A linear metal string $[Cr_7(\mu_7\text{-teptra})_4Cl_2]$ complex with delocalized heptachromium(II) multiple bonds ($teptraH_3$ = tetrapyridyltriamine)

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Received (in Cambridge, UK) 22nd June 1999, Accepted 21st July 1999

A heptachromium(II) metal chain helically wrapped by four all-*syn* type $teptra^{3-}$ ligands with delocalized Cr^{II}–Cr^{II}–Cr^{II}–Cr^{II}–Cr^{II}–Cr^{II}–Cr^{II} multiple bonds is found in the complex $[Cr_7(\mu_7\text{-teptra})_4Cl_2]$. The band structure of a hypothetical one-dimensional chromium string based on this structure is calculated and shows metallic behavior for the string structure.

The bonding interaction of the metal string in oligonuclear linear metal chain complexes, which have the potential as molecular metal-wires is an important and exciting topic.[1–12] Bonding information and the electronic configurations of metal centers on oligonuclear metal complexes from trinuclear metal complexes with *syn–syn* bis(α-pyridyl)amido (dpa) ligand $[M_3(\mu_3\text{-dpa})_4X_2]$, (M = Cu,[1] Ni,[2] Co,[3,6] Cr,[7] Ru,[4] Rh[4]) and from pentanuclear metal complexes with all-*syn* tris(α-pyridyl)diamido (tpda) ligand $[M_5(\mu_5\text{-tpda})_4X_2]$, (M = Ni,[5,8] Co,[5,8] Cr[10,11]) have been described and discussed in detail. Although the Ni–Ni bond order is zero, the Ni–Ni distance altered predictably from 2.379(2) Å for the terminal one to 2.307(1) Å for the intermediate one and to 2.220(2) Å for the innermost one in the heptanickel $[Ni_7(\mu_7\text{-teptra})_4Cl_2]$ complex.[12] The next target of study is the linear oligochromium(II) complexes with a strong Cr–Cr bond (bond order 1.5). In this system, the Cr–Cr distances are found to be 2.36(1) Å in trichromium $[Cr_3(\mu_3\text{-dpa})_4Cl_2]$,[7] and 2.284(1) and 2.2405(8) Å in pentachromium $[Cr_5(\mu_5\text{-tpda})_4Cl_2]$.[11] Here we report the synthesis and structure of the heptachromium(II) metal string complex, $[Cr_7(\mu_7\text{-teptra})_4Cl_2]$, and the band structure of a hypothetical one-dimensional metal string based on the structure of this complex.

The title compound, $[Cr_7(\mu_7\text{-teptra})_4Cl_2]$, was synthesized by using anhydrous $CrCl_2$ and $teptraH_3$ ligand as the starting materials and naphthalene as the solvent under an argon atmosphere.† Bu^tOK was used as a base to deprotonate the amine groups of the $teptraH_3$ ligand. The $teptraH_3$ ligand was synthesized in the same manner as previously reported.[13,14] The crystal structure of $[Cr_7(\mu_7\text{-teptra})_4Cl_2]$ is shown in Fig. 1.‡ The space group of the title compound is $P2_1/c$ with a whole molecule and six THF molecules in an asymmetric unit. The structure is essentially identical to those of $[Ni_7(\mu_7\text{-teptra})_4X_2]$, (X = Cl^-, NCS^-)[9,12] with the linear heptachromium chain being wrapped helically by four all-*syn* type $teptra^{3-}$ ligands. The complex exhibits an approximate D_4 symmetry. According to our structural analysis, the Cr–Cr bond lengths are symmetrically distributed in the range 2.211(2)–2.291(2) Å. Logically, the bonding mode in the Cr^{II}_7 unit favors a delocalized arrangement (**I**) over a localized arrangement (**II**).

$$\mathrm{Cl{-}Cr{=}Cr{=}Cr{=}Cr{=}Cr{=}Cr{=}Cr{-}Cl}$$

I

$$\mathrm{Cl{-}Cr{\equiv}Cr\cdots Cr{\equiv}Cr\cdots Cr{\equiv}Cr\cdots Cr{-}Cl}$$

II

However, our study shows that the inner chromium ions (Cr(2)–Cr(6)) have anisotropic ellipsoidal structures with a larger thermal parameter in the direction of the metal axis. Although they still have reasonable values (av. U_{11}, U_{22}, U_{33} are 0.078, 0.041, 0.033, respectively), the disordered form of **II** can not be completely excluded. Three types of Cr–Cr bond lengths, with small differences among them, are observed. The averaged values of the bond length are 2.286(2) Å for the terminal Cr–Cr bonds, 2.243(2) Å for the intermediate Cr–Cr bonds and 2.213(2) Å for the innermost Cr–Cr bonds. A comparison of the Cr–Cr distances among the tri-, penta-, and heptachromium(II) complexes are shown in Fig. 2. All of the Cr–Cr distances in $[Cr_7(\mu_7\text{-teptra})_4Cl_2]$ are shorter than those in $[Cr_3(\mu_3\text{-dpa})_4Cl_2]$ (2.36(1) Å),[7] and are comparable with 2.284(1) Å of the terminal Cr–Cr bond, and 2.2405(8) Å of the inner Cr–Cr bond in $[Cr_5(\mu_5\text{-tpda})_4Cl_2]$. In a previous report,[12] the probability of

