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First reductive dimerization of a polycyclic azine†

Jean-Claude Berthet,*[a] Pierre Thuéry,[a] Cécile Baudin,[b] Bruno Boizot[b] and Michel Ephritikhine*[a]

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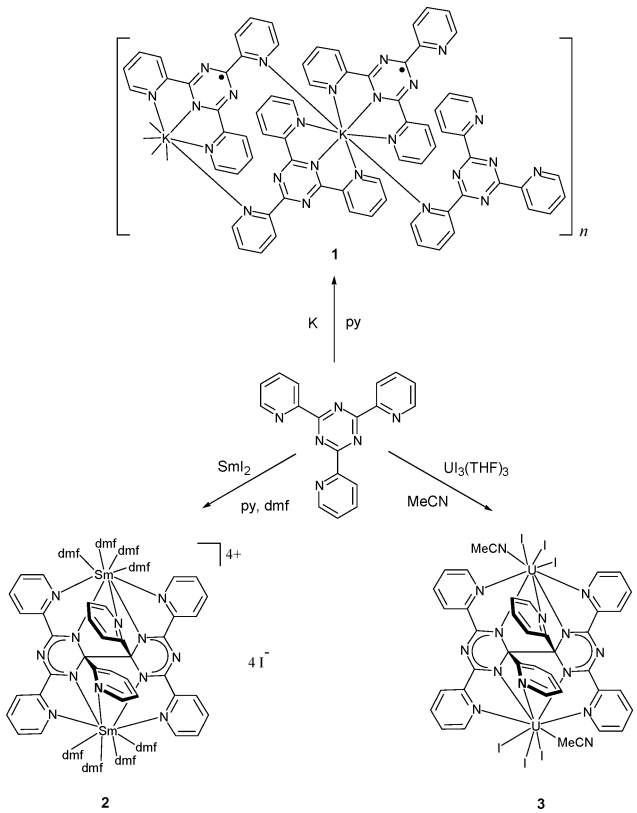
The tptz molecule is reduced by potassium into its anion-radical in the compound $K(tptz)_2$ (1), whereas it is reductively coupled by SmI_2 and $UI_3(py)_4$ into the bis-triazinide ligand in the dinuclear complexes $[Sm_2(tptz–tptz)(DMF)_8][I]_4\cdot3.5DMF$ (2·3.5DMF) and $U_2I_6(tptz–tptz)(MeCN)_2\cdot2MeCN$ (3·2MeCN) where each metal ion occupies a pentadentate N_5 cavity of the $[tptz–tptz]^{2-}$ ligand.

Reductive coupling reactions of unsaturated substrates promoted by low-valent metal species are of considerable interest in organic synthesis, and lanthanide complexes occupy a prominent position in these processes.[1] While various metal reagents were found to be efficient in the coupling of imines,[2] examples of reductive dimerization of azines are very rare, being limited to those of pyridine, pyridazine and benzaldehyde azine mediated by divalent lanthanide or titanium complexes.[3,4] Reactions of $Yb(C_5Me_5)_2(OEt_2)$ and $U(C_5H_4R)_3$ (R = ^{t}Bu or $SiMe_3$) with aromatic azines also involved metal-to-ligand electron transfer and gave dinuclear complexes where the two ytterbium(III) and uranium(IV) centres are bridged by the non-coupled nitrogen ligand in its dianionic form, as illustrated with $[Yb(C_5Me_5)_2]_2$(2,2′-bipyrimidine)[5] and $[U(C_5H_4R)_3]_2$(μ-pyrazine).[6] In other cases, such reactions afforded 1 : 1 adducts with a radical-anionic ligand which did not undergo further dimerization; representative examples of these complexes are given by $Sm^{III}(C_5Me_5)_2(bipy^{-\bullet})$[3a] and the series of $M^{III}(C_5Me_5)_2(terpy^{-\bullet})$ derivatives (M = U, Ce,[7] Sm, Yb[8]) which are of interest for their reactivity[7] and their electronic and magnetic properties.[9] Here we report on the synthesis and X-ray crystal structures of the complexes obtained by the reaction of 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tptz) with SmI_2 and $UI_3(py)_4$, representing the first reductive dimerization of a polycyclic azine; we also present the synthesis and crystal structure of the potassium salt of the tptz anion-radical.

