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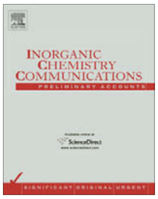

1-D networks formed by metal···sulfur van der Walls contacts: Novel tetrazole–thiolato Pd(II) and Pt(II) complexes

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ABSTRACT

Pd(II)– and Pt(II)–azido complexes, $[M(N_3)(PMe_3)_2(C\text{–}L)]$ {LH = 2-(2′)-thienyl pyridine; M = Pd (**1**), Pt(**2**)}, which contain σ-bonded heterocycles (L), were treated with aryl isothiocyanate ($Me_2C_6H_3$–NCS) to afford the corresponding Pd(II) and Pt(II) tetrazole–thiolato complexes, *trans*-$\{M[SCN_4(2,6\text{-}Me_2C_6H_3)](PMe_3)_2(C\text{–}L)\}$ **{**M = Pd (**3**), Pt (**4**)**}**. Complexes **3** and **4** have a 1-D helical network formed by the intermolecular M···S van der Waals contacts.

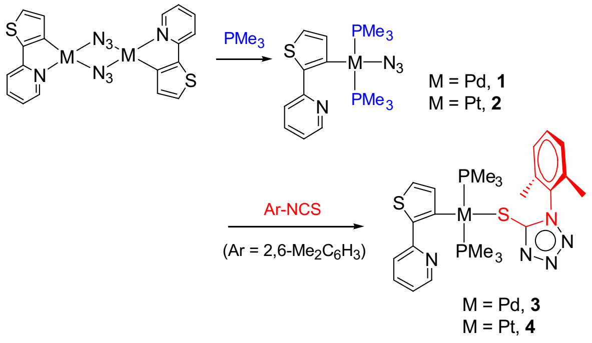
Thiophene compounds with extended π-electron bonds have been intensively studied because of their potential usefulness in the construction of self-assembled compounds and electronic or chemical devices [1–8]. In particular, (α-position)-pyridyl-substituted thiophene derivatives exhibit interesting various coordination behaviors as well as electronic or electroluminescent properties [9–23].

Recently, we reported the preparation of the pyridyl thienylene complexes of group 10 metals $[M(N_3)L(C,N\text{–}L)]$, which contain *C,N*-chelated ligands and azido groups [24,25]. The azido groups in these complexes are photo-sensitive and undergo reactions with organic unsaturated compounds to give heterocycles such as tetrazoles by the dipolar cycloaddition. In addition, the cyclometalated complexes with *C,N*-donor ligands turned out to be labile toward phosphines. In this paper, we report the preparation and structures of tetrazole–thiolato Pd(II) and Pt(II).

The starting complexes $[M(\mu\text{-}N_3)(C,N\text{–}L)]_2$ (LH = 2-(2′)-thienyl pyridine; M = Pd [25], Pt [26,27]), which were prepared from $[M(\mu\text{-}Cl)(C,N\text{-}L)]_2$ and excess NaN_3, were cleaved by excess PMe_3 to give the corresponding azido complexes $[M(N_3)(PMe_3)_2(C\text{–}L)]$ {M = Pd (**1**), Pt (**2**)} [25,28], in which the original *C,N*–L ligand is now a *C*-coordinated ligand (Scheme 1). Subsequent treatments of complexes 1 and 2 with $Me_2C_6H_3$–NCS afforded the corresponding tetrazole–thiolato complexes, *trans*-$\{M[SCN_4(2,6\text{-}Me_2C_6H_3)](PMe_3)_2(C\text{–}L)\}$ {M = Pd (**3**), Pt (**4**)} [29], which have been formed by the 1,3-dipolar cycloaddition of Ar–NCS into the metal–azido bond (Scheme 1). The IR spectra of complexes **1** and **2** display a strong N_3 stretch at 2032–2042 cm^{-1}, which are absent in complexes **3** and **4**. A singlet of the $^{31}P\{^1H\}$ spectra of the complexes **1**–**4** supports their *trans*-square-planar geometry.

