Four quadruple metal–metal bonds lined up: linear nonachromium(II) metal string complexes†

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Through a new pyrazine-modulated pentapyridyltetraamine ligand, H_4N_9-mpz, linear nonachromium(II) complexes with four quadruple metal–metal bonds were successfully obtained, and their structure, magnetic and electrochemistry properties were studied.

Extended metal atom chain (EMAC) complexes are very important to a fundamental understanding of metal–metal interactions and in potential applications such as molecular metal wire and switches.[1] A series of tri-,[2] tetra-,[3] penta-,[4] hexa-,[5] hepta-,[6] and nona-nuclear[7] metal string complexes have been synthesized by employing oligo-α-pyridylamino ligands (Scheme 1). The typical structure of this family includes a linear metal chain, which is helically wrapped by four oligo-α-pyridylamido ligands, with all the pyridine nitrogen and amido nitrogen atoms coordinated in a *syn* form. The adjacent pyridyl rings are not coplanar due to the repulsion of the β-H atoms, and the dihedral angle between adjacent pyridyl rings is about 45°. When an EMAC contains 17 metal atoms, the twisted, wrapping ligand will fulfil a single term around the metal array line and it is theoretically possible to extend the system to an infinite one-dimensional molecule. Thus synthesis of longer EMACs is one of the targets of research and great effort has been made towards this end over the past decade. However, synthetic difficulty increases and yield decreases with an increase in the number of metal atoms and length of the molecules. On the other hand, our previous research revealed that the longer the EMAC is, the more easily it undergoes oxidation, which destabilizes the compound.[8] The longest EMAC molecule obtained to date contains nine metal atoms of nickel,[7] seven of chromium[6] and cobalt,[9] and five of ruthenium. Recently we designed a series of new ligands, pyrazine-modulated oligo-α-pyridylamino ligands, by including pyrazine instead of pyridine
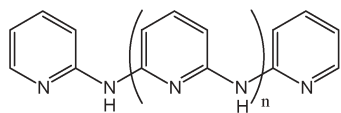
Scheme 1 Oligo-α-pyridylamino ligands.

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ring(s) in the oligo-α-pyridylamino ligands.[10] The introduction of one or more nitrogen-rich aromatic rings, pyrazine, to the ligand significantly improves the reactivity leading to the EMAC, and the products are more resistant to oxidation than the relevant oligo-α-pyridylamino EMAC. Through the reaction of pyrazine-modulated pentapyridyltetraamine (H_4peptea, Scheme 1, $n = 3$), we successfully obtained single crystals of linear nonachromium(II) complexes, which are the highest nuclearity chromium(II) EMACs reported to date.[7] Here we report a new pyrazine-modulated pentapyridyltetraamine ligand, N^2,N^6-bis-[6-(pyridin-2-ylamino)-pyridin-2-yl]pyrazine-2,6-diamine (H_4N_9-mpz)‡ (Scheme 2S), and its nonachromium(II) complexes $[Cr_9(\mu_9\text{-}N_9\text{-mpz})_4Cl_2]$ (**1**)§ and $[Cr_9(\mu_9\text{-}N_9\text{-mpz})_4(NCS)_2]$ (**2**).¶

The ligand H_4N_9-mpz was synthesized on the basis of the Buchwald's palladium-catalyzed procedures (Scheme 2S) *via* the cross-coupling of *N*-pyridin-2-yl-pyridine-2,6-diamine and 2,6-dichloropyrazine,[11] and characterized by IR, ^{1}H NMR and MS(FAB). The chloride complex $[Cr_9(\mu_9\text{-}N_9\text{-mpz})_4Cl_2]$ (**1**) was synthesized by the reaction of anhydrous $CrCl_2$ with the ligand H_4N_9-mpz in an argon atmosphere at high temperature (180–200 °C) employing naphthalene as solvent and Bu^tOK as a base to deprotonate the amine group. The thiocyanate species $[Cr_9(\mu_9\text{-}N_9\text{-mpz})_4(NCS)_2]$ (**2**) was obtained through the substitution of axial chloride ligands from **1**.

