Linear Five-Centred Chromium Multiple Bonds Bridged by Four $tpda^{2-}$ Ligands [$tpda^{2-}$ = tripyridyldiamido dianion] – Synthesis and Structural Studies

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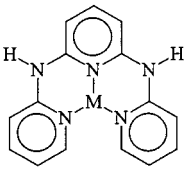
The linear pentanuclear chromium complexes $[Cr^{II}_5(\mu_5\text{-tpda})_4Cl_2]$ (**1**), $[Cr^{II}_5(\mu_5\text{-tpda})_4(NCS)_2]$ (**2**), $[Cr^{III}Cr^{II}_4(\mu_5\text{-tpda})_4F_2](BF_4)$ (**3**), and $[Cr^{III}Cr^{II}_4(\mu_5\text{-tpda})_4F(OTf)](OTf)$ (**4**), with four all-*syn* tri(α-pyridyl)diamido dianion ($tpda^{2-}$) ligands, have been prepared and structurally characterized. Compounds **1** and **2** possess a delocalized $Cr^{(II)}$–$Cr^{(II)}$–$Cr^{(II)}$–$Cr^{(II)}$–$Cr^{(II)}$ five-centred metal–metal bond of order 1.5. In both **1** and **2** two values for Cr^{II}–Cr^{II} bond lengths are found both; the outer ones connected with axial ligands are 2.284(1) and 2.285(2) Å, and the inner ones are 2.2405(8) and 2.246(1) Å, for **1** and **2,** respectively. When compound **1** reacts with 2 equiv. of $AgBF_4$ or Ag(OTf), a oxidation reaction takes place and one of the terminal chromium(II) ions is oxidized to produce $[Cr^{III}Cr^{II}_4(\mu_5\text{-tpda})_4F_2]BF_4$ (**3**) or $[Cr^{III}Cr^{II}_4(\mu_5\text{-tpda})_4F(OTf)](OTf)$ (**4**). Two short Cr–Cr distances [1.969(2) and 2.138(2) Å for **3**, 1.846(1) and 1.922(1) Å for **4**] are found, with the presence of two quadruple bonds among four adjacent Cr^{II} ions. The fifth Cr^{III} ion, which is separated from the neighboring Cr^{II} ion by 2.487(2) Å for **3** and 2.610(1) Å for **4**, is simply a square pyramidal unit with no metal–metal bonding interaction.

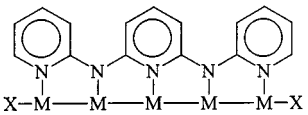
Introduction

The coordination chemistry of oligo-α-pyridylamino ligands[1] is an interesting topic, not only on the subject of the synthetic varieties of *all-anti* and *all-syn* complexes, but also as concerns the specific conformations and chemical properties of these complexes.[1–9]



All *anti*-form

M = Fe, Co, Ni, Cu, Zn



All *syn*-form

M = Co, Ni

Previous reports on the extension of di-nuclear metal complexes[10–12] to metal string complexes supported by oligo-α-pyridylamino ligands were focused on the tri-nuclear $[M_3(dpa)_4X_2]$ (M = Cr,[2] Co,[3,4] Ni,[5] Cu,[6] Rh,[7] Ru;[7] dpa^- = dipyridylamido anion), and pentanuclear $[M_5(tpda)_4X_2]$ (M = Co, Ni; $tpda^{2-}$ = tripyridyldiamido dianion) systems.[8,9] There is good correlation between the metal–metal distance obtained from structural analysis and the bond order predicted by qualitative M. O. calculations for the tri-nuclear metal string complexes $[M_3(dpa)_4X_2]$. The M–M distances are affected by the axial ligands, and the magnetic behavior of the M^{II}_5 unit in $[Ni_5(tpda)_4X_2]$ and $[Co_5(tpda)_4X_2]$ complexes has been studied in detail. In order to achieve a complete bonding scheme for five-centred metal–metal multiple bonds, the early transition metal string complexes $[Cr_5(tpda)_4Cl_2]$ (**1**), $[Cr_5(tpda)_4(NCS)_2]$ (**2**) have been synthesized. In addition, two oxidation products of $[Cr^{III}Cr^{II}_4(tpda)_4F_2](BF_4)$ (**3**) and $[Cr^{III}Cr^{II}_4(tpda)_4F(CF_3SO_3)](CF_3SO_3)$ (**4**) are reported. The structural analyses are described and discussed in detail (see Table 5).

