NO_3)_2 \cdot 5\ H_2O$ (**1**), bis(μ-pyrimidine-2-thiolato-N^1,*S*)-bis{[bis(1-methylimidazol-2-yl) ketone]palladium(II)} nitrate $[Pd_2(bmik)_2(pymt)_2](NO_3)_2 \cdot 5\ H_2O$ (**2**), and bis(μ-1-methylimidazole-2-thiolato-N^3,*S*)-bis{[bis(1-methylimidazol-2-yl) ketone]palladium(II)} nitrate $[Pd_2(bmik)_2(meimt)_2](NO_3)_2 \cdot 4.5\ H_2O$ (**3**). In the cases of **1** and **3** the bridging thiolate ligands show head-to-head orientation. For complex **2** a head-to-tail orientation of the pyrimidine-2-thiolates was found. The metal-metal distances vary from 2.963 Å in complex **3** and 2.915 Å in **1** to the shortest of 2.886 Å in **2**. In addition to the X-ray crystallography the three compounds were characterized by ^{1}H-NMR and IR spectroscopy.

Metal complexes of heterocyclic thione donors like thioamides are of considerable interest since they are known to have a widely ranging spectrum of potential uses, e.g. in analytical chemistry, in polymer industry, and in medical-biological systems, where their bacteriostatic and cytostatic properties are useful[1]. Under appropriate conditions they exhibit a very versatile and intriguing coordination chemistry. The three thioamides pyridine-2-thione (pytH), pyrimidine-2-thione (pymtH), and 1-methyl-4-imidazoline-2-thione (meimtH) are known to coordinate to platinum and palladium as neutral monodentate ligands by the exocyclic sulfur donor atom (Figure 1A)[2–7]. Pyridine-2-thione and pyrimidine-2-thione can act as anionic chelating ligands (Figure 1C)[3,8,9] as well as anionic μ-*N*,*S*-bridging ligands (Figure 1D; Table 1)[2,10–17]. The most versatile coordination behavior is exhibited by pyridine-2-thione which is also known to coordinate to platinum and palladium as an anionic monodentate (Figure 1B)[8] and as an anionic triply bridging ligand (Figure 1E)[2,13].

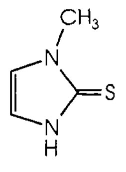
In a series of investigations we have studied the synthesis and chemical properties of platinum and palladium bis(imidazole) complexes with bridging secondary ligands[18,19,20]. Especially the platinum complexes of chelating bis(imidazole) ligands have been shown to display significant antitumor activity[19]. In this paper we report on the synthesis of the products obtained by the reaction of the diaqua[bis(1-methylimidazol-2-yl) ketone]palladium(II) nitrate complex ($[Pd(bmik)(H_2O)_2](NO_3)_2$) with pyridine-2-thione (pytH), pyrimidine-2-thione (pymtH), and 1-methyl-4-imidazoline-2-thione (meimtH). X-ray diffraction studies of these complexes revealed that the three thioamides act in all cases as anionic bridging secondary ligands. They connect two of the bmik-chelated palladium centers to dinuclear molecular units. Compounds presented and discussed in this paper are: $[(bmik)Pd(pyt)_2Pd(bmik)](NO_3)_2 \cdot 5\ H_2O$ (**1**), $[(bmik)Pd(pymt)_2Pd(bmik)]NO_3)_2 \cdot 5\ H_2O$ (**2**), and $[(bmik)Pd(meimt)_2Pd(bmik)](NO_3)_2 \cdot 4.5\ H_2O$ (**3**). Further characterization methods used are ^{1}H-NMR and IR spectroscopy.



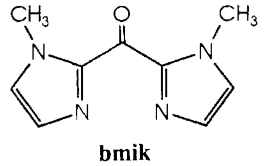
pymtH



pytH



meimtH



bmik

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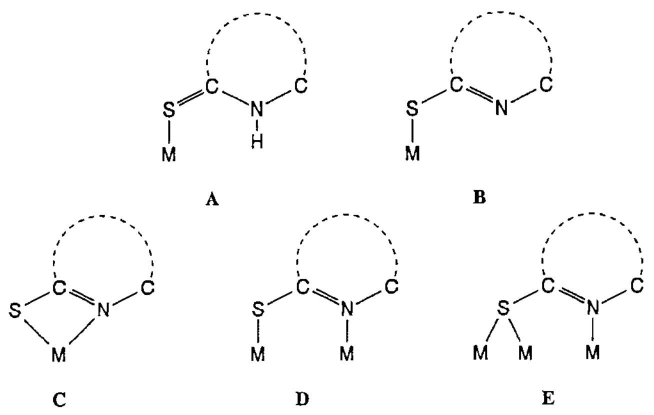

Figure 1. The different possible coordination modes of heterocyclic thiolates to platinum and palladium

Results and Discussion

Synthesis of Dinuclear Thioamide-Bridged Complexes of Palladium(II)

Pyridine-2-thione, pyrimidine-2-thione, and 1-methyl-4-imidazoline-2-thione are treated with an acidic aqueous solution ($\mathrm{pH} < 2$) of diaqua[bis(1-methylimidazol-2-yl) ketone]palladium(II) nitrate $[\mathrm{Pd(bmik)(H_2O)_2}](\mathrm{NO_3})_2$. This reaction is accompanied by a color change from pale orange to deep red. This differs from a previous report[21] where 1-methyl-4-imidazoline-2-thione was found not to react at all with palladium(II) salts at a pH less than 3.5, presumably due to protonation of both the ring nitrogen and the exocyclic sulfur atom.