Complexes **3** and **4** were determined by X-ray diffraction [30]. The molecular structure of complex **3** with the atom-numbering scheme is shown in Fig. 1a. The coordination sphere of Pd can be described as square-planar. The molecular plane (P1, P2, S2, C1) is nearly planar with an average atomic displacement of 0.017(1) Å, and the Pd metal lies 0.058(1) Å above this plane. The Pd metal is further bound to the S atom in the neighboring molecule by van der Waals contacts (Pd···S = 3.568(1) Å). These contacts connect the molecules approximately along the *b*-axis to give a 1-D helical network (Fig. 1b).

The molecular structure of complex **4** is presented in Fig. 2a. The molecular plane (P1, P2, S2, C1) of this square-planar complex



Scheme 1.

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is also nearly planar with an average atomic displacement of 0.0255(8) Å, and the Pt metal lies 0.0539(8) Å above this plane. The tetrazolato ring is significantly twisted from the phenyl ring (C2–C7) by 76.8(1)°, probably due to the presence of the two methyl groups at C3 and C9 atoms. In contrast, the thiophenyl and pyridyl rings are essentially coplanar with a dihedral angle of 2.0(1)°. As in complex **3**, the Pt metal in complex **4** interacts with the S atom in the neighboring molecule (Pt···S = 3.6018(8) Å) to create a 1-D helical network along the *b*-axis. A space filling model (Fig. 2b) clearly demonstrates the helical structure. For compari-