Results and Discussions

The synthetic procedures for compounds **1**, **2**, **3**, and **4** are summarized in Scheme 1. Compound **1** can be synthesized under nitrogen using anhydrous $CrCl_2$ and the H_2tpda ligand as the starting materials, and naphthalene as the solvent. *t*BuOK was used as a base to deprotonate the H atom on the amido group of the H_2tpda ligand. Compound **2** was synthesized via the axial ligand replacement method with the NCS^- ligand instead of the Cl^- ligand in **1**. Compounds **3** and **4** are the products of the oxidation reactions of compound **1** with **2** equiv. of $AgBF_4$ and AgOTf, respectively. The presence of the F^- ion in **3** and **4** can be explained by considering the dissociation in THF of the BF_4^- and $SO_3CF_3^-$ anion, respectively.[2a]

For compounds **1** and **2**, each structure basically consists of a linear chain of five chromium atoms bridged by four $tpda^{2-}$ ligands. The steric crowding of the β-carbon hydrogen atoms on the pyridyl rings forces the $tpda^{2-}$ ligand to

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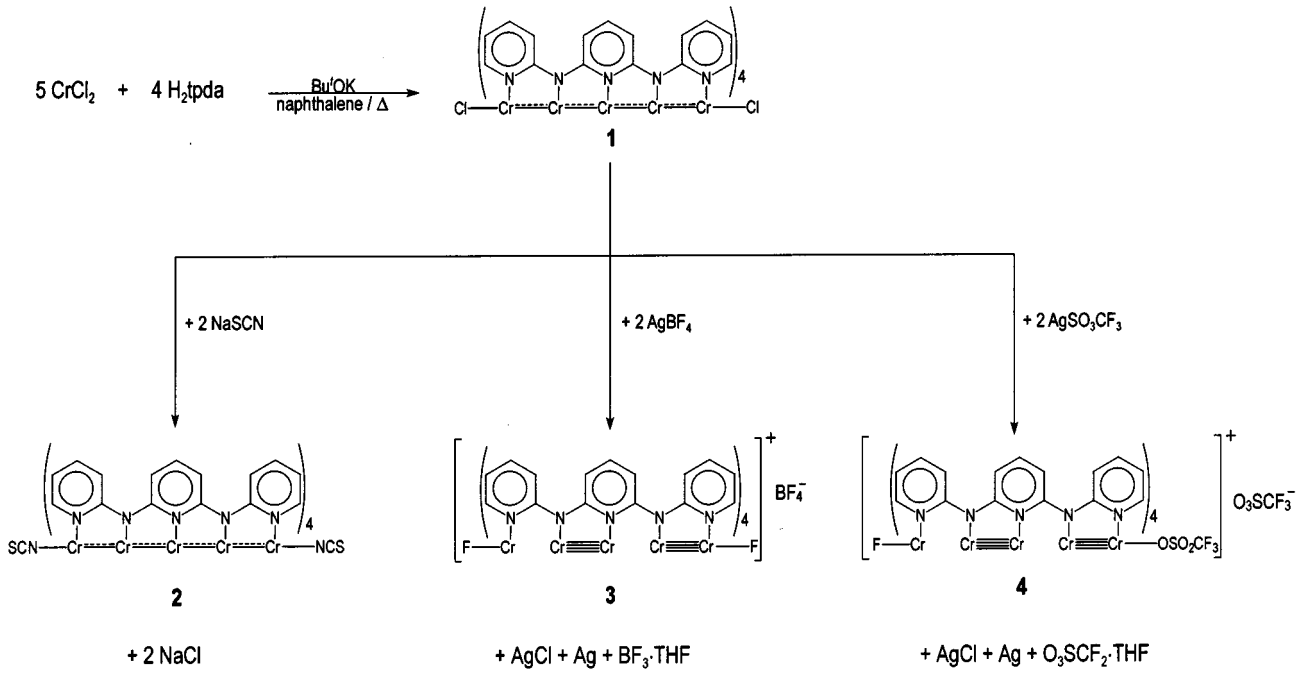