In the present reaction single crystals were formed upon slow evaporation of the solvent at 6°C. The X-ray diffraction analyses of the crystals revealed that the dinuclear complexes **1**, **2**, and **3** were formed. The metal centers with the chelating ligand bis(1-methylimidazol-2-yl) ketone are bridged by the anionic thiolates in the μ-*N,S* mode (Figure 1 D) to dinuclear molecular units. This is quite remarkable, since the reaction medium was acidic at all times. As known for a long time the thioamides exist in two tautomeric forms, the thione and the iminethiol form. Usually, a base is added to the reaction mixture of a palladium or platinum salt and a thione in order to abstract the acidic proton which is involved in the thione-iminethiol tautomerism and to promote in this way its coordination as an anionic ligand[2,10,11].

Crystal Structure of 1

Figure 2 shows a plot of the molecular cation of **1**. Selected interatomic distances and angles are listed in the legend of Figure 2. The unit cell consists of two cations, four nitrate anions, and ten molecules of crystal water. One of the nitrate anions was found to be disordered, three different positions at slightly different sites could be located. Each of the palladium atoms is coordinated by one chelating bis(1-methylimidazol-2-yl) ketone molecule. In addition, they are μ-*N,S*-bridged by two pyridine-2-thiolate molecules which show a head-to-head orientation. The resulting square-planar coordination spheres of Pd(1) and Pd(2) consist of four nitrogen donors and of two nitrogen and two sulfur donor atoms, respectively. The intramolecular metal-metal distance in the dinuclear complex cation is 2.915 Å. This is 0.075 Å longer than in the corresponding α-pyridonate-bridged complex $[\mathrm{(bmik)Pd(\alpha\text{-}pyridonate)_2Pd(bmik)}](\mathrm{NO_3})_2$[18] (Pd···Pd 2.840 Å). In contrast, the tilt (dihedral) angle τ between the two adjacent metal coordination planes in the bridged unit is smaller in **1** than in the α-pyridonate-bridged complex (15.6°, 24.4°, respectively). The same observation was made by a comparison of the $[\mathrm{Pt_2(en)_2(pyt)_2}]\mathrm{Cl_2}$ complex with its α-pyridonate analogue[11]. The decreased tilt angle is in accordance with the larger bite of the bridging pyridine-2-thiolate molecules (2.72 Å) as compared to α-pyridonate (2.34 Å). Along the Pd···Pd vector an average torsion or twist angle of the coordination planes of $\omega = 27.6°$ is observed. Pd(1) lies 0.018 Å below, Pd(2) 0.055 Å above the least-squares plane through the $\mathrm{PdN_4}$ and $\mathrm{PdN_2S_2}$ coordination units, respectively. They are oriented towards each other. Two dimeric cations form a tetranuclear unit. They are related to one another by a crystallographic inversion center that lies in the center of the Pd(2)···Pd(2a) vector. The four palladium atoms of two dimers show an approximately linear arrangement [Pd(1)···Pd(2)···Pd(2a): 173.9°]. The intermolecular Pd···Pd distance is 3.660 Å. The bonding distances in the two crystallographically independent bmik ligands show only small differences. Due to the disorder of the nitrate anion consisting of N(12), O(6), O(7), and O(8) the deviation from its expected geometry is larger in this compound.

Crystal Structure of 2

Compound **2** represents the first example of a doubly thioamide-bridged complex with the thiolates in the head-to-tail orientation (Figure 3). The unit cell of **2** consists of two dinuclear cations, four nitrate anions and ten molecules of crystal water. The asymmetric unit contains only one half of the cation. The other half is generated by a crystallographic twofold rotation axis. Accordingly, the dinuclear cation possesses C_2 symmetry. Two metal centers are bridged by two pyrimidine-2-thiolates forming dinuclear molecular units. The distance of 2.886 Å between the two palladium atoms is the shortest one of the three complexes reported here, although the bite of the bridging ligands is almost the same. As the bridging ligands have a head-to-tail orientation, all palladium atoms in this compound have a $\mathrm{PdN_3S}$ coordination sphere. The metal atoms deviate from the square coordination planes such that they are oriented within a dinuclear unit towards each other. Pd(1) lies 0.031 Å below, Pd(1a) due to symmetry 0.031 Å above the best least-squares planes through $\mathrm{PdN_3S}$. The molecular cations are stacked such that they form a chain structure separated by the nitrate anions. The result is a $[-\mathrm{Pd}-\mathrm{Pd}-(\mathrm{NO_3})-]_n$ chain (Figure 4). Two oxygen atoms of the nitrate anions are bridging the palladium atoms of two dinuclear cations. The $\mathrm{Pd\cdots O_{nitrate}}$ distance amounts to 3.1 Å, the corresponding Pd···Pd···O angle is 178.5°. Due to the separation by the nitrate anions the intermolecular distance of the palladium atoms is very large (7.120 Å). The bite of the pyrimidine-