The crystal structures of **1** and **2** are shown in Fig. 1S and Fig. 1.‖ The molecule consists of nine Cr(II) atoms in a linear chain with the M–M–M bond angles in a range of 178–180°. The atoms of axial ligands bonded to the terminal metal atoms, chloride or nitrogen atoms of NCS^-, are collinear with the M_9 axis. The length of the whole molecule of **1** is 23 Å, and molecule **2** is 25 Å. This is the longest chain obtained since $[Ni_9(\mu_9\text{-peptea})_4Cl_2]$, which contains a nine-nickel chain.[7] Four ligands wrapped around the metal string in *syn-syn* form as a nonadent anion helix. The N–Cr–Cr–N torsion angles for adjacent Cr(II) are between 18 and 23°, and the average value of total torsion angles for one ligand, *i.e.* N–Cr(1)–Cr(1A)–N, is 159°. The Cr–Cr bond distances fall into two categories, the shorter one is in the range 1.973–2.097 Å with an average of 2.025 Å, which is consistent with the reference values of the short limit for quadruple Cr–Cr bonds (Table 1).[12] The longer Cr–Cr distances range from 2.397 to 2.497 Å. Thus complexes **1** and **2** are composed of four quadruple Cr–Cr bonds and a single terminal Cr(II) atom coordinated in a pyramidal Cl–Cr–N_4 unit, in the same style as tri- and penta-chromium EMAC. It is noticeable that the four quadruple Cr–Cr bonds and the single Cr(II) are aligned in a straight chain; this may result from the steric force of the ligand H_4N_9-mpz for
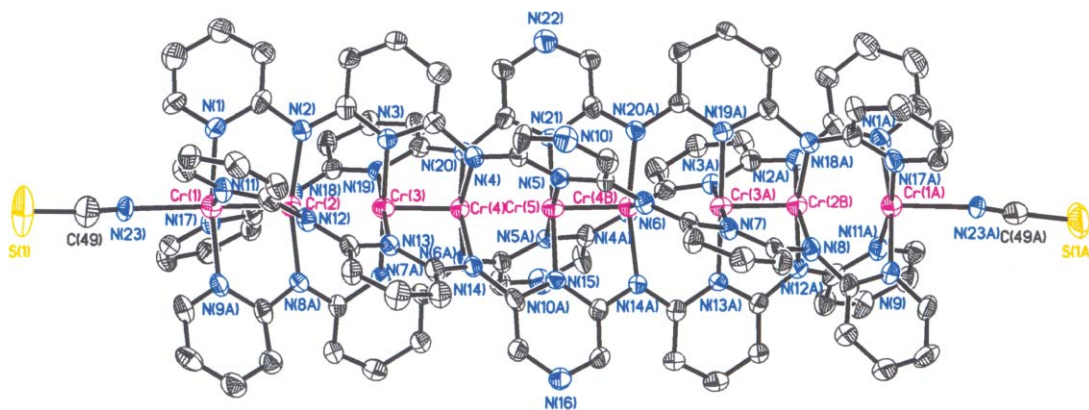
Fig. 1 The molecular structure of [$Cr_9(\mu_9$-N_9-mpz)$_4$(NCS)$_2$] (**2**). Label A represents symmetric related positions, and label B non-symmetric related positions (disordered positions). Thermal ellipsoids are drawn at the 30% probability level. The hydrogen atoms have been omitted for clarity.

Table 1 Selected bond lengths (Å) for **1** and **2**

	Cr(1)–Cr(2)	Cr(2)–Cr(3)	Cr(3)–Cr(4)	Cr(4)–Cr(5)	Cr(4B)–Cr(5)	Cr(4B)–Cr(3A)	Cr(3A)–Cr(2B)	Cr(2B)–Cr(1A)
1	2.097(4)	2.425(4)	2.024(3)	2.397(3)	2.017(3)	2.404(4)	2.046(4)	2.475(4)
2	2.055(5)	2.450(5)	1.984(4)	2.426(4)	1.973(4)	2.438(5)	2.007(5)	2.497(5)
	Cr(1)–$N_{av.}$	Cr(2)–$N_{av.}$	Cr(3)–$N_{av.}$	Cr(4)–$N_{av.}$	Cr(5)–$N_{av.}$	Cr(2B)–$N_{av.}$	Cr(4B)–$N_{av.}$	
1	2.105(6)	2.038(6)	2.055(6)	2.034(7)	2.034(9)	2.029(7)	2.033(7)	
2	2.089(9)	2.035(9)	2.047(8)	2.035(9)	2.032(11)	2.026(9)	2.033(9)	