Although the tptz ligand is present in a large number of d and f element complexes, no data on the preparation and structure of the anion-radical $tptz^{-\bullet}$ were available up until now. Treatment of tptz with a slight excess of potassium or K(Hg) in pyridine led rapidly to a dark blue suspension. The analytically pure powder of $K(tptz)_2$ (**1**) was isolated in 57% yield after extraction of the reaction mixture in pyridine, and dark blue crystals of **1** were obtained upon slow diffusion of pentane into a pyridine solution (Scheme 1).‡ The free anion-radical nature of **1** in the solid state



Scheme 1 Synthesis of the complexes. Note that the radical in **1** is fully delocalized on both tptz ligands.

was demonstrated by EPR measurements; the mean paramagnetic centre is characterized by an axial type tensor ($g_\perp = 2.0038$, $g_{//} = 2.0025$; 298 K, 0.01 mW). At 123 K and at a higher applied microwave power (10 mW), the spectrum is far more complicated with apparition of hyperfine and/or superhyperfine structures resulting from the interaction with the nitrogen neighbours (ESI†).

A view of the 1D structure of **1** is shown in Fig. 1 together with selected bond lengths and angles.§ The potassium ions occupy the terdentate sites of two tptz ligands which are symmetry-related by a two-fold axis, and are linked to the nitrogen atoms of the third pyridyl group of two adjacent tptz ligands to form infinite chains. The coordination geometry of the metal centre can be described as a very distorted square anti-prism with the square bases N1–N2–N3–N6″ and N1′–N2′–N3′–N6‴ (rms deviation 0.463 Å) forming a dihedral angle of 8.57(13)°. The tptz ligand is planar (rms deviation 0.081 Å); the two ligands attached to the same K atom form a dihedral angle of 37.10(2)° and the metal is at 0.3703(10) Å from these planes. The K–N distances in the terdentate site which average 2.93(2) Å are smaller than the K–N6 distance of 3.311(2) Å; these values can be compared with those found in the

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† Electronic supplementary information (ESI) available: EPR spectra. CCDC reference numbers 726184–726186. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b909547k

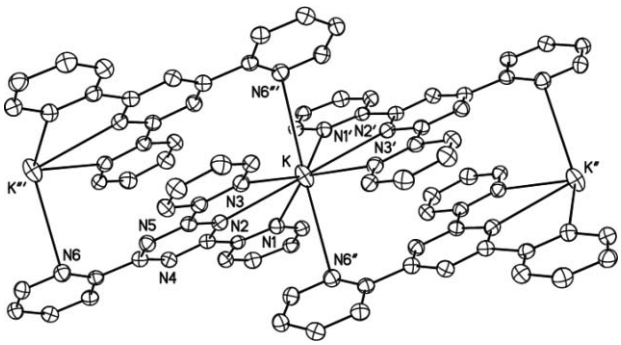

Fig. 1 View of the 1D structure of **1**. The H atoms have been omitted. Displacement ellipsoids are drawn at the 40% probability level. Symmetry codes: $' = 2 - x, y, 3/2 - z$; $'' = x, 2 - y, z + 1/2$; $''' = 2 - x, 2 - y, 1 - z$. Selected bond lengths (Å) and angles (°): K–N1 2.946(2), K–N2 2.942(2), K–N3 2.902(2), K–N6″ 3.311(2); N1–K–N2 55.94(6), N2–K–N3 56.73(6), N1–K–N6″ 80.50(6), N2–K–N6″ 77.87(6), N3–K–N6″ 80.64(6), N6″–K–N6‴ 143.22(8).