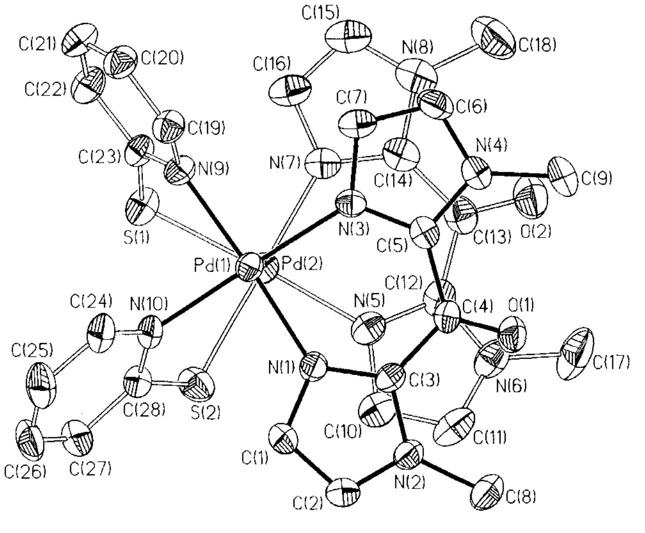

Figure 2. Molecular structure and atomic numbering scheme for the cation of **1**. Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at the 30% probability level. Shown is a view down the Pd···Pd vector. Selected interatomic distances [Å] and angles [deg] for the $[Pd_2(bmik)_2(pyt)_2]^{2+}$ cation of **1** are: Pd(1)−Pd(2) 2.915(1), Pd(1)−N(1) 2.022(5), Pd(2)−S(1) 2.290(2), Pd(1)−N(3) 2.024(5), Pd(2)−S(2) 2.288(2), Pd(1)−N(9) 2.030(5), Pd(2)−N(5) 2.081(6), Pd(1)−N(10) 2.011(5), Pd(2)−N(7) 2.086(5); N(1)−Pd(1)−Pd(2) 97.0(1), S(1)−Pd(2)−Pd(1) 81.8(1), N(1)−Pd(1)−N(3) 89.3(2), S(2)−Pd(2)−Pd(1) 80.3(1), N(1)−Pd(1)−N(9) 174.5(2), S(2)−Pd(2)−S(1) 86.5(1), N(3)−Pd(1)−Pd(2) 88.1(1), N(5)−Pd(2)−Pd(1) 102.3(1), N(3)−Pd(1)−N(9) 93.7(2), N(5)−Pd(2)−S(1) 175.2(2), N(9)−Pd(1)−Pd(2) 87.7(1), N(5)−Pd(2)−S(2) 91.7(2), N(10)−Pd(1)−Pd(2) 89.8(1), N(5)−Pd(2)−N(7) 88.4(2), N(10)−Pd(1)−N(1) 89.9(2), N(7)−Pd(2)−Pd(1) 102.3(1), N(10)−Pd(1)−N(3) 177.6(2), N(7)−Pd(2)−S(1) 93.2(2), N(10)−Pd(1)−N(9) 87.3(2), N(7)−Pd(2)−S(2) 177.3(1)

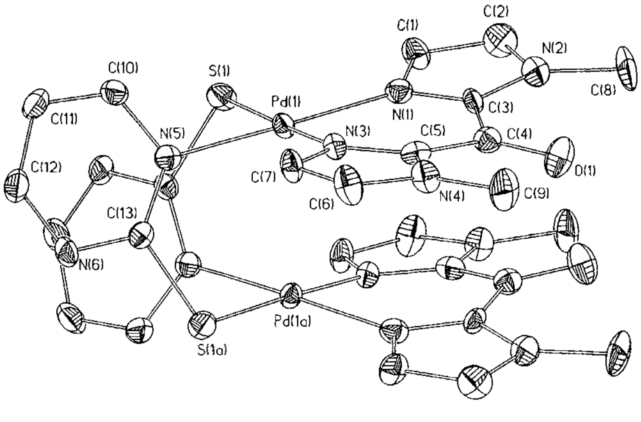

Figure 3. Molecular structure and atomic numbering scheme for the cation of **2**. Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at the 50% probability level. Interatomic distances [Å] and angles [deg] for the $[Pd_2(bmik)_2(pymt)_2]^{2+}$ cation of **2** are: Pd(1)−Pd(1a)[a] 2.886(1), Pd(1)−S(1) 2.288(2), Pd(1)−N(3) 2.053(6), Pd(1)−N(1) 2.037(7), Pd(1)−N(5) 2.037(6); S(1)−Pd(1)−Pd(1a) 83.96(6), N(3)−Pd(1)−Pd(1a) 98.7(2), N(1)−Pd(1)−Pd(1a) 95.6(2), N(3)−Pd(1)−S(1) 1.76.7(2), N(1)−Pd(1)−S(1) 92.5(2), N(5)−Pd(1)−Pd(1a) 85.8(2), N(1)−Pd(1)−N(3) 89.2(2), N(5)−Pd(1)−S(1) 87.3(2), N(1)−Pd(1)−N(5) 178.6(3), N(5)−Pd(1)−N(3) 91.0(2). − [a] Symmetry transformation used to generate equivalent atoms: $a = -x + 1/2, y, -z + 1/2$