oligo-α-pyridylamino ligands favoring linear metal string structures. However, a weak Cr–Cr bond through the Cr9 core with σ-character was not excluded in spite of the long distances between quadruple Cr–Cr bonds (2.397 to 2.497 Å), considering that the Cr–Cr bond was observed in trichromium EMAC [$Cr_3(\mu_3$-depa)$_4$Cl$_2$] even the Cr–Cr distance is 2.378 Å.[2c] There are two equally occupied positions for Cr(2) and Cr(4), whereas Cr(1), Cr(3) and Cr(5) are not disordered. Thus the molecule is oriented in two directions as: Cr1Cr2---Cr3Cr4---Cr5Cr4B---Cr3Cr2B---Cr1 or Cr1---Cr2BCr3---Cr4BCr5---Cr4Cr3---Cr2Cr1, and each form is adopted with an occupancy of 50%.

The redox properties of EMACs are an important topic in the research of inherence of metal–metal bonding and their potential application as molecular devices. Previous studies showed that EMACs exhibited rich redox properties. The cyclic voltammograms show three oxidative waves at $E_{1/2}$ = +0.38, +0.50, and +0.92 V for **1**, and $E_{1/2}$ = +0.42, +0.52, and +0.94 V for **2** (Fig. 2). The first and second oxidation processes are overlapped and can be well resolved by using differential pulse techniques. All electrochemical processes are reversible and involve one-electron abstraction as evidenced by thin-layer spectroelectrochemical measurements.[13] Displacement of chlorides with thiocyanates results in slightly anodic shifts. The first oxidation peaks for both **1** and **2** corresponded to the loss of one electron from isolated Cr(II) according to the research on oxidized products of complexes $Cr_3(\mu_3$-dpa)$_4$Cl$_2$ [Hdpa = di(2-pyridyl)amine] and $Cr_5(\mu_5$-tpda)$_4$Cl$_2$ [H$_2$tpda = N,N′-bis(α-pyridyl)-2,6-diaminopyridine], and the resulting species was $Cr_9{}^{19+}$ with the backbone $\left(Cr^{II}\!\!\equiv\!\!Cr^{II}\right)_4$–$Cr^{III}$.[2d,4a]

The magnetic behaviour of **1** and **2** are similar and obey the Curie–Weiss law. Plots of thermal magnetic susceptibility and $\chi_M T$ are shown in Fig. 3. The $\chi_M T$ values of **1** and **2** at room temperature (300 K) were 3.20 and 3.11 emu K mol^{-1}, respectively, which correspond to the value of the quintet ground state (for four unpaired electrons $\chi_M T$ = 3 emu K mol^{-1}). Based on the structural results, the first approximation attributes the magnetic contribution only to the high-spin, terminal Cr(II) atom that is non-bonded to other Cr(II) atoms, and the CrCr bond is diamagnetic with eight electrons localized within the Cr–Cr quadruple bond.

From 300 to 16 K, $\chi_M T$ for both **1** and **2** decreased only slightly upon cooling. A fit with the Curie–Weiss Law gave g = 2.07 and θ = −5.54 K for **1** and g = 2.03 and θ = −2.20 K for **2**. An obvious decrease of $\chi_M T$ was observed below 16 K, which was due to zero-field splitting and an incorporation of intermolecular interaction.

In summary, through the reaction of the pyrazine-modulated pentapyridyltetraamine ligand, we successfully obtained single crystals of linear nonachromium complexes, which are the highest
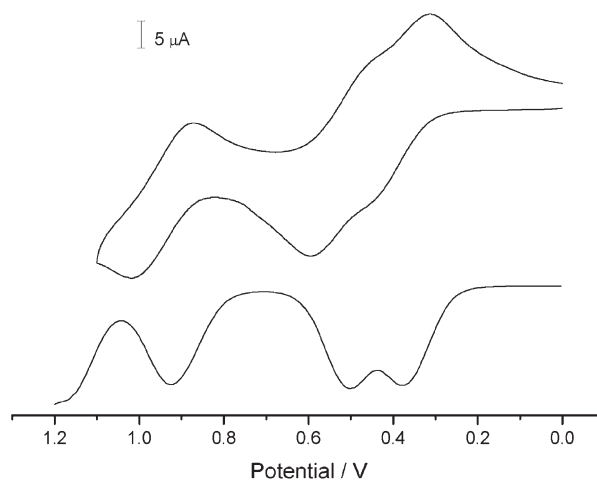

