Linear trinuclear three-centred metal–metal multiple bonds: synthesis and crystal structure of $[M_3(dpa)_4Cl_2]$ [M = Ru^{II} or Rh^{II}, dpa = bis(2-pyridyl)amido anion]

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The synthesis and X-ray crystal structures of the linear trinuclear metal complexes, $[M^{II}_3(dpa)_4Cl_2]$ (M = Ru or Rh), with a *syn–syn* bis(2-pyridyl)amido (dpa) ligand, possessing a short M–M–M three-centred multiple bond [Ru–Ru 2.2537(5) Å; Rh–Rh 2.3920(5) Å] are described.

The nature of metal–metal bonding in dinuclear metal complexes is well understood.[1–3] Presently, the extension of dinuclear metal complexes to oligonuclear metal-chain complexes is rare.[4–10] One special series of solids with a partially filled band resulting from a linear chain of metal ions has been investigated.[4] A representative example is the KDP′ salt, $K_2Pt(CN)_4Br_{0.3}\cdot 3H_2O$;[5] others include d^7–d^8 mixed-valence oligonuclear metal complexes, possessing partial σ bonds.[6–10] We report here on the synthesis and structure of quadruply bridged linear trinuclear metal ions with a *syn–syn* configuration of the bridged bis(2-pyridyl)amido (dpa) ligand. These complexes possess a short, delocalized, three-centred $\mathrm{Ru^{II}\underline{\cdots}Ru^{II}\underline{\cdots}Ru^{II}}$ bond [2.2537(5) Å] or a $\mathrm{Rh^{II}–Rh^{II}–Rh^{II}}$ bond [2.3920(5) Å] and are the first examples of three-centred multiple metal–metal bond complexes.

High-temperature interaction of $Ru_2(OAc)_4Cl$ with K (dpa) (1.5 mol equiv.), prepared *in situ* from Hdpa and $KOBu^t$ in butanol, afforded $[Ru_3(dpa)_4Cl_2]$ in low yield.†

The structure of $[Ru_3(dpa)_4Cl_2]$ is shown in Fig. 1.‡ A crystallographic C_2 axis runs through the Ru(1) atom and is perpendicular to the metal–metal bond. The three Ru^{II} ions and two chloride ions are almost collinear, with Ru(2′)–Ru(1)–Ru(2) 171.17(4)° and Ru(1)–Ru(2)–Cl 174.10(8)°. The Ru(2)–Cl distance, 2.596(2) Å, is long, showing that this bond is weak. The *syn–syn* conformation of the four dipyridylamido ligands allows each of the nitrogen atoms to coordinate with separate ruthenium ions helically. The average torsional angle along the meal–metal bond of each coordinated nitrogen atom is 21.7°. The structure is essentially isostructural to those of $[M_3(dpa)_4Cl_2]$ (M = Co^{II}, Rh^{II}, Ni^{II}, Cu^{II}). A comparison with these structures is given in Table 1.

The symmetrical delocalized three-centred multiple bond is apparently unique and is a novel feature of the trinuclear ruthenium(II) complex. According to MO analyses, the dinuclear complexes M_2L_8 contain metal–metal orbitals in the order: $\sigma < \pi^2 \ll \delta < \delta^* \ll \pi^{*2} < \sigma^*$.[1–3] Extension from di- to trinuclear complexes M_3L_{12} generates orbitals in the sequence of $\sigma < \pi^2 \ll \delta \approx n^4$ (not degenerate but close in energy) $\approx \delta^* < \pi^{*2} \ll \sigma^*$.§ The 18 d electrons of trinuclear Ru^{II} ions fill up to the ninth orbital (δ*) resulting in an overall bond order of three over the Ru_3 unit. This configuration accounts for diamagnetism of the trinuclear ruthenium complex. The Ru–Ru bond length of 2.2537(5) Å (bond order 1.5) is shorter than that of $[Ru_2(OAc)_4Cl]\cdot 2H_2O$, 2.267(1) Å,[14] which has a bond order of 2.5 and that of $[Ru_2(OAc)_4(thf)_2]$, 2.261(3) Å,[15] which has a bond order of 2.0.