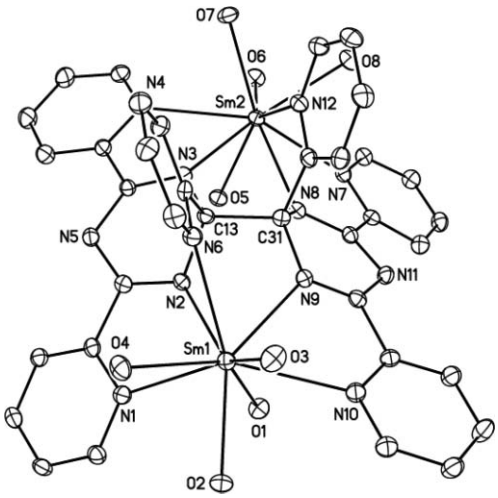

Fig. 2 View of the cation of **2**. The H atoms have been omitted and only the O atoms of the DMF ligands are represented. Displacement ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (°): Sm1–N1 2.657(3), Sm1–N2 2.465(3), Sm1–N6 2.694(3), Sm1–N9 2.518(3), Sm1–N10 2.653(3), Sm2–N3 2.543(3), Sm2–N4 2.653(3), Sm2–N7 2.656(3), Sm2–N8 2.477(3), Sm2–N12 2.651(3), C13–C31 1.584(5), C13–N2 1.469(5), C13–N3 1.455(5), C31–N8 1.472(4), C31–N9 1.456(5); N1–Sm1–N2 62.44(10), N2–Sm1–N9 63.38(10), N9–Sm1–N10 62.63(10), N1–Sm1–N6 103.03(10), N2–Sm1–N6 62.30(10), N9–Sm1–N6 71.81(9), N10–Sm1–N6 116.83(10).

cationic eight-coordinate complexes $[K(phen)_3(H_2O)]_2[ClO_4]_2$[10a] and $[K(phen)_3]_2[BPh_4]_2$[10b] which vary from 2.800(5) to 3.167(6) Å. The data are not precise enough to determine if there is, or not, a difference between the C–C and C–N bond lengths and those measured in the free[11a] or coordinated[11b] neutral tptz molecule.

In contrast to its reaction with potassium, treatment of tptz with SmI_2 in pyridine or acetonitrile led to the dimerization of the anion-radical $tptz^{-\bullet}$ and formation of the dinuclear species $[Sm_2(tptz–tptz)][I]_4$ (**2**) isolated as an orange powder in good yield (> 80%). Crystallization of this compound from a mixture of dimethylformamide and diethyl ether gave orange crystals of $[Sm_2(tptz–tptz)(DMF)_8][I]_4 \cdot 3.5DMF$ (**2**·3.5DMF).