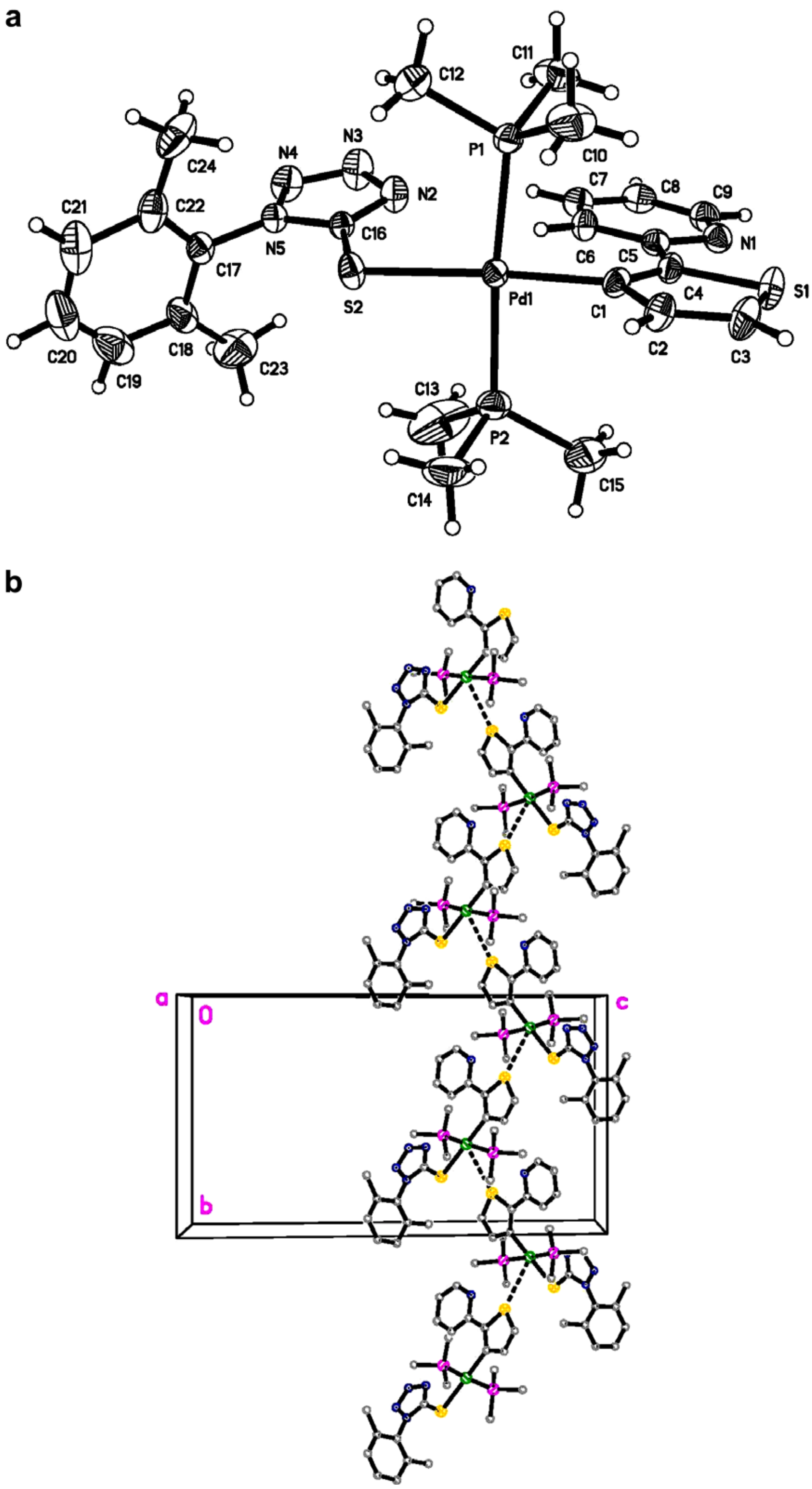

Fig. 1. (a) *ORTEP* drawing of **3** showing the atom-labelling scheme and 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (°): Pd1–C1 2.004(3), Pd1–P2 2.296(1), Pd1–P1 2.312(1), Pd1–S2 2.390(1), S2–C16 1.707(3), N2–N3 1.353(4), N3–N4 1.310(4), N4–N5 1.348(4), N5–C16 1.347(4); P2–Pd1–P1 173.71(4), P2–Pd1–S2 89.21(4), P1–Pd1–S2 95.79(4), C3–S1–C4 91.2(2), C16–S2–Pd1 103.3(1), C16–N2–N3 106.2(3), N4–N3–N2 111.2(3), N3–N4–N5 105.6(3), C16–N5–N4 109.2(3). (b) Projection of complex **3** perpendicular to the (100) plane, showing a 1-D network approximately along the *b*-axis.