The trirhodium complex $[Rh_3(dpa)_4Cl_2]$ was prepared similarly. The structure of $[Rh_3(dpa)_4Cl_2]$ is shown in Fig. 2‡ and is isomorphous with $[Ru_3(dpa)_4Cl_2]$. The Rh–Rh distance, 2.3920(5) Å, is comparable to that of the Rh–Rh dinuclear complex $[Rh_2(OAc)_4(H_2O)_2]$, 2.3855(5) Å, which has a bond order of 1.0. A comparison of dinclear metal–metal bonds and linear trinuclear metal–metal bonds is given in Table 2. For the linear trinuclear metal complexes, the energy of three-centred σ and π bonding orbitals are much lower than those of the δ (weak or negligible), *n* and σ* orbitals. The bond order of trinuclear metal complexes remains at 1.5 as the configuration of the metal ion changes from d^2 (δ, n, δ* empty) to d^6 (δ, n, δ* filled) and

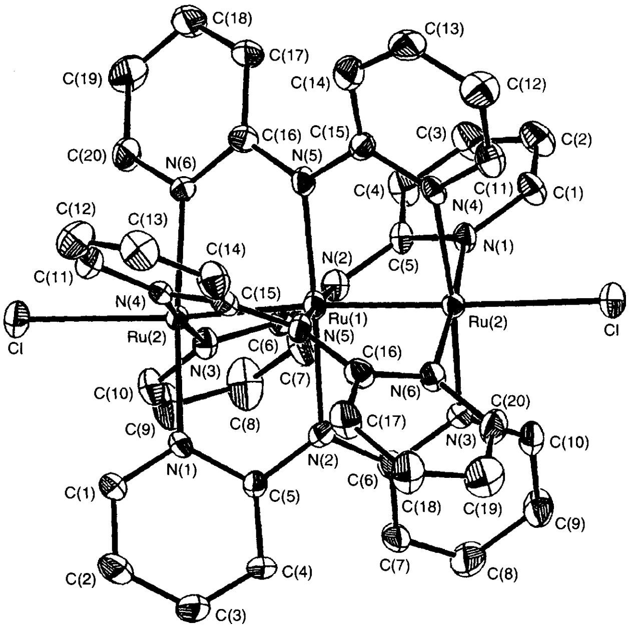

Fig. 1 ORTEP view of $[Ru^{II}_3(dpa)_4Cl_2]$ (along the metal–metal bond axis). Pertinent bond lengths (Å) and angles (°): Ru(1)–Ru(2) 2.2537(5), Ru(2)–Cl 2.596(2), Ru(1)–N, 2.033(6)–2.098(6), av. 2.06(3); Ru(2)–N, 2.064(6)–2.166(6), av. 2.11(4); Ru(2)–Ru(1)–Ru(2′), 171.15(4), Ru(1)–Ru(2)–Cl, 174.08(9), Cl–Ru(2)–N, 90.9(2)–94.0(2), av. 92(1); Ru(1)–Ru(2)–N, 84.1(2)–90.8(2), av. 88(3); N–Ru(2)–N, 88.6(2)–91.4(2), av. 90(1); Ru(2)–Ru(1)–N, 85.9(2)–94.2(2), av. 90(3); N–Ru(1)–N, 88.3(3)–90.8(3), av. 90(1). Torsional angles, N–Ru–Ru–N, 20.8–22.8, av. 21.7.