Scheme 1. Synthetic routes for compounds **1**, **2**, **3** and **4**

bind helically with the metal ion. Both are essentially isostructural with $[M_5(\mu_5\text{-tpda})_4X_2]$ (M^{II} = Co, X = Cl^-, NCS^-, N_3^-, CH_3CN and M^{II} = Ni, X = Cl^-, CN^-, NCS^-, N_3^-, CH_3CN).[8,9] Complex **1** crystallizes in the *C*2/*c* space group with the Cr(3) atom located at the crystallographic 2-fold axis. The molecular structure of **1** is shown in Figure 1. Complex **2** crystallizes in the *I*4/*m* space group with the Cr(3) atom located at the crystallographic 4/*m* symmetry, and the asymmetric unit contains only one eighth of the complex. The atomic positions of the complex **2** are averaged, because the right-turn and left-turn helical complexes are seriously disordered in the crystal. The eight nitrogen atoms from the amido group (occupancy 0.5) coordinated to chromium ions [Cr(2)], and the α-carbon atoms of the pyridyl groups have high anisotropic thermal parameters. One of the helical structures of **2** is shown in Figure 2. All of the Cr ions and two axial ligands for **1** and **2** are nearly co-linear. The five-centred Cr^{II} delocalized

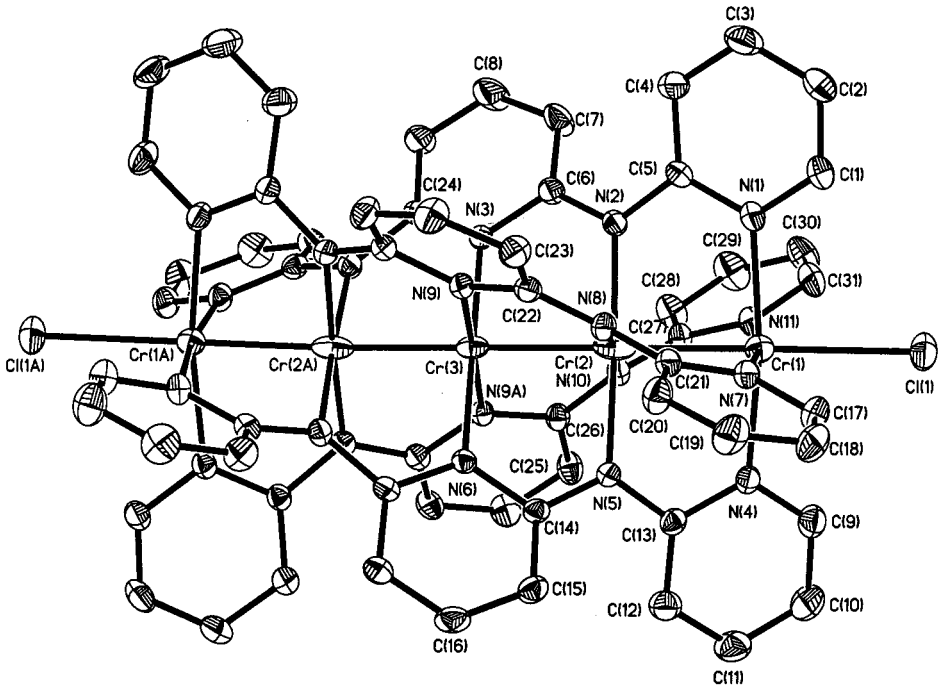


Figure 1. Crystal structure of $[Cr_5(\mu_5\text{-tpda})_4Cl_2]$ **1**. Atoms are shown as 20% vibrational thermal ellipsoids