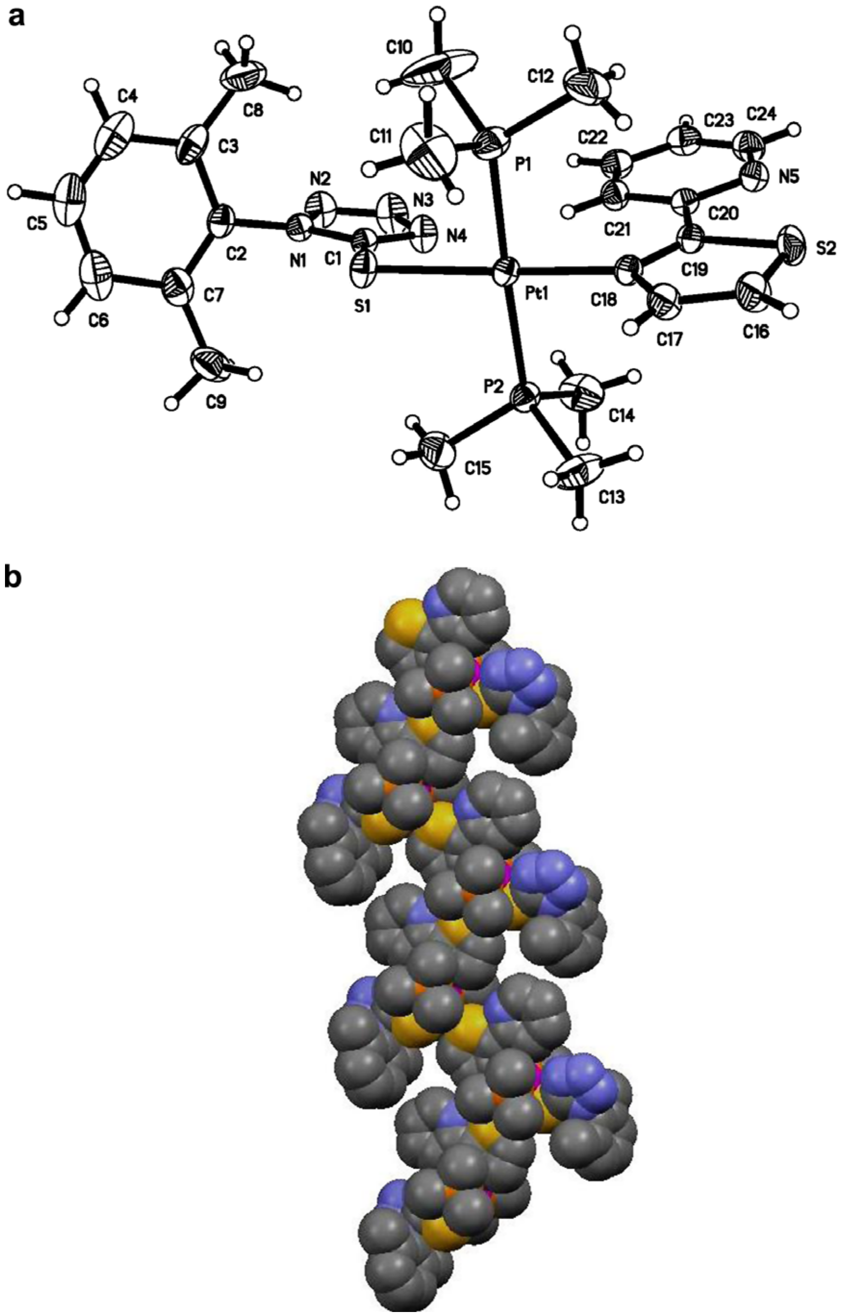

Fig. 2. (a) *ORTEP* drawing of **4**. Selected bond lengths (Å) and angles (°): Pt1–C18 2.015(3), Pt1–P1 2.2847(9), Pt1–P2 2.2960(8), Pt1–S1 2.3826(7), S1–C1 1.713(3), N1–N2 1.366(3), N2–N3 1.296(4), N3–N4 1.354(4), N1–C11.342(3); P1–Pt1–P2 174.99(3), P1–Pt1–S1 88.42(3), P2–Pt1–S1 94.59(3), C1–S1–Pt1 104.09(9), C16–S2–C19 91.49(16), C1–N1–N2 108.4(2), N3–N2–N1 105.9(2), N2–N3–N4 111.4(2), C1–N4–N3 106.1(2). (b). A space filling model of the packing of complex **4** showing its helical structure: (a) red, Pt; yellow, S; orange, P; purple, N; grey, C. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

son, the van der Waals radii of Pd, Pt, and S atoms are 1.63, 1.72, and 1.80 Å, respectively. The van der Waals contacts (or interactions) of metal–ligand and metal–metal types are known to increase the dimensionality of coordination polymers or lead to the formation of high-dimensional networks. Some recent polymers and networks containing such contacts are $[Cu_4I_4\{\mu\text{-}PhS(CH_2)_4SPh\}_2]_n$ [33], $\{Fe(3\text{-bromo-4-picoline})_2[AuI(CN)_2]_2\}_n$ [34], and especially silver species [35–40].

In summary, we prepared novel tetrazole–thiolato complexes, *trans*-$\{M[SCN_4(2,6\text{-}Me_2C_6H_3)](PMe_3)_2(C\text{–}L)\}$ (LH = 2-(2′)-thienyl pyridine; M = Pd, Pt) by treating the corresponding azido complexes $[M(N_3)(PMe_3)_2(C\text{–}L)]$ with $Me_2C_6H_3\text{–}NCS$. X-ray diffraction studies revealed that these complexes have 1-D helical networks, formed by the metal···sulfur van der Waals contacts.