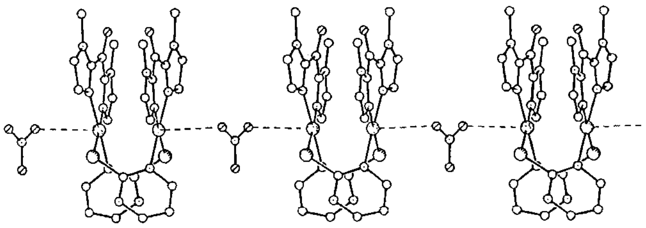

Figure 4. $[-Pd-Pd-(NO_3)-]_n$ chain of **2**

2-thiolate [S(1a)···N(5)] is 2.71 Å. In accordance with the comparatively larger Pd···Pd distance (2.886 Å) the square palladium coordination planes are tilted by $\tau = 15.6°$ relative to each other. Along the Pd···Pd vector a torsion of the palladium bonding planes of $\omega = 28.1°$ is observed. The Pd−N and the Pd−S distances lie in the same range as in similar compounds. The second nitrogen donor atom of the pyrimidine ring [N(6)] is not coordinated to a metal atom and shows hydrogen bonding to a crystal water molecule [N(6)···O(10) 2.87 Å].

Crystal Structure of 3

Compound **3** is the first example of a complex with 1-methylimidazole-2-thiolate (meimt) in the μ-*N*,*S*-bridging mode. Figure 5 shows plots of the two crystallographically independent molecular cations. The asymmetric unit of the unit cell includes two molecular cations, four nitrate anions, and nine molecules of crystal water. The two palladium atoms of a cation are μ-*N*,*S*-bridged by two 1-methylimidazole-2-thiolate units in the head-to-head mode. One palladium atom of each dinuclear molecular unit has a PdN_4 coordination sphere [Pd(2) and (Pd(3)]. The other palladium atom [Pd(1) and Pd(4)] is coordinated by the sulfur atoms of the 1-methylimidazole-2-thiolate unit, in addition to the bis(imidazole) ligand. The two $[Pd_2(bmik)_2(meimt)_2]^{2+}$ units themselves as well as their orientation to each other differ considerably. The Pd(4) atom shows significantly smaller Pd−S distances in comparison with Pd(1) [Pd(4)−S(3) 2.273, Pd(4)−S(4) 2.280 and Pd(1)−S(1) 2.292, Pd(1)−S(2) 2.295 Å], while the PdN_4 coordination spheres are equal within the limits of error.

The two crystallographically independent dimeric units form two tetranuclear units, as shown in Figure 6. The metal-metal distances amount to: Pd(1)···Pd(2) 2.963 (intramolecular), Pd(1)···Pd(1a) 3.859 (intermolecular), Pd(3)···Pd(4) 2.970 (intramolecular), Pd(4)···Pd(4a) 4.434 Å (intermolecular). The larger intramolecular metal-metal distance in **3** (2.963, 2.970 Å) as compared to **1** and **2** is in accordance with the larger bite of the 1-methylimidazole-2-thiolate unit (2.76, 2.80 Å) in contrast to that of pyridine-2-thiolate (2.71 Å) and pyrimidine-2-thiolate (2.72 Å). The angles Pd(1a)···Pd(1)···Pd(2) and Pd(4a)···Pd(4)···Pd(3) are 161.8 and 150.7°, respectively. Dihedral tilt angles of $\tau = 12.2°$ [Pd(1), Pd(2)] and $\tau = 11.8°$ [Pd(3), Pd(4)] are observed between the coordination planes of the palladium atoms. An average torsion of the square planes of the palladium atoms of $\omega = 19.6°$ [Pd(1)···Pd(2)] and 16.0° [Pd(3)···Pd(4)] is observed along the Pd···Pd vectors. There is an orientation of the metal atoms in one dinuclear unit towards each other similar to the analogous compounds **1** and **2**. Pd(3) lies 0.002 Å below and Pd(4) 0.061 Å above