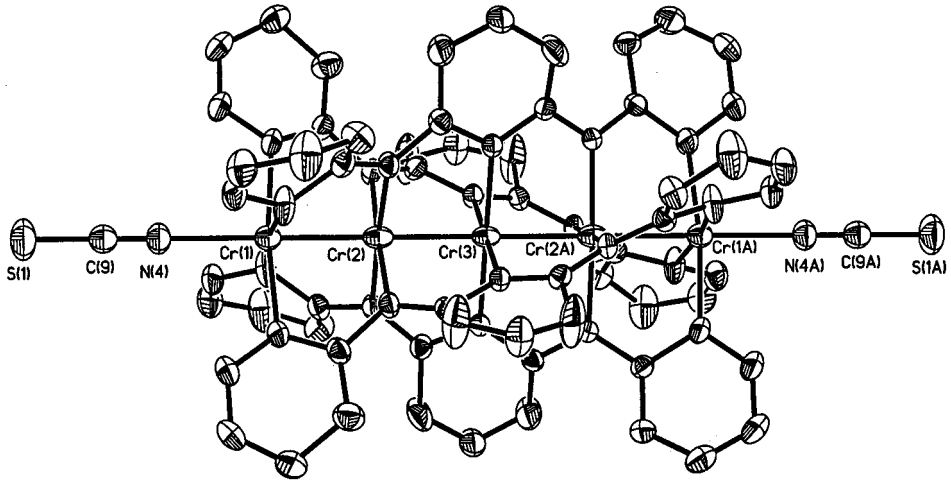


Figure 2. Crystal structure of $[Cr_5(\mu_5\text{-tpda})_4(NCS)_2]$ **2**. Atoms are shown as 20% vibrational thermal ellipsoids

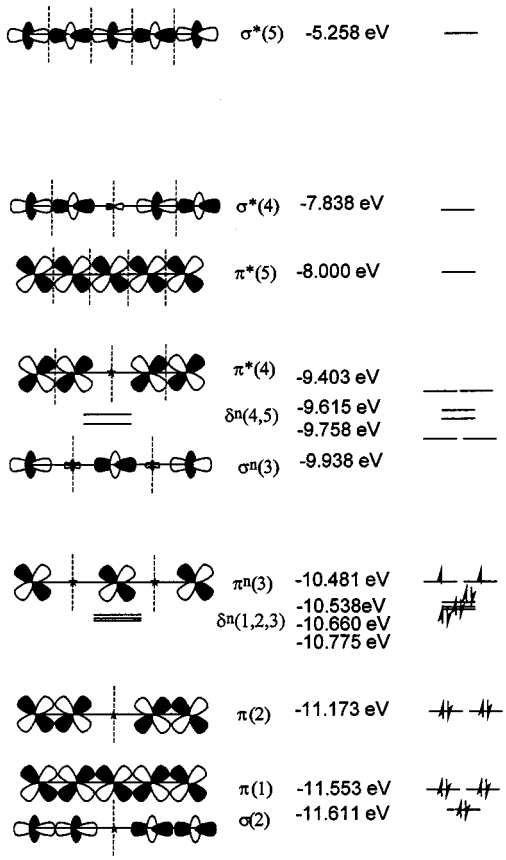


Figure 3. The qualitative molecular orbital diagram of linear five $Cr^{II}-Cr^{II}-Cr^{II}-Cr^{II}-Cr^{II}$ system for $[Cr_5(\mu_5\text{-tpda})_4Cl_2]$ **1**