Table 1 Structural comparison of $[M_3(dpa)_4Cl_2]$ trinuclear metal complexes (M = Co^{II}, Rh^{II}, Ni^{II}, Cu^{II}, Ru^{II})

	Co[11]	Ni[12]	Cu[13]	Ru	Rh
M–Cl	2.432(3) 2.361(4)	2.325(3)	2.465(1)	2.596(2)	2.586(1)
M–M	2.290(3) 2.472(3)	2.443(1)	2.471(1)	2.2537(5)	2.3920(5)
M–N (py)	1.96(1) 2.12(1)	2.10(1)	2.05(2)	2.11(4)	2.08(1)
M–N (amido)	1.90(1)	1.89(1)	1.96(2)	2.07(3)	2.01(1)

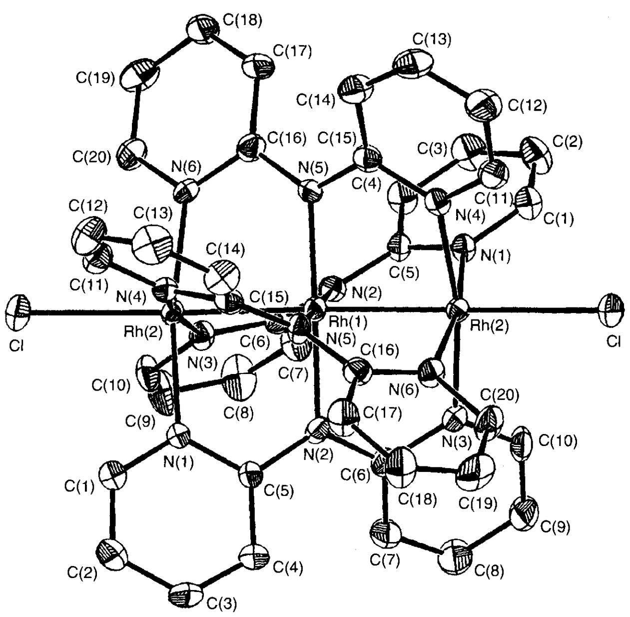

Fig. 2 ORTEP view of $[Rh^{II}_3(dpa)_4Cl_2]$ (along the metal–metal bond axis). Pertinent bond lengths (Å) and angles (°): Rh(1)–Rh(2) 2.3920(5), Rh(2)–Cl 2.586(1), Rh(1)–N, 2.008(5)–2.020(5), av. 2.01(1); Ru(2)–N, 2.069(5)–2.091(6), av. 2.08(1). Torsional angles, N–Rh–Rh–N,19.8–21.0 av. 20.4; Rh(2)–Rh(1)–Rh(2′), 177.13(4), Rh(1)–Rh(2)–Cl, 178.32(8), Cl–Rh(2)–N, 94.5(1)–95.4(1), av. 95.0(3); Rh(1)–Rh(2)–N, 84.0(1)–86.3(1), av. 85(1); N–Rh(2)–N, 89.0(2)–90.2(2), av. 89.6(5); Rh(2)–Rh(1)–N, 88.8(2)–91.5(2), av. 90(1); N–Rh(1)–N, 89.4(3)–90.4(3), av. 90(1).

Table 2 Comparison of dinuclear and trinuclear metal–metal bonds

Complex	Configuration	Bond order	M–M bond length
$[Mo_2(OAc)_4]$[17]	$\sigma^2\pi^4\delta^2$	4	2.093(1)
$[Ru_2(OAc)_4Cl]\cdot 2H_2O$ [14]	$\sigma^2\pi^4\delta^2\delta^*\pi^{*2}$	2.5	2.267(1)
$[Ru_2(OAc)_4(thf)_2]$[15]	$\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*2}$	2.0	2.261(3)
$[Rh_2(OAc)_4(OH_2)_2]ClO_4\cdot H_2O$[18]	$\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*3}$	1.5	2.316(2)
$[Rh_2(OAc)_4(H_2O)_2]$[16]	$\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}$	1.0	2.3855(5)
$[Ru^{II}_3(dpa)_4Cl_2]$	$\sigma^2\pi^4\delta^2n^8\delta^{*2}$	1.5	2.2537(5)
$[Rh^{II}_3(dpa)_4Cl_2]$	$\sigma^2\pi^4\delta^2n^8\delta^{*2}\pi^{*3}$	0.75	2.3920(5)

decreases to 0.75 and to 0 for the d^7 to d^8 trinuclear metal complexes.