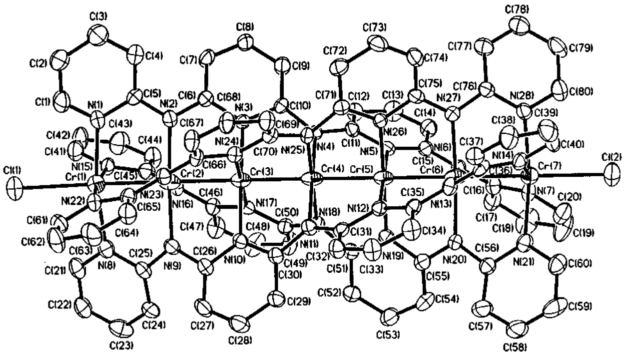
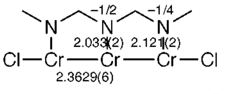
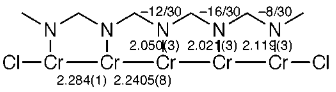


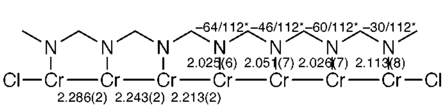
Fig. 1 Crystal structure of $[Cr_7(\mu_7\text{-teptra})_4Cl_2]$ (ORTEP side view). Atoms are shown as 30% vibrational thermal ellipsoids. Pertinent bond lengths (Å) and angles (°): Cr(1)–Cr(2) 2.291(2), Cr(2)–Cr(3) 2.243(2), Cr(3)–Cr(4) 2.211(2), Cr(4)–Cr(5) 2.215(2), Cr(5)–Cr(6) 2.243(2), Cr(6)–Cr(7) 2.280(2), Cr(1)–$N_{av.}$ 2.113(8), Cr(2)–$N_{av.}$ 2.026(7), Cr(3)–$N_{av.}$ 2.051(7), Cr(4)–$N_{av.}$ 2.025(6), Cr(5)–$N_{av.}$ 2.054(7), Cr(6)–$N_{av.}$ 2.024(7), Cr(7)–$N_{av.}$ 2.113(8), Cr(1)–Cl(1) 2.557(3), Cr(7)–Cl(2) 2.544(3), Cl(1)–Cr(1)–Cr(2) 178.6(1), Cr(1)–Cr(2)–Cr(3) 179.35(9), Cr(2)–Cr(3)-Cr(4) 179.74(9), Cr(3)–Cr(4)–Cr(5) 179.58(9), Cr(4)–Cr(5)–Cr(6) 179.79(8), Cr(5)–Cr(6)–Cr(7) 179.7(1), Cr(6)–Cr(7)–Cl(2) 179.6(1).



Trichromium(II) complex[15]



Pentachromium(II) complex[11]



Heptachromium(II) complex

Fig. 2 Comparisons of Cr–Cr and Cr–N distances among tri-, penta- and heptachromium(II) complexes. *: Probability of negative charge distribution on the N atoms according to 112 resonance structures.

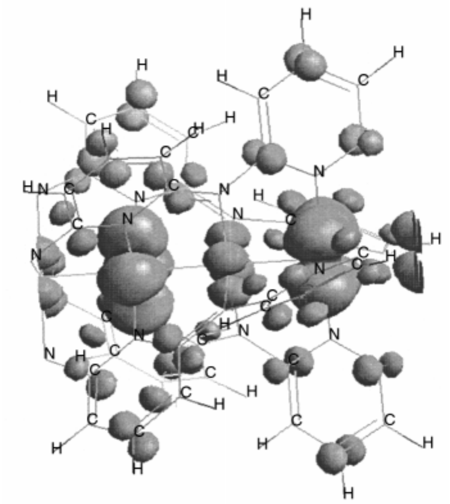


Fig. 3 The HOMO orbital of the $[Cr_4(\mu_4\text{-dpda})_4]_n$ chain.

negative charge distribution on the seven N atoms by 112 resonance structures are shown to be −30/112, −60/112, −46/112, and −64/112 from the terminal N atom to the central N atom, respectively (Fig. 2). This charge distribution is qualitatively similar to the calculated net atomic charges obtained from EHMO and Gaussian/DFT calculations.[12] The results indicate that the bond length of the Cr–N bond should depend on the bonding interaction between the N and Cr atoms. The larger the negative charge is on the N atom, the stronger is the Cr–N bond and the shorter is the Cr–N bond distance. This prediction is proven directly from the Cr–N distances obtained from structural analyse. In Fig. 2, the two terminal Cr–N bond distances are obviously the longest. The Cr–N bond distance neighboring the terminal Cr–N bond and the central Cr–N bond distance are the shortest. This result is in good agreement with the prediction based on the charge distributions.