multiple bond is the focus of this study. Two types of Cr−Cr bond lengths are found in **1** and **2**. The outer ones connected to the axial ligands are 2.284(1) and 2.285(2) Å, and the inner ones are 2.2405(8) and 2.246(1) Å, for **1** and **2** respectively. Both are shorter than those found in trinuclear complexes {2.365(1) Å in $[Cr_3(dpa)_4Cl_2]$[2]} and dichromium(II) tetracarboxylate complexes {2.29−2.53 Å in $[Cr_2(O_2CR)_4X_2]$[10]}, but much longer than those in super-short dichromium(II) complexes bridged by N,N-containing ligands {e.g. 1.843(2) Å in $[Cr_2(MeNC(Ph)NMe)_4]$,[19] 1.870(3) Å in $[Cr_2(Me\text{-pyridylamido})_4]$,[20] 1.858(1) Å in $[Cr_2(PhN_3Ph)_4]$[21]}. They are also comparable with the values of 2.28 Å and 2.23 Å found in the $[Co_5(\mu_5\text{-tpda})_4X_2]$ complex, which exhibits a double bond among the $Co^{II}{}_5$ unit.[8] The qualitative molecular orbital analysis of the Cr−Cr−Cr−Cr−Cr system, according to the atomic coordinates of **1** derived from the X-ray data, is shown in Figure 3. The bonding features among the five Cr atoms are similar to those of $[Co_5(tpda)_4(NCS)_2]$ and $[Ni_5(tpda)_4(NCS)_2]$, with a linear combination of the d_{z^2} orbitals of the five Cr atoms forming five σ orbitals, the (d_{xz}, d_{yz}) of the five Cr atoms forming ten π orbitals and the ($d_{x^2-y^2}$ or d_{xy}) orbitals of the five Cr atoms forming five nonbonding orbitals.[9] A total of twenty d electrons of Cr^{II} ions fill up to n_π degenerate orbitals leading to the configuration of $\sigma_1{}^2\sigma_2{}^2\pi_1{}^4\pi_2{}^4\delta_{n1}{}^2\delta_{n2}{}^2\ \delta_{n3}{}^2\pi_{n(dxz)}{}^1\pi_{n(dyz)}{}^1$. This configuration shows that two unpaired electrons are delocalized among the $Cr^{II}-Cr^{II}-Cr^{II}-Cr^{II}-Cr^{II}$ unit and that the bond order is 1.5 for each $Cr^{II}-Cr^{II}$ bond (the δ bonds are regarded as nonbonding orbitals for the helical conformation of the $tpda^{2-}$ ligand). The temperature independent magnetic susceptibility measurement of compound **1** is shown in Figure 4 with μ = 4.0 B.M, which is consistent with the M.O. prediction. This measured magnetic value is larger than the spin-only value (μ = 2.82 B.M), and this may be due to the orbital contribution of π-nonbonding orbitals. [The magnetic moment (μ_{eff}) is 3.6 B. M. for $[Cr_3(dpa)_4Cl_2]$ which is also larger than spin-only value (2.82).] If the M−M distances in the $[M_5(\mu_5\text{-tpda})_4X_2]$ system are compared with the distances for those systems having the axial ligands Cl^- and NCS^- for different metal centers (listed in Table 1) it can be seen that, i) in the Ni case, the outer M−M distance is obviously changed from 2.385(2) Å to 2.369(2) Å when the axial ligand is changed from Cl^- to NCS^- with the Ni−Ni bond order being zero,[8,9] ii) in compounds **1** and **2**, the outer Cr−Cr distance is nearly the same [2.284(1) and 2.285(2) Å] whether the axial ligand is Cl^- or NCS^-, with the Cr−Cr bond order being 1.5. These results indicate that, in the $[M_5(\mu_5$-

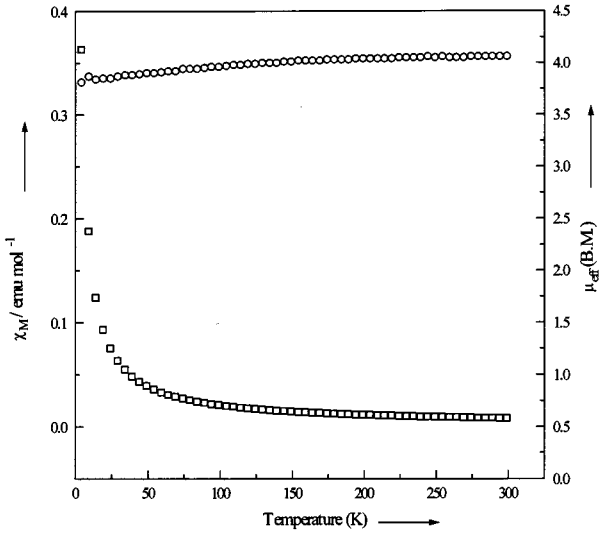
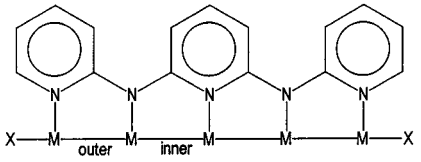


Figure 4. Magnetic measurement for compound **1**. □ indicates the observed magnetic susceptibility (χ_M) and ○ the observed effect magnetic moment (μ_{eff})

Table 1. Comparison of M−M bond length [Å] in $[M_5(tpda)_4X_2]$ complexes (M = Cr, Co, Ni; X = Cl, NCS)



Compound	Outer M−M distance	Inner M−M distance	Bond order
$[Cr_5(tpda)_4Cl_2]$ (**1**)	2.284(1)	2.2405(8)	1.5
$[Cr_5(tpda)_4(NCS)_2]$ (**2**)	2.285(2)	2.246(1)	1.5
$[Co_5(tpda)_4Cl_2]$[a]	2.281(4)	2.234(4)	0.5
$[Co_5(tpda)_4(NCS)_2]$[a]	2.277(2), 2.274(2)	2.232(2), 2.229(2)	0.5
$[Ni_5(tpda)_4Cl_2]$[a]	2.385(2)	2.305(1)	0.0
$[Ni_5(tpda)_4(NCS)_2]$[a]	2.367(2), 2.371(2)	2.289(2), 2.294(2)	0.0