Acknowledgment

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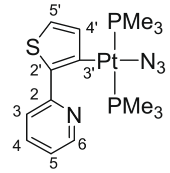
[27] Synthesis of $[Pt(\mu\text{-}N_3)(C,N\text{-}L)]_2$ (HC,N-L = 2-(2′-thienyl)pyridine) and $[Pt(N_3)(PMe_3)_2(C\text{–}L)]$(**2**): To a homogeneous DMSO (100 ml) solution of $[Pt(\mu\text{-}Cl)(C,N\text{-}L)]_2$ (0.882 g, 1.13 mmol) was added a H_2O (3 ml) solution of NaN_3 (0.220 g, 3.38 mmol). After stirring for 18 h, excess H_2O was added to the mixture under ice bath to give dark yellow precipitates. The solids were filtered and washed with H_2O and diethyl ether. The product was dried under vacuum to give brown solids of $[Pt(\mu\text{-}N_3)(C,N\text{-}L)]_2$ (0.819 g, 91%).

[28] To a Schlenk flask containing $[Pt(\mu\text{-}N_3)(C,N\text{-}L)]_2$ (0.304 g, 0.38 mmol) were sequentially added CH_2Cl_2 (5 ml) and PMe_3 (136 µl, 1.53 mmol). The heterogeneous brown solution immediately turned to an orange solution. After stirring for 3 h at room temperature, the reaction mixture was completely evaporated under vacuum to give dark yellow solids. The solids were filtered and washed with hexane (5 ml). Recrystallization from CH_2Cl_2/diethyl ether gave pale yellow crystals of **2** (0.332 g, 79%). IR (KBr, cm^{-1}): 2042 (N_3). ^1H NMR($CDCl_3$ in 300 MHz, δ): 1.26 (t, 18 H, $J = 3.7$, $J_{PtH} = 30$ Hz, PMe_3), 7.00 (d, 1H, $J = 5.1$ Hz, $H^{4'}$), 7.08 (ddt, 1H, $J = 1.1$, 4.9, 9.8 Hz, H^5), 7.26 (d, 1H, $J = 4.9$ Hz, $H^{5'}$), 7.66 (dt, 1H, $J = 7.8$ Hz, H^3), 8.53 (d, 1H, $J = 3.0$ Hz, H^4), 9.43 (d, 1H, $J = 8.0$ Hz, H^6). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, δ): 13.2 (t, $J_{CP} = 7.5$ Hz, $P(CH_3)_3$), 119.1 (s, C^3), 120.5 (s, C^5), 126.3 (s, $C^{5'}$), 127.0 (s, $C^{4'}$), 135.8 (s, C^4), 136.5 (s, $C^{2'}$), 149.2 (s, $C^{3'}$), 149.5 (br, C^6), 155.6 (s, C^2). $^{31}P\{^1H\}$ NMR (120 MHz in $CDCl_3$, δ): −12.8 (s, $J_{PtP} = 2639$ Hz). Anal. Calcd. for $C_{15}H_{24}N_4P_2SPt$: C, 32.79; H, 4.40; N, 10.20. Found: C, 32.71; H, 4.52; N, 9.75.