An attempt to isolate linear trinuclear metal complexes of early transition metals is being undertaken.

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Footnotes

† $[Ru_2(OAc)_4Cl]$ (0.95 g, 2 mmol) and dipyridylamine (Hdpa, 0.51 g, 3 mmol) were placed in a Erlemyer Flask, to which naphthalene (10 g) was added. The mixture was heated (*ca.* 160–180 °C) for 20 min to remove water. Then *n*-butanol (3 ml) was added and heating continued until the *n*-butanol was almost completely evaporated. A solution of potassium *tert*-butoxide (0.34 g) in *n*-butanol (20 ml) was added dropwise. Heating was continued until the remaining *n*-butanol was evaporated completely. After the mixture was cooled, *n*-hexane was added to wash out the naphthalene. The remaining solid was extracted with dichloromethane and recrystallized from CH_2Cl_2–*n*-hexane. Dark green-brown crystals were obtained (yield 2%). The IR spectrum is almost the same as for the previously reported nickel(II), cobalt(II) and copper(II) complexes[11–13] with absorptions at 1597s, 1587s, 1541m, 1458vs and 1420vs cm^{-1}, with an absence of absorption due to the N–H stretching mode in the region of 3300 cm^{-1}. The electronic spectrum (CH_2Cl_2 solution), shows maxima at 295 nm (ε 7.15 × 10^4 dm^3 mol^{-1} cm^{-1}) and 357 nm (3.22 × 10^4). The ^1H NMR spectrum (CD_2Cl_2), shows signals at δ 6.35m, 6.68m, 7.06m, 7.35m, 7.46m, 7.99m and 8.15m; mass spectrum at: *m/z* 1054 (M^+).

The trirhodium complex $[Rh_3(dpa)_4Cl_2]$ was prepared similarly. The IR spectrum is almost the same as above with absorptions at 1599s, 1588s, 1541m, 1460vs and 1420vs cm^{-1}, and no bond due to N–H. The electronic spectrum (CH_2Cl_2 solution), shows maxima at 277 nm (ε 5.05 × 10^4 dm^3 mol^{-1} cm^{-1}) and 305 nm (5.97 × 10^3). μ_{eff} = 1.9 μ_B; mass spectrum: *m/z* 1060 (M^+).

‡ *Crystal data* for $[Ru_3(dpa)_4Cl_2]\cdot CH_2Cl_2$: orthorhombic, space group *Pnn*2, a = 14.181(3), b = 13.289(2), c = 11.090(5) Å, U = 2088(1) $Å^3$, D_c = 1.738 g cm^{-3}, Z = 2; CAD4 diffractometer with graphite-monochromated Mo-Kα radiation, ψ-scan absorption correction; 1941 unique reflections (2θ < 50°) were measured and 1522 with $I > 2\sigma(I)$ were used in the refinement. Refinement of the positional and anisotropic thermal perameters for all non-hydrogen atoms (276 variables) converged to R = 0.027 and R_w = 0.026.

For $[Rh_3(dpa)_4Cl_2]\cdot CH_2Cl_2$: orthorhombic, space group *Pnn*2, a = 14.148(3), b = 13.306(2), c = 11.128(5) Å, U = 2095.0(5) $Å^3$, D_c = 1.760 g cm^3, Z = 2, 2532 unique reflections (2 θ < 55°) were measured and 1943 with $I > 2\sigma$ (I) were used in the refinement. R = 0.029, Rw = 0.030. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§The molecular-orbital calculation is based on the extended Hückel methods (EHMO), using the program ICON.[19] The basis functions of Ru, Rh, Cl, C, N and H and the results of MO analysis were presented as supplementary material and seen by the referees.

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