The crystal structure of the cation of **2** (Fig. 2) exhibits a pseudo two-fold axis of symmetry passing through the middle of the new C–C bond, C13–C31, between the two triazinide fragments of the $[tptz–tptz]^{2-}$ ligand. This ligand contains two pentadentate cavities, N1–N2–N6–N9–N10 and N3–N4–N7–N8–N12, which are occupied by the Sm1 and Sm2 ions, respectively. These ions are also bound to four DMF molecules and their environment can be seen as a distorted tricapped trigonal prism; around Sm1, the trigonal faces are defined by O2–O3–O4 and O1–N2–N9, while N1, N6 and N10 are in capping positions. Each half of the tptz–tptz molecule acts simultaneously as a tridentate and bidentate ligand, adopting a $\mu\text{-}\kappa^3 : \kappa^2$ ligation mode similar to that encountered with tptz itself in dinuclear complexes like $(CuCl_2)_2(\mu\text{-tptz})\cdot MeOH$[12a] and $[Hg(CO_2CF_3)_2]_2(\mu\text{-tptz})$.[12b] The C13 and C31 atoms are at 0.483(5) and 0.429(5) Å, respectively, from the planar pentadienide-like C_2N_3 fragment of the corresponding triazinide units (rms deviations 0.044 and 0.032 Å). The C–N distances at C13 and C31, which average 1.463(9) Å, are typical single-bond values while the remaining eight C–N distances narrowly spread in the double-bond range with a mean value of 1.33(2) Å; the angles around C13 and C31, which vary from 106.1(3) to 114.0(3)°, are close to the ideal tetrahedral value of 109.28°. The pyridyl groups attached to C13 and C31 form a dihedral angle of 40.37(12)° and dihedral angles of 82.73(12) and 76.86(12)° with the mean planes of the corresponding triazinide rings while the other pyridyl groups are rotated with respect to the C_3N_3 rings by 3.8(2)–17.7(2)°. These structural features of the tris(pyridyl) triazinide moieties are similar to those found in the rhenium(I) compound $Re(CO)_3(\mu\text{-tptz–OMe})ReBr(CO)_3$ where tptz–OMe results from the nucleophilic attack of methanol on the triazine ring.[13] The Sm–N(triazinide) distances are smaller than the Sm–N(pyridyl) distances, with average values of 2.50(3) and 2.66(1) Å, respectively; these distances can be compared with those measured in Sm(III) tptz complexes, 2.61(2) Å in $Sm(tptz)(NO_3)_3\cdot H_2O$[14] and 2.61(2) Å in $Sm(tptz)(H_2O)_4Fe(CN)_6\cdot 8H_2O$.[14b]

While CeI_3 reacted with 1 or 2 mol equivalents of tptz in acetonitrile or pyridine to give the Lewis base adducts $CeI_3(tptz)(MeCN)_2$ and $[CeI_2(tptz)_2L_2]I$ (L = MeCN, py),[15] the 1 : 1 mixture of $UI_3(py)_4$ and tptz in acetonitrile afforded a pale brown powder of $U_2I_6(tptz–tptz)$ which recrystallized as orange crystals of $U_2I_6(tptz–tptz)(MeCN)_2\cdot 2MeCN$ (**3**·2MeCN). Such clear differentiation between lanthanide(III) and uranium(III) complexes involving $U^{III} \rightarrow U^{IV}$ oxidation was previously revealed with the metallocenes $M(C_5H_4R)_3$ (M = Ce, U; R = ^{t}Bu or $SiMe_3$) in their reaction with pyrazine which gave $Ce(C_5H_4R)_3$(pyrazine) and $[U(C_5H_4R)_3]_2(\mu\text{-pyrazine})$, respectively;[6] in that case, the azine molecule was not coupled and was transformed into its dianionic form. Although the quality of the refinement for **3** is low, the overall structure of the complex was clearly established and shows the presence of the coupled tptz molecule which adopts the same coordination mode and geometry as in **2** (Fig. 3).

In conclusion, the reactions of tptz with the reducing species K, SmI_2 and $UI_3(py)_4$ follow different pathways. While the free anion-radical $K(tptz)_2$ is isolated from the reduction with potassium metal, reactions of tptz with SmI_2 or $UI_3(py)_4$ provide the first examples of reductive coupling of a polycyclic azine molecule. The syntheses of **2** and **3** are likely to involve an electron transfer from the Sm^{II} or U^{III} ion to the aromatic nitrogen ligand, as expected

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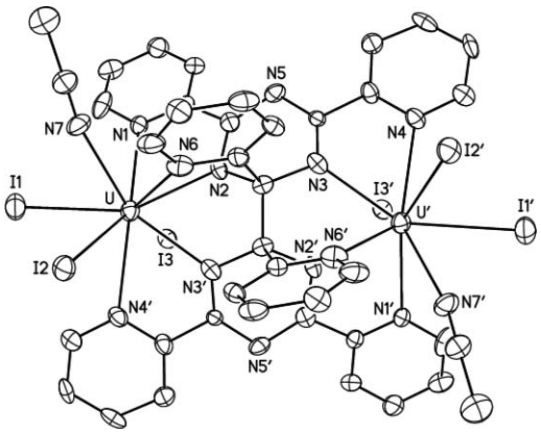