[29] Synthesis of *trans*-$\{M[SCN_4\,(2,6\text{-}Me_2C_6H_3)](PMe_3)_2\,(C\text{–}L)\}$(M = Pd, **3**; Pt = **4**): To a Schlenk flask containing $[Pd(N_3)(PMe_3)_2\,(C\text{–}L)]$ (**1**, 0.228 g, 0.50 mmol) were added CH_2Cl_2 (4 ml) and 2,6-dimethylphenyl isothiocyanate (0.121 g, 0.74 mmol). After stirring for 18 h, the solvent was removed, and then the resulting residue was solidified with *n*-hexane. The solids were filtered and washed with hexane (5 ml × 2). Recrystallization from CH_2Cl_2/*n*-hexane gave the white crystals of *trans*-$\{PdS[CN_4(R)](C\text{–}L)(PMe_3)_2\}$ (**3**, 0.141 g, 46%). ^1H NMR ($CDCl_3$, δ): 1.08 (br s, 18H, $P(CH_3)_3$), 2.07 (s, 6H, Me), 7.08 (d, 1H, $J = 5.0$ Hz, $H^{4'}$), 7.10 (ddt, 1H, $J = 1.1$, 4.8, 9.8 Hz, H^5), 7.21(d, 2H, $J = 7.3$ Hz, Ph), 7.32(t, 1H, $J = 7.8$ Hz, Ph), 7.39 (d, 1H, $J = 4.6$ Hz, $H^{5'}$), 7.92 (dt, 1H, $J = 8.0$ Hz, H^3), 8.54 (m, 1H, H^4), 9.72 (br, 1H, H^6). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 14.1 (t, $J_{PC} = 14$ Hz, $P(CH_3)_3$), 17.9 (s, Me), 120.5 (s, C^3), 121.1 (s, C^5), 126.6 (s, $C^{5'}$), 128.5, 130.1,133.8, 134.2 (s, $C^{4'}$), 136.2, 137.1 (s, C^4), 140.6 (s, $C^{2'}$), 146.8 (s, $C^{3'}$), 149.2 (s, C^6), 155.0 (s, C^2), 163.5). $^{31}P\{^1H\}$NMR ($CDCl_3$, δ): −14.6 (s). Anal. Calcd. for $C_{24}H_{33}N_5P_2S_2Pd$: C, 46.19; H, 5.33; N, 11.22. Found: C, 46.15; H, 5.59; N, 11.08. The complex, *trans*-$\{PtS[CN_4(R)](C\text{–}L)(PMe_3)_2\}$ (**4**, 0.162 g, 54%) was analogously prepared. ^1H NMR ($CDCl_3$, δ): 1.19 (t, $J = 3.7$, $J_{PtH} = 30$ Hz, $P(CH_3)_3$), 2.06 (s, 6H, Me), 7.08–7.37(m, 6H, Ph), 7.91 (dt, 1H, $J = 7.7$ Hz, H^3), 8.53 (m, 1H, H^4), 9.89 (br, 1H, H^6). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 13.4 (t, $J_{PC} = 19$ Hz, $P(CH_3)_3$), 17.8 (s, Me), 120.7 (s, C^3), 121.2 (s, C^5), 126.7 (s, $C^{5'}$), 128.5, 130.0,133.5, 136.0, 136.1, 136.8 (s, C^4), 139.4 (t, $J_{CP} = 12$ Hz, $C^{3'}$), 146.8 (s, $C^{2'}$), 148.9 (s, C^6), 155.7 (s, C^2), 161.2. $^{31}P\{^1H\}$NMR ($CDCl_3$, δ): −16.9 (s, $J_{PtP} = 2575$ Hz). Anal. Calcd. for $C_{24}H_{33}N_5P_2S_2Pt$: C, 40.45; H, 4.67; N, 9.83. Found: C, 40.25; H, 4.76; N, 9.56.

[30] All X-ray data were collected with a Bruker Smart APEX2 diffractometer equipped with a Mo X-ray tube. Collected data were corrected for absorption with SADABS based upon the Laue symmetry by using equivalent reflections [31]. All calculations were carried out with the use of SHELXTL programs [32]. Crystal data for **3**: $Mr = 624.01$, colorless, monoclinic $P2_1/c$, $a = 8.8658(2)$ Å, $b = 13.4779(3)$ Å, $c = 24.3206(4)$ Å, $\beta = 96.462(1)$ Å, $V = 2887.7(1)$ Å^3, $Z = 4$, $d_{cal} = 1.435$ g cm^{-3}, crystal size = 0.40 × 0.38 × 0.34 mm^3, $F(000) = 1280$, No. of reflns measured = 42941, No. of reflns unique = 7202, No. of reflns with $I > 2\sigma(I) = 4078$, No. of params refined = 307, $GOF = 1.003$, $R_1 = 0.0416$, $wR_2 = 0.0807$. Crystal data for **4**: $Mr = 712.70$, colorless, monoclinic $P2_1/c$, $a = 8.88709(3)$ Å, $b = 13.5076(4)$ Å, $c = 24.3251(8)$ Å, $\beta = 96.860(1)$ Å, $V = 2893.8(2)$ Å^3, $Z = 4$, $d_{cal} = 1.636$ g cm^{-3}, crystal size = 0.38 × 0.28 × 0.24 mm^3, $F(000) = 1408$, No. of reflns measured = 80741, No. of reflns unique = 6918, No. of reflns with $I > 2\sigma(I) = 5109$, No. of params refined = 295, $GOF = 0.987$, $R_1 = 0.0242$, $wR_2 = 0.0567$.

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