[a] Ref.[8] and ref.[9]

tpda)$_4X_2$] system, the outer M−M distance could be affected or not affected by the axial ligands, and that the bonding strength of M−M bond is an important factor. When the M−M interaction is weak {in $[Ni_5(tpda)_4X_2]$ case}, the outer M−M distance is easily affected by the different axial ligands,[9] but the M−M distance is not influenced by the axial ligand when the metal−metal bond is strong {in the case of $[Cr_5(tpda)_4X_2]$}. However, such structural characterizations should be studied further by synthesizing more $[M_5(\mu_5\text{-tpda})_4X_2]$ complexes, with different metal center and axial ligands, and supporting the results by theoretical calculations.

Compounds **3** and **4** crystallize in $P2_1/n$ and $P2_1/c$ space groups, respectively, with both molecules residing in general positions. As for the compounds **1** and **2**, all of the Cr ions and two axial ligands are nearly co-linear and the five Cr centers are also helically wrapped by four $tpda^{2-}$ ligands. One of the terminal Cr^{II} atoms in these compounds is oxidized to Cr^{III}, connected with the axial ligand F^-, and the other terminal Cr^{II} ion is connected with the axial ligand F^- and $CF_3SO_3^-$ (**3** and **4**, respectively). The crystal structures of **3** and **4** are shown in Figures 5 and 6. Four unsym-

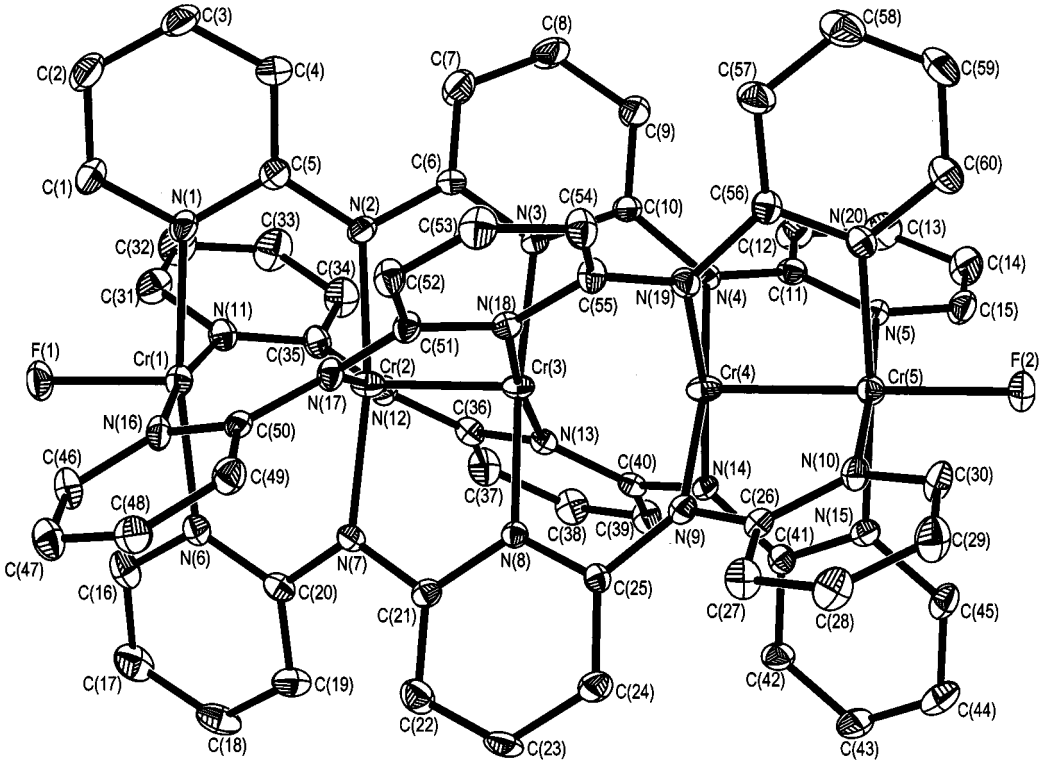


Figure 5. Crystal structure of $[Cr_5(\mu_5\text{-tpda})_4F_2]^+$ **3**. Atoms are shown as 20% vibrational thermal ellipsoids