The electronic band structure of the molecular polynuclear metal-wire is calculated for a hypothetical infinite one-dimensional metal-wire created by extending the length of the linear metal complex. In light of the D_4 symmetry of the metal complex, $[Cr_7(\mu_7\text{-teptra})_4Cl_2]$, a model metal-wire is constructed with $[Cr_4(\mu_4\text{-dpda})_4]_n$ (dpda = dipyridyldiamido moiety) taken from the crystal structure of the $[Cr_7(\mu_7\text{-teptra})_4Cl_2]$, as the repeat unit. The molecular structure of this model is then optimized and the band structure is calculated.§ The results indicate that the linear complex is a metal since the Fermi level is located within the HOMO band and there is thus no band gap. The HOMO orbital (Fig. 3) of this hypothetical metal-wire is delocalized and mainly constitutes of the d_{xy} and the $d_{x^2-y^2}$ orbitals of chromium and the p orbitals of carbon in the $dpda^{2-}$ ligands. The LUMO is localized on the chromium chain, and is composed of the d_{z^2} orbital of chromium. This model shows that the chromium metal-wire can likely serve as a conducting wire in, for example, nanostructure applications.

In summary, we have demonstrated a seven-centered metal multiple bonding scheme for early transition metal ions. The variations of the M–M distances in the Ni_7 system with a weak antiferromagnetic interaction and in the Cr_7 system with a strong M–M bonding have been described and compared. In both cases, the M–M distances converge to *ca.* 2.22 Å. Studies on the application of metal string complexes as molecular metal-wires are in progress.

The authors thank the National Science Council of the Republic of China for financial support. The authors also thank the National Center for High-performance Computing (NCHC) for providing computational facilities.

Notes and references

† *Preparation and characterization of* $[Cr_7(\mu_7\text{-teptra})_4Cl_2]$. Anhydrous $CrCl_2$ (1.40 g, 11.4 mmol) and $\text{teptra}H_3$ (1.00 g, 2.8 mmol) were placed in an Erlenmeyer flask, and naphthalene (10 g) was added under nitrogen in a glove box. The mixture was heated (about 160–180 °C) for 20 h under argon. Then a solution of potassium *tert*-butoxide (1.04 g, 9.3 mmol) in *tert*-butyl alcohol (10 mL) was added dropwise. The mixture was refluxed for 18 h continuously. After the mixture had cooled, hexane was added to wash out naphthalene. The remaining solid was extracted with CH_2Cl_2 and recrystallized from DMF–THF. Deep brown crystals were obtained. (Yield: 40%), IR (KBr) ν/cm^{-1} = 1600, 1580, 1546 (C=C). UV/Vis (CH_2Cl_2) $\lambda_{\text{max}}/\text{nm}$ ($\varepsilon/\text{dm}^3\ \text{mol}^{-1}\ \text{cm}^{-1}$) = 285 ($1.79 \times 10^5$), 338 ($1.28 \times 10^5$), 409 ($1.36 \times 10^5$), 503 ($1.34 \times 10^4$); 534 ($1.14 \times 10^4$), 745 ($1.44 \times 10^4$). MS(FAB): *m/z* (%) 1844 (85) $[M]^+$, 1809 (100) $[M - Cl]^+$, 1721 (21) $[Cr_6(\mu_6\text{-teptra})_4]^+$.

‡ *Crystal data* for $[Cr_7(\mu_7\text{-teptra})_4Cl_2]\cdot 6THF$, $Cr_7Cl_2N_{28}C_{104}H_{104}O_6$, M = 2277.05, monoclinic, space group $P2_1/c$, a = 35.2674(2), b = 15.0195(3), c = 19.6563(4) Å, β = 98.615(1)°, V = 10276.9(3) Å^3, D_c = 1.472 g cm^{-3}, Z = 4, μ = 0.834 mm^{-1}. The crystal was sealed in a capillary with the mother liquor since it cracked immediately after leaving the solution. Data were collected on a SMART CCD diffractometer with graphite-monochromated Mo-Kα radiation at 295 K. SADABS absorption correction (T_{min} 0.65 and T_{max} 0.83), a total of 38720 reflections were measured and 13181 unique reflections ($2\theta < 45°$, R_{int} = 0.0514) were used in the refinement. Full-matrix least-square refinement on F^2 (1070 variables) converged to $R(F)$ = 0.103 and $R(wF^2)$ = 0.265 ($I > 2\sigma(I)$) and $R(F)$ = 0.145 and $R(wF^2)$ = 0.297 (all data). The THF molecules were refined using 'similarity restraints' in SHELXTL. CCDC 182/1340. See http://www.rsc.org/suppdata/cc/1999/1667/ for crystallographic files in .cif format.

§ *Computational details*. The *ab initio* quantum mechanical calculations were performed with CASTEP 3.9 code.[16,17] Gradient-corrected density functional theory[18,19] (DFT) is used to calculate the electronic ground state of the system. We expand the valence electronic wavefunctions in plane waves up to a 290 eV cut-off and represent the nuclei and core electrons by ultrasoft pseudopotentials. Details of the computational study of the molecular metal-wire for Ni, Co, and Cr complex chains will be published in a separate paper.

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Communication 9/05001I