Fig. 2 Cyclic voltammogram (top) and differential pulse voltammograph (bottom) of **1** in CH_2Cl_2 with 0.1 M TBAP.
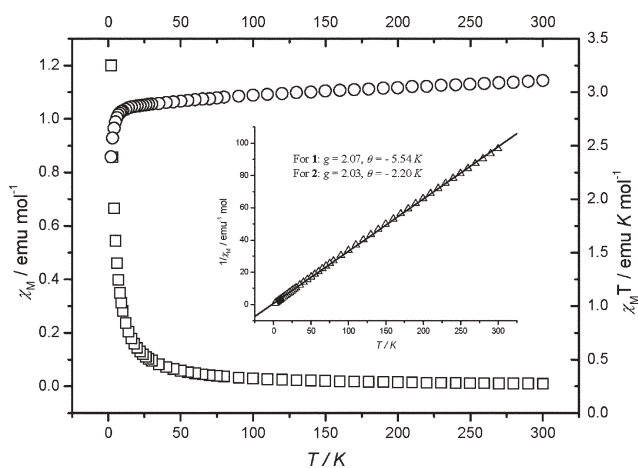
Fig. 3 Temperature-dependent $\chi_M T$ ($\bigcirc$, right axis) and molar magnetic susceptibility ($\square$, left axis) for compound **2**. Inset: reciprocal dependence of the magnetic susceptibility on temperature. The solid lines result from least-square fits of the Curie–Weiss Law.

nuclearity EMACs reported to date. Further investigations on high nuclearity chromium(II) EMACs with pyrazine-modulated ligands are currently underway in our group.

Notes and references

‡ Synthesis of N^2,N^6-bis-[6-(pyridin-2-ylamino)pyridin-2-yl]pyrazine-2,6-diamine (H$_4$N$_9$-mpz). The reaction of 2,6-dichloropyrazine (10 g, 0.067 mol) and N-pyridin-2-yl-pyridine-2,6-diamine (29.96 g, 0.061 mol) in the presence of Pd$_2$(dba)$_3$ (1.229 g, 2 mol%), BINAP (1.671 g, 4 mol%) and Bu^{t}ONa (21.67 g, 0.225 mol) in benzene (600 mL) for 72 h gave H$_4$N$_9$-mpz. The crude product was recrystallized from acetone and gave pure H$_4$N$_9$-mpz as a light yellow solid (yield 30.6%). IR (KBr) ν/cm^{-1}: 3402m, 3270m, 3191m, 3103m, 3050m, 1598m, 1558m, 1516m, 1434vs, 1354m, 1301m, 1260m, 1246m, 1226m, 1192m, 1151m, 996w, 771m, 668w; UV/Vis (DMF) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 270 (4.33 × 10^4), 321 (2.48 × 10^4), 370 (3.70 × 10^4), 467 (7.46 × 10^2); ^{1}H NMR (400 MHz, (CD$_3$)$_2$SO): δ 9.42 (s, 4H), 8.57 (s, 2H), 8.20–8.19 (m, 2H), 7.81–7.79 (d, J = 8.46 Hz, 2H), 7.64–7.60 (m, 2H), 7.56–7.52 (t, J = 8.01 Hz, 2H), 7.23–7.19 (t, J = 8.12 Hz, 4H), 6.86–6.83 (m, 2H); MS(FAB): m/z (%) 449 (45) [M]$^+$; EA (%) C$_{24}$H$_{20}$N$_{10}$·CH$_3$OH: calc. C 62.49, H 5.03, N 29.15; found: C 62.45, H 4.67, N 29.30%.