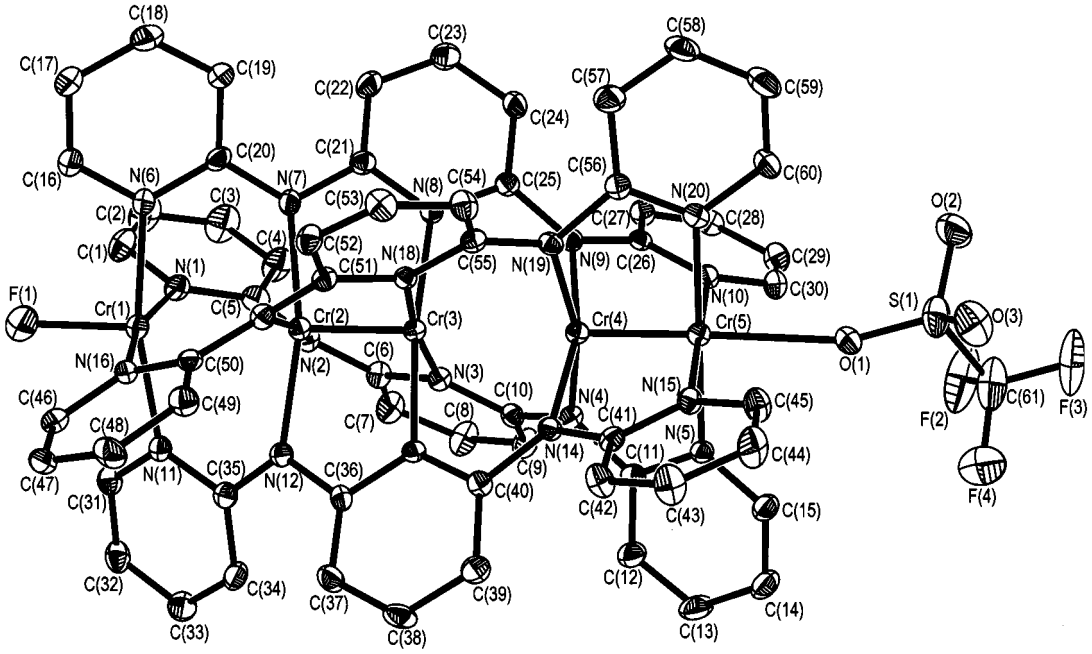
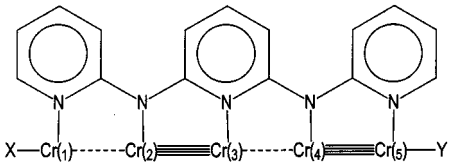


Figure 6. Crystal structure of $[Cr_5(\mu_5\text{-tpda})_4F(SO_3CF_3)]^+$ **4**. Atoms are shown as 20% vibrational thermal ellipsoids

metric Cr−Cr distances listed in Table 2 are observed in both compounds. Two short Cr−Cr distances [1.969(2) and 2.138(2) Å for **3**, 1.846(1) and 1.922(1) Å for **4**] are found along with the presence of two quadruple bonds among four adjacent Cr^{II} ions. The longer distances of 1.922(1), 1.969(2), and 2.138(2) Å are comparable with those found in the dichromium(II) complexes (1.937−2.354 Å) bridged by N,N- or N,O-containing ligands (e.g. formamidinate and 2-oxopyridinates),[10] and in the trichromium(II) complexes bridged by the dpa^- ligand {1.9952(8) Å in $[Cr_3(dpa)_4Cl(BF_4)]$}.[2] The shortest distance of 1.846(1) Å is comparable with those found in the super-short dichromium(II) complexes which are bridged by N,N-containing ligands {e.g. 1.843(2) Å in $[Cr_2(MeNC(Ph)NMe)_4]$,[19] 1.870(3) Å in $[Cr_2(Me\text{-}pyridylamido)_4]$,[20] 1.858(1) Å in $[Cr_2(PhN_3Ph)_4]$[21]}. Complexes **3** and **4** are so far the only cases found in the literature where two Cr−Cr quadruple bonds co-exist in a molecule. In the dichromium(II) complex an unusually wide range of Cr−Cr bond lengths (1.828−2.541 Å) are exhibited.[10] The presence or absence of axial ligand was found to be the determining factor over the Cr−Cr bond length when considering the same bridging ligands. In complexes **3** and **4**, the influence of the axial ligand on the Cr−Cr quadruple bond is also significant (Table 2). The intermediate Cr(2)−Cr(3) bond lengths [**3**, 1.969(2) Å; **4**, 1.846(1) Å] are obviously shorter than the terminal Cr(4)−Cr(5) bond lengths [**3**, 2.138(2) Å; **4**, 1.922(1) Å] with one axial ligand (**1**, F^-; **2**, $SO_3CF_3^-$) connected to Cr(5). Meanwhile, the terminal Cr(4)−Cr(5) distance is shortened from 2.138(2) Å to 1.922(1) Å when the axial ligand connected on Cr(5) is changed from a strong σ-donating F^- ligand to a weak $CF_3SO_3^-$ ligand. The distances [Cr(3)−Cr(4)] between the two quadruple bonds are long [2.419(2) and 2.596(1) Å for **3** and **4** respectively] which can be explained by the absence of a metal−metal bonding interaction. The fifth Cr^{III} [Cr(1)] ion connected with F^-, which is separated from the neighboring Cr^{II} ion by 2.487(2) and 2.610(1) Å (**3** and **4** respectively), is simply