Fig. 3 View of **3**. The H atoms have been omitted. Displacement ellipsoids are drawn at the 20% probability level. Symmetry code: ′ = 2 − *x*, *y*, 1/2 − *z*. Selected bond lengths (Å) and angles (°): U–N1 2.662(17), U–N2 2.412(16), U–N3′ 2.466(19), U–N4′ 2.660(18), U–N6 2.750(19), C13–C13′ 1.49(4), C13–N2 1.51(3), C13–N3 1.45(3); N1–U–N2 63.2(6), N2–U–N3′ 62.9(6), N3′–U–N4′ 63.2(6), N1–U–N6 97.0(6), N2–U–N6 59.7(6), N3′–U–N6 73.5(6), N4′–U–N6 122.4(6).

from the reduction potential of the tptz molecule (−1.41 V *vs.* Ag/AgCl in MeCN),[16] followed by dimerization of the anion-radical tptz$^{-\bullet}$. The various factors which determine the outcome of the reduction of an azine molecule by a low-valent metal species are intricate, as previously noted with the reaction of pyridazine and $M(C_5Me_5)_2$ which afforded the radical-anion for M = Yb[3b] and the dianionic coupled ligand for M = Sm,[3a] while 2,2′-bipyrimidine was transformed into the corresponding dianion in the presence of $Yb(C_5Me_5)_2$.[3b] In relation with the nature of the metal, the azine molecule and the solvent, the lifetime and localization of the radical should have a major influence on its reactivity.