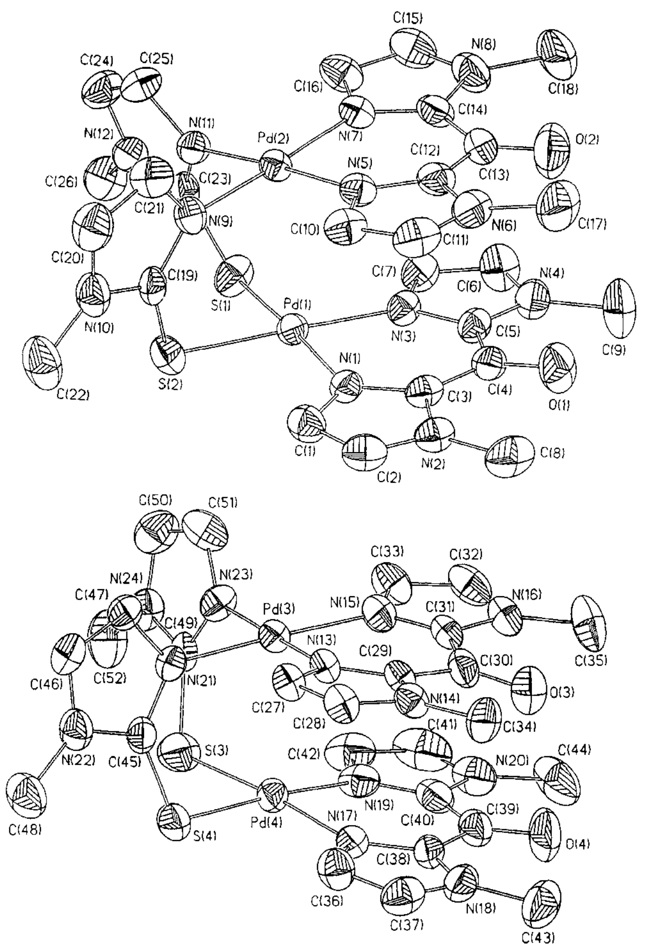

Figure 5. Molecular structure and atomic numbering scheme for the two crystallographically independent cations of **3**. Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at the 30% probability level. Selected interatomic distances [Å] and angles [deg] for the two crystallographically independent $[Pd_2(bmik)_2(meimt)_2]^{2+}$ cations of **3** are: Pd(1)–Pd(2) 2.963(1), Pd(1)–S(1) 2.292(3), Pd(1)–S(2) 2.290(3), Pd(1)–N(1) 2.091(7), Pd(1)–N(3) 2.075(7), Pd(2)–N(5) 2.029(7), Pd(2)–N(7) 2.020(7), Pd(2)–N(9) 2.015(7), Pd(2)–N(11) 1.999(7); S(1)–Pd(1)–Pd(2) 85.5(1), S(2)–Pd(1)–Pd(2) 86.8(1), S(2)–Pd(1)–S(1) 86.9(1), N(1)–Pd(1)–S(1) 175.6(2), N(1)–Pd(1)–S(2) 92.9(2), N(1)–Pd(1)–Pd(2) 98.9(2), N(3)–Pd(1)–Pd(2) 95.2(2), N(3)–Pd(1)–S(1) 91.4(2), N(3)–Pd(1)–S(2) 177.2(2), N(3)–Pd(1)–N(1) 88.7(3), N(5)–Pd(2)–Pd(1) 91.2(2), N(7)–Pd(2)–Pd(1) 96.5(2), N(7)–Pd(2)–N(5) 90.5(3), N(9)–Pd(2)–Pd(1) 85.4(2), N(9)–Pd(2)–N(5) 91.6(3), N(9)–Pd(2)–N(7) 177.2(3), N(11)–Pd(2)–Pd(1) 86.2(2), N(11)–Pd(2)–N(5) 177.3(3), N(11)–Pd(2)–N(7) 90.5(3), N(11)–Pd(2)–N(9) 87.5(3) and Pd(3)–Pd(4) 2.970(1), Pd(3)–N(13) 2.005(7), Pd(3)–N(15) 2.024(8), Pd(3)–N(21) 2.006(7), Pd(3)–N(23) 2.024(7), Pd(4)–S(3) 2.273(3), Pd(4)–S(4) 2.279(3), Pd(4)–N(17) 2.067(8), Pd(4)–N(19) 2.073(8); N(13)–Pd(3)–Pd(4) 96.5(2), N(13)–Pd(3)–N(15) 89.4(3), N(13)–Pd(3)–N(21) 89.7(3), N(13)–Pd(3)–N(23) 176.9(3), N(15)–Pd(3)–Pd(4) 91.4(2), N(15)–Pd(3)–N(23) 92.9(3), N(21)–Pd(3)–Pd(4) 86.2(2), N(21)–Pd(3)–N(15) 177.4(3), N(21)–Pd(3)–N(23) 88.1(3), N(23)–Pd(3)–Pd(4) 85.5(2), S(3)–Pd(4)–Pd(3) 87.4(1), S(3)–Pd(4)–S(4) 85.8(1), S(4)–Pd(4)–Pd(3) 86.5(1), N(17)–Pd(4)–Pd(3) 95.3(2), N(17)–Pd(4)–S(3) 176.1(2), N(17)–Pd(4)–S(4) 91.6(2), N(17)–Pd(4)–N(19) 88.7(3), N(19)–Pd(4)–Pd(3) 98.5(2), N(19)–Pd(4)–S(3) 93.6(3), N(19)–Pd(4)–S(4) 175.0(2)

its best least-squares plane through PdN_4 and PdN_2S_2, respectively. In the other dimeric cation both palladium atoms lie above the best least-squares planes through their coordination spheres [Pd(1) 0.051, Pd(2) 0.004 Å]. The bonding distances within the bis(1-methylimidazol-2-yl) ketone ligand do not differ significantly from each other. The ligands are approximately planar. The geometry of the nitrate anions shows the expected planarity.