§ Synthesis of [Cr$_9$(μ_9-N$_9$-mpz)$_4$Cl$_2$] (**1**). Anhydrous CrCl$_2$ (0.637 g, 5.1 mmol), H$_4$N$_9$-mpz (0.448 g, 1.0 mmol) and naphthalene (40 g) were heated at *ca.* 170–180 °C under argon and then a solution of potassium *tert*-butoxide (0.561 g, 5.0 mmol) in *n*-butyl alcohol (4 mL) was added dropwise. After reaction *n*-hexane was added to wash out the naphthalene. Compound **1** was extracted and recrystallized in CH$_2$Cl$_2$–benzene (1 : 1) (yield 1.0%). IR (KBr) ν/cm^{-1}: 1603m, 1582m, 1550m, 1447m, 1410s, 1353m, 1326s, 1270m, 1197m, 1156m, 1104w, 1118w, 1046w, 1020m, 779m, 736m, 668m; UV/Vis (CH$_2$Cl$_2$) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 230 (1.11 × 10^5), 278 (1.39 × 10^5), 349 (9.36 × 10^4), 369 (9.46 × 10^4), 390 (9.73 × 10^4), 600 (6.20 × 10^3), 756 (6.82 × 10^3), 809 (8.34 × 10^3); MS(FAB): m/z (%) 2316 (65) [M]$^+$, 2283 (100) [M − Cl]$^+$; EA (%) [Cr$_9$(μ_9-N$_9$-mpz)$_4$Cl$_2$]·CH$_2$Cl$_2$·2CH$_3$OH: calc. C 48.23, H 3.03, N 22.72; found: C 48.38, H 3.38, N 21.94%.

¶ Synthesis of [Cr$_9$(μ_9-N$_9$-mpz)$_4$(NCS)$_2$] (**2**). [Cr$_9$(μ_9-N$_9$-mpz)$_4$Cl$_2$] (0.03 g, 0.013 mmol) and NaNCS (0.004 g, 0.051 mmol) in CHCl$_3$ (30 mL) were stirred for 2 d. The solvent was removed under reduced pressure and the product recrystallized from a CHCl$_3$–diethyl ether solution (1 : 4). Deep red-brown crystals were obtained (yield 82%). IR (KBr) ν/cm^{-1}: 3418m, br, 2036m, 1603m, 1582m, 1551m, 1472m, 1409s, 1325s, 1268m, 1196m, 1155s, 1119w, 1103w, 1020m, 972w, 834w, 778m, 736m, 648w; UV/Vis (CH$_2$Cl$_2$) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 236 (1.05 × 10^5), 280 (1.32 × 10^5), 361 (9.13 × 10^4), 393 (9.50 × 10^4), 655 (3.80 × 10^3), 757 (7.99 × 10^3), 809 (8.27 × 10^3); MS(FAB): m/z (%) 2360 (4) [M − NCS]$^+$; EA (%) [Cr$_9$(μ_9-N$_9$-mpz)$_4$(NCS)$_2$]: calc. C 40.49, H 2.46, N 30.11; found: C 40.66, H 2.32, N 29.42%.

‖ Crystal data for **1**: [Cr$_9$(μ_9-N$_9$-mpz)$_4$Cl$_2$]·2C$_6$H$_6$·2C$_6$H$_{14}$·C$_2$H$_5$OC$_2$H$_5$, M_w = 2719.45, monoclinic, space group $C2/c$, a = 44.392(3), b = 14.3963(10), c = 18.6471(12) Å, β = 95.391(4)°, V = 11864.3(14) Å^3, Z = 4, μ = 0.907 mm^{-1}, 46 502 reflections collected, 10 382 independent, final $R1$ = 0.0788 for $I > 2\sigma(I)$; $wR2$ = 0.2618 for all data. Crystal data for **2**: [Cr$_9$(μ_9-N$_9$-mpz)$_4$(NCS)$_2$]·2C$_6$H$_{14}$·CHCl$_3$, M_w = 2653.74, monoclinic, space group $C2/c$, a = 43.5722(13), b = 14.4390(5), c = 19.2834(6) Å, β = 98.1689(17)°, V = 12008.8(7) Å^3, Z = 4, μ = 0.948 mm^{-1}, 31 810 reflections collected, 10 533 independent, final $R1$ = 0.1077 for $I > 2\sigma(I)$, $wR2$ = 0.3432 for all data. Structures of **1** and **2** were solved both by $C2/c$ and Cc space groups, and the results showed that in both compounds the $C2/c$ data are superior. The details were included in CIF files. CCDC 623204 and 623205. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b614597c.

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