Notes and references

‡ Synthesis and characterizing data. All manipulations were carried out under argon. $K(tptz)_2$ (**1**): (a) a flask was charged with tptz (100.0 mg, 0.32 mmol) and K (15.0 mg, 0.38 mmol) in pyridine (5 mL). Rapidly the solution turned dark blue, and a blue suspension was obtained after 15 h at 20 °C. The solid was extracted in pyridine for 20 h by a soxhlet, and was then washed with pyridine (5 mL) and a 2 : 1 mixture of THF : pyridine (5 mL). After drying under vacuum, **1** was isolated as a dark blue powder (65 mg, 57%). Found: C, 63.87; H, 3.73; N, 25.13; K, 5.75. $KC_{36}N_{12}H_{24}$ (M = 663.78) requires C, 65.14; H, 3.64; N, 25.32; K, 5.89%. (b) In an NMR tube, tptz (10.0 mg, 0.032 mmol) was reacted with 2% K(Hg) (65 mg, 0.032 mmol of K) in pyridine (1 mL) for 1 h at 20 °C. After filtration, slow diffusion of pentane (1.5 mL) into the dark blue solution led to the formation of dark blue crystals of **1**.
$[Sm_2(tptz–tptz)][I]_4$: (a) a flask was charged with SmI_2 (25.0 mg, 0.062 mmol), tptz (19.3 mg, 0.062 mmol) and freshly distilled MeCN (1 mL). The orange suspension was heated at 100 °C for 10 h. After filtration, the orange powder of $[Sm_2(tptz–tptz)][I]_4$ was washed with MeCN (1 mL) and dried under vacuum (39.0 mg, 88%). Found: C, 29.86; H, 1.76; N, 11.95. $Sm_2C_{36}H_{24}I_4N_{12}$ (M = 1433.07) requires C, 30.17; H, 1.69; N, 11.73%. Diffusion of Et_2O into a DMF solution of the powder afforded orange crystals of $[Sm_2(tptz–tptz)(DMF)_8][I]_4$·3.5DMF (**2**·3.5DMF). (b) The same reaction with SmI_2 (200 mg, 0.49 mmol) and tptz (154.5 mg, 0.49 mmol) in pyridine (20 mL) gave an orange solution with yellow microcrystals. Evaporation of the solvent and addition of ~5 mL MeCN led to an orange suspension after 12 h stirring (287 mg, 81%). Found: C, 29.79; H, 1.83; N, 11.72. The poor solubility of the complex in the usual organic solvents precluded recording of the NMR spectra.
U_2I_6(tptz–tptz): a flask was charged with $UI_3(py)_4$ (150 mg, 0.160 mmol), tptz (50.1 mg, 0.160 mmol) and acetonitrile (20 mL). The solution immediately turned red and deposited a brown powder. After 2 h at 100 °C, the powder of U_2I_6(tptz–tptz) was filtered off, washed with Et_2O (10 mL) and dried under vacuum (137.6 mg, 69%). Found: C, 24.41; H, 1.47; N, 9.20. $U_2I_6C_{36}N_{12}H_{24}$ requires C, 23.22; H, 1.30; N, 9.03%. Orange crystals of $U_2I_6(tptz–tptz)(MeCN)_2$·2MeCN (**3**·2MeCN) were obtained by crystallization from acetonitrile. Complex **3** in pyridine is ^{1}H NMR and EPR silent (in the solid state and in a frozen solution).
§ Crystal data for **1**: $C_{36}H_{24}KN_{12}$, M = 663.77, monoclinic, space group $C2/c$, a = 17.7227(18), b = 10.9183(12), c = 16.0694(17) Å, β = 104.505(6)°, V = 3010.4(6) Å^3, Z = 4, T = 100(2) K. Refinement of 222 parameters on 2822 independent reflections out of 10 673 measured reflections (R_{int} = 0.092) led to R_1 = 0.054 (observed data), wR_2 = 0.124 (all data), S = 1.021, $\Delta\rho_{min}$ = −0.41, $\Delta\rho_{max}$ = 0.26 e Å^{-3}.
Crystal data for **2**: $C_{70.5}H_{104.5}I_4N_{23.5}O_{11.5}Sm_2$, M = 2273.58, triclinic, space group $P\bar{1}$, a = 12.9092(3), b = 14.1646(6), c = 25.1108(11) Å, α = 85.764(2), β = 89.355(3), γ = 80.132(2)°, V = 4511.3(3) Å^3, Z = 2, T = 100(2) K. Refinement of 1049 parameters on 17 063 independent reflections out of 160 534 measured reflections (R_{int} = 0.044) led to R_1 = 0.032 (observed data), wR_2 = 0.079 (all data), S = 1.034, $\Delta\rho_{min}$ = −1.40, $\Delta\rho_{max}$ = 2.42 e Å^{-3}.
Crystal data for **3**: $C_{44}H_{36}I_6N_{16}U_2$, M = 2026.35, monoclinic, space group $C2/c$, a = 25.314(2), b = 13.4164(9), c = 16.0957(10) Å, β = 90.106(8)°, V = 5466.5(7) Å^3, Z = 4, T = 100(2) K. Refinement of 337 parameters on 5005 independent reflections out of 18 972 measured reflections (R_{int} = 0.151) led to R_1 = 0.077 (observed data), wR_2 = 0.214 (all data), S = 1.008, $\Delta\rho_{min}$ = −1.91, $\Delta\rho_{max}$ = 1.34 e Å^{-3}.
Data were collected on a Nonius Kappa-CCD area-detector diffractometer and processed with HKL2000.[17] Absorption effects were corrected with DELABS (PLATON)[18] or SCALEPACK.[17] The structures were solved by direct methods and refined by full-matrix least-squares on F^2 with SHELXTL.[19] All non-hydrogen atoms were refined with anisotropic displacement parameters. In **2**, one solvent DMF molecule is disordered around an inversion centre and it was refined with restraints on bond lengths and displacement parameters. Restraints were also applied in **3**, particularly for the very badly resolved acetonitrile solvent molecules. The carbon-bound hydrogen atoms were introduced at calculated positions. The drawings were done with SHELXTL.[19]

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