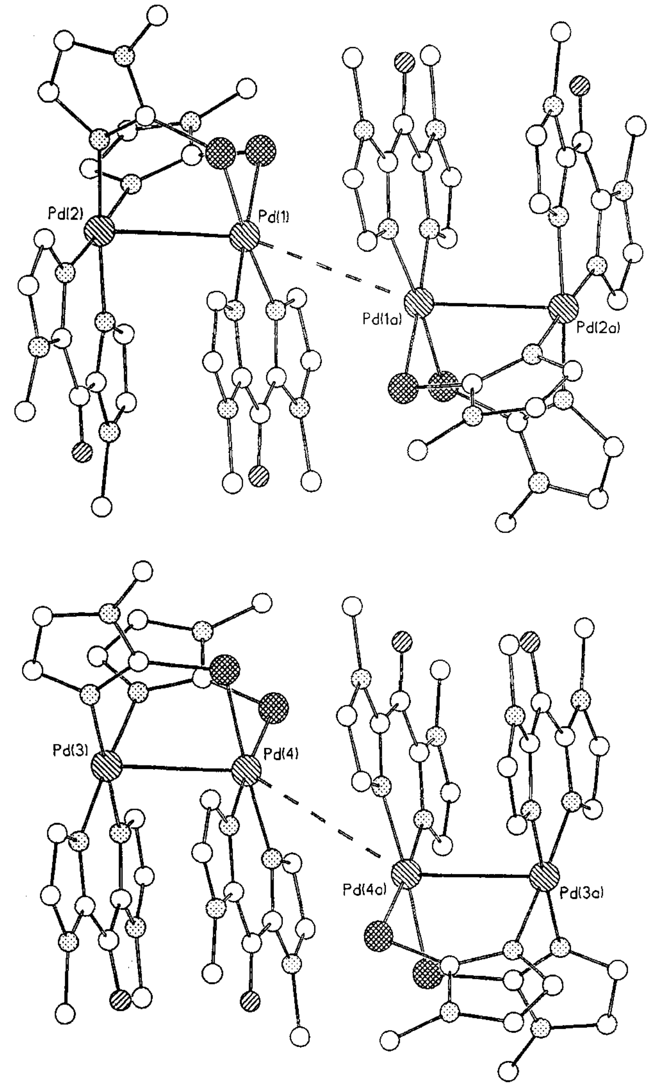

Figure 6. Different orientation of the two dimeric units of **3** towards each other

Conclusions

Besides the two structurally comparable platinum complexes $[Pt_2(en)_2(pyt)_2]Cl_2$[10,11] and $[Pt_2(en)_2(4\text{-mepyt})_2]Cl_2$[11] (Table 1) the three compounds **1**, **2**, and **3** represent the first examples of dinuclear doubly thiolate-bridged complexes of palladium which have been prepared analogously to amide-bridged complexes. In accordance with the significantly larger bite of the thioamides as compared to amides, e.g. α-pyridone, the compounds have larger metal-metal distances and smaller tilt angles (τ) between adjacent metal coordination planes in the dinuclear units. The torsion angles (ω) of these three compounds are relatively large (27.6° in **1**, 28.1° in **2**, 19.6 and 16.0° in **3**). No significant stacking interaction of the imidazole planes of the bmik ligands is supposed to exist (see Figure 2). It is interesting to notice that the shorter the metal-metal distance the larger the torsion angle. This is true for complexes **1**, **2**, and **3**. Comparison of complex **4** (Pd···Pd = 3.083 Å, ω = 32.6°) with complex **5** (Pd···Pd = 3.101 Å, ω = 34.3°) shows that in this case it is the other way round. The fact that the metal-metal distances in the platinum thiolate-bridged complexes **4** and **5** are significantly longer than in the palladium complexes **1**, **2**, and **3** (Table 1) is essentially attributed to a steric effect due to the chelating ligands rather than to the different metal atoms. An appropriate explanation for this finding is that the bmik ligand is almost planar in contrast to the en ligand. The shortest metal-metal distances of compounds in the +II oxidation state are observed in the complexes **6** and **7** which are quadruply bridged[2,12,14]. The shortest metal-metal distances of thioamide-bridged dinuclear complexes were, as expected, found in platinum(III) complexes[12,15–17]. The palladium-sulfur distances of 2.273 to 2.295 Å lie in the same range as in similar compounds[2,4,8,21].

Table 1. Crystallographically characterized dinuclear complexes of platinum and palladium, doubly or quadruply bridged by anionic thioamides. en = ethylenediamine, 4-mepyt = 4-methylpyridine-2-thiolato, 2-tu = 2-thiouracilato

Compound	Oxidation state	M-M Distance (Å)	Literature
$[Pd_2(bmik)_2(pyt)_2](NO_3)_2$ (**1**)	2	2.915	this work
$[Pd_2(bmik)_2(pymt)_2](NO_3)_2$ (**2**)	2	2.886	this work
$[Pd_2(bmik)_2(meimt)_2](NO_3)_2$ (**3**)	2	2.963, 2.970	this work
$[Pt_2(en)_2(pyt)_2]Cl_2$ (**4**)	2	3.083	10, 11
$[Pt_2(en)_2(4\text{-}mepyt)_2]Cl_2$ (**5**)	2	3.101	11
$[Pd_2(pyt)_4]$ (**6**)	2	2.677	2, 14
$[Pt_2(4\text{-}mepyt)_4]$ (**7**)	2	2.680	12
$[Pt_2(pyt)_4Cl_2]$ (**8**)	3	2.532	12
$[Pt_2(pymt)_5Cl]$ (**9**)	3	2.547	17
$[Pt_2(pymt)_4Cl_2]$ (**10**)	3	2.518	16
$[Pt_2(2\text{-}tu)_4I_2]$ (**11**)	3	2.546	16
$[Pt_2(pymt)_4Br(Br/pymt)]$ (**12**)	3	2.553	16
$[Pt_2(pymt)_4I_2]$ (**13**)	3	2.554	15

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Experimental

IR: Perkin-Elmer 683 (KBr pellets). – ^1H NMR: Bruker WH 300, at 300 MHz. The complexes were dissolved in $D_2O/[D_6]$acetone (1:1) with TMS as internal reference. – Elemental analyses: Perkin Elmer Dia CHN 240.

[Bis(1-methylimidazol-2-yl)ketone]dichloropalladium(II) $[Pd(bmik)Cl_2]$ was prepared from K_2PdCl_4 and bmik by analogy with a published procedure[18].

Pyridine-2-thione (pytH), *Pyrimidine-2-thione* (pymtH), *and 1-Methyl-4-imidazoline-2-thione* (meimtH) were obtained from Fluka Feinchemikalien GmbH and used without further purification.

Bis(μ-pyridine-2-thiolato-N,S)-bis{[bis(1-methylimidazol-2-yl) ketone]palladium(II)} Nitrate $[Pd_2(bmik)_2(pyt)_2](NO_3)_2 \cdot 5\ H_2O$ (**1**), *Bis(μ-pyrimidine-2-thiolato-N^1,S)-bis{[bis(1-methylimidazol-2-yl) ketone]palladium(II)} Nitrate* $[Pd_2(bmik)_2(pymt)_2](NO_3)_2 \cdot 5\ H_2O$ (**2**), *and Bis(μ-1-methylimidazole-2-thiolato-N^3,S)-bis{[bis(1-methylimidazol-2-yl) ketone]palladium(II)} Nitrate* $[Pd_2(bmik)_2(meimt)_2](NO_3)_2 \cdot 4.5\ H_2O$ (**3**) were obtained by the reaction of $[Pd(bmik)(H_2O)_2]^{2+}$ with the thioamides as follows: An aqueous solution of $[Pd(bmik)(H_2O)_2]^{2+}$ was prepared by adding 0.170 g (1.0 mmol) of $AgNO_3$ to a suspension of 0.188 g (0.50 mmol) of $Pd(bmik)Cl_2$ in 10 ml of water. After the suspension had been stirred for 3 h at room temp. the resulting AgCl precipitate was removed together with unreacted $Pd(bmik)Cl_2$ by centrifugation, and a clear orange-brownish solution was obtained. The pH value of this solution is less than 2 due to the acidic reaction of $[Pd(bmik)(H_2O)_2]^{2+}$ in water. Then 0.35 mmol of solid pyridine-2-thione (39 mg), pyrimidine-2-thione (39 mg), or 1-methyl-4-imidazoline-2-thione (40 mg) was added to the centrifugate. Within a few seconds (in the case of meimtH) up to some minutes the color of the solutions turned red. After incubation for 20 h at 40°C the reaction was complete. The products were crystallized by decreasing the temperature to 6°C.

1: Red crystals (head-to-head isomer) suitable for X-ray structure analysis were obtained in 20% yield (total yield after further evaporation: 53%). – IR (KBr): $\tilde{\nu}$ = 3110 cm^{-1} (m, br), 3060 (m), 3020 (m), 1630 (s), 1590 (s), 1545 (m), 1525 (w), 1485 (s), 1470 (w), 1450 (s), 1410 (s), 1405 (s), 1350 (s, br), 1285 (m), 1260 (w), 1180 (m), 1160 (w), 1140 (m), 1090 (m), 1060 (m), 1025 (w), 985 (w), 900 (s), 830 (w), 810 (w), 770 (m), 730 (m), 720 (m), 690 (w), 680 (w), 645 (w), 600 (m), 575 (w), 495 (w), 460 (w), 450 (w), 370 (w). – ^1H NMR ($D_2O/[D_6]$acetone): δ = 3.87, 3.96 (m, 12H, NCH_3, bmik), 6.96, 7.07 [d, 4H, 5-H, imidazole (bmik)], 7.25 [d, 4H, 4-H, imidazole (bmik)], 7.29, 7.42, 7.47, 7.92 (m, 8H, pyridine-2-thiolate). – $C_{28}H_{28}N_{12}O_8Pd_2S_2 \cdot 5\ H_2O$ (1027.6): calcd. C 34.4, H 3.3, N 14.3; found C 34.2, H 3.4, N 14.5.

2: The crystals (head-to-tail isomer) are orange and could be obtained in 20% yield (total yield: 59%). – IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1} (m, br), 3030 (w), 1630 (s), 1610 (s), 1545 (m), 1485 (s), 1450 (s), 1410 (s), 1350 (s, br), 1180 (m), 1140 (w), 1120 (w), 900 (s), 870 (m), 830 (w), 770 (m), 720 (m), 560 (m), 550 (w). – ^1H NMR ($D_2O/[D_6]$acetone): δ = 4.04, 4.15 (m, 12H, NCH_3, bmik), 7.35, 7.49 [d, 4H, 5-H, imidazole (bmik)], 7.61 [d, 4H, 4-H, imidazole (bmik)], 6.20, 8.48, 9.24 (m, 6H, pyrimidine-2-thiolate). – $C_{26}H_{26}N_{14}O_8Pd_2S_2 \cdot 5\ H_2O$ (1029.6): calcd. C 31.4, H 3.3, N 19.7; found C 31.3, H 3.4, N 19.6.

3: Red crystals (head-to-head isomer) were collected (yield 24%). A second batch was obtained from further concentration of the filtrate, providing a total yield of 64%. – IR (KBr): $\tilde{\nu}$ = 3110 cm^{-1} (m, br), 3030 (w), 2940 (w), 1620 (s), 1530 (m), 1480 (m), 1450 (m), 1410 (s), 1380 (s), 1350 (w), 1280 (m), 1180 (m), 1160 (m), 1120 (w), 1085 (w), 1050 (w), 965 (w), 900 (s), 820 (w), 790 (w), 725 (m), 700 (m), 690 (w), 640 (w), 600 (m), 560 (w), 510 (w), 465 (w), 360 (w). – ^1H NMR ($D_2O/[D_6]$acetone): δ = 3.38, 3.55 (m, 6H, NCH_3, 1-methylimidazole-2-thiolate), 3.87, 4.00 [m, 12H, NCH_3, (bmik)], 6.25, 6.84, 6.92, 7.00, 7.08, 7.16, 7.21, 7.30, 7.33, 7.38, 7.40 [imidazole (bmik) and meimt]. – $C_{26}H_{30}N_{14}O_8Pd_2S_2 \cdot 4.5\ H_2O$ (1023.6): calcd. C 30.8, H 3.8, N 19.3; found C 30.9, H 3.6, N 19.5.

Crystallographic Data Collection and Structure Determination[24]: Details of crystal structure determinations and intensity data treatments are summarized in Table 2. In all three structures the coordinates of the palladium atoms were obtained from Patterson maps (program SHELXS-86[22]). A series of full-matrix least-squares refinement cycles on $|F|^2$ (program SHELXL-93[23]) followed by Fourier syntheses gave all the remaining atoms except the hydrogen atoms. The hydrogen atoms in all three structures were placed at calculated positions and constrained to "ride" on the carbon atom

Table 2. Crystallographic data and details of refinement of **1**, **2**, and **3**

		1	**2**	**3**
empirical formula		$C_{28}H_{28}N_{12}O_8S_2Pd_2 \cdot 5H_2O$	$C_{26}H_{26}N_{14}O_8S_2Pd_2 \cdot 5H_2O$	$C_{26}H_{30}N_{14}O_8S_2Pd_2 \cdot 4.5H_2O$
molecular mass (g mol^{-1})		1027.62	1029.61	1023.62
unit cell dimensions	a (Å)	11.136(2)	9.926(2)	13.834(3)
	b (Å)	12.852(2)	11.526(2)	16.291(4)
	c (Å)	15.088(2)	16.281(3)	19.421(4)
	α (deg)	69.43(1)		94.02(2)
	β (deg)	78.55(1)	94.70(3)	104.57(2)
	γ (deg)	85.31(1)		110.74(2)
cell volume	V (Å^3)	1981.3(5)	1856.4(6)	3899.9(15)
Z		2	2	4
density calc. (g cm^{-3})		1.716	1.842	1.743
crystal system		triclinic	monoclinic	triclinic
space group symbol		$P\bar{1}$	P2/n	$P\bar{1}$
diffractometer		Siemens R3	Syntex $P2_1$	Siemens R3
radiation, λ (Å)		Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073
monochromator		graphite	graphite	graphite
crystal size (mm)		0.38 × 0.35 × 0.25	0.05 × 0.30 × 0.20	0.15 × 0.20 × 0.13
temperature (K)		293	156	293
data collecting mode		θ-2θ-scan	θ-2θ-scan	ω-scan
theta range		$4° < 2θ < 54°$	$4° < 2θ < 54°$	$4° < 2θ < 54°$
range of hkl		$0 < h < 14$	$0 < h < 12$	$0 < h < 17$
		$-16 < k < 16$	$0 < k < 14$	$-20 < h < 19$
		$-18 < l < 19$	$-20 < l < 20$	$-24 < l < 24$
no. of reflns. measured		9172	4314	17835
no. of independent reflns.		8718	4082	17095
no. of obs. reflns. with $I > 2σ(I)$		5688	2651	10354
μ (mm^{-1})		1.09	1.16	1.11
absorption correction		ψ-scan, empirical	ψ-scan, empirical	ψ-scan, empirical
min. trans., max. trans.		0.660, 0.761	0.706, 0.944	0.801, 0.866
no. of l.s. parameters		524	296	978
$R[F>4σ(F)]^a$		0.0542	0.0661	0.0822
$wR(F^2)^b$		0.1408	0.1424	0.2040
a		0.0563	0.0411	0.0819
b		2.5849	8.2265	8.4533

[a] $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. – [b] $wR = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$; $w = 1/[σ^2(F_o^2) + (a \cdot P)^2 + b \cdot P]$ where $P = [\max(F_o^2 \text{ or } 0) + 2F_c^2]/3$.

to which they are attached. The isotropic thermal parameters for the aromatic hydrogen atoms and for the methyl protons were refined with 1.2 times and 1.5 times the U_{eq} value of the corresponding carbon atom, respectively. All atoms of the molecular cations of **1**, **2**, and **3** except the hydrogen atoms were refined anisotropically.

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