Table 2. Selected bond lengths [Å] for $[Cr_5(tpda)_4F_2](BF_4)$ and $[Cr_5(tpda)_4F(OTf)](OTf)$



Compound	Cr(1)−X[a]	Cr(1)−Cr(2)	Cr(2)−Cr(3)	Cr(3)−Cr(4)	Cr(4)−Cr(5)	Cr(5)−Y[a]
$[Cr_5(tpda)_4F_2](BF_4)$	1.840(4)	2.487(2)	1.969(2)	2.419(2)	2.138(2)	1.931(4)
$[Cr_5(tpda)_4F(OTf)](OTf)$	1.863(5)	2.610(1)	1.846(1)	2.596(1)	1.922(1)	2.353(5)

[a] X = F^-, Y = F^- or $SO_3CF_3^-$.

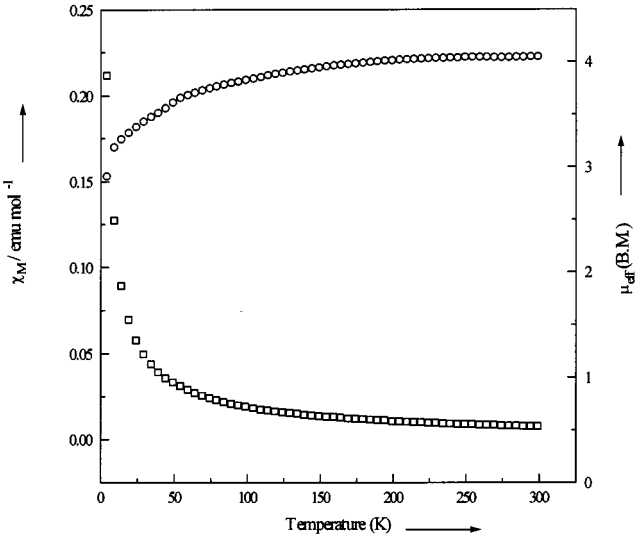
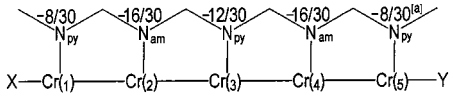


Figure 7. Magnetic measurement for compound **3**. □ indicates the observed magnetic susceptibility (χ_M) and ○ the observed effect magnetic moment (μ_{eff})

a square pyramidal $F-Cr^{III}-N_4$ unit without a metal−metal bonding interaction. The $Cr^{III}-F$ distances of 1.840(4) Å (**3**) and 1.863(5) Å (**4**) are comparable with those of 1.824(7) and 1.802(6) Å in the $[Cr_3(dpa)_4F(BF_4)](BF_4)$ complex.[2] The magnetic measurement of compound **3** is shown in Figure 7. The temperature independent magnetic moment of μ_B = 4.0 B.M. indicates that there are three unpaired electrons. These can be assigned to the $Cr^{3+}(d^3)$ species; the two quadruply bonded fragments would not be expected to contribute to the paramagnetism of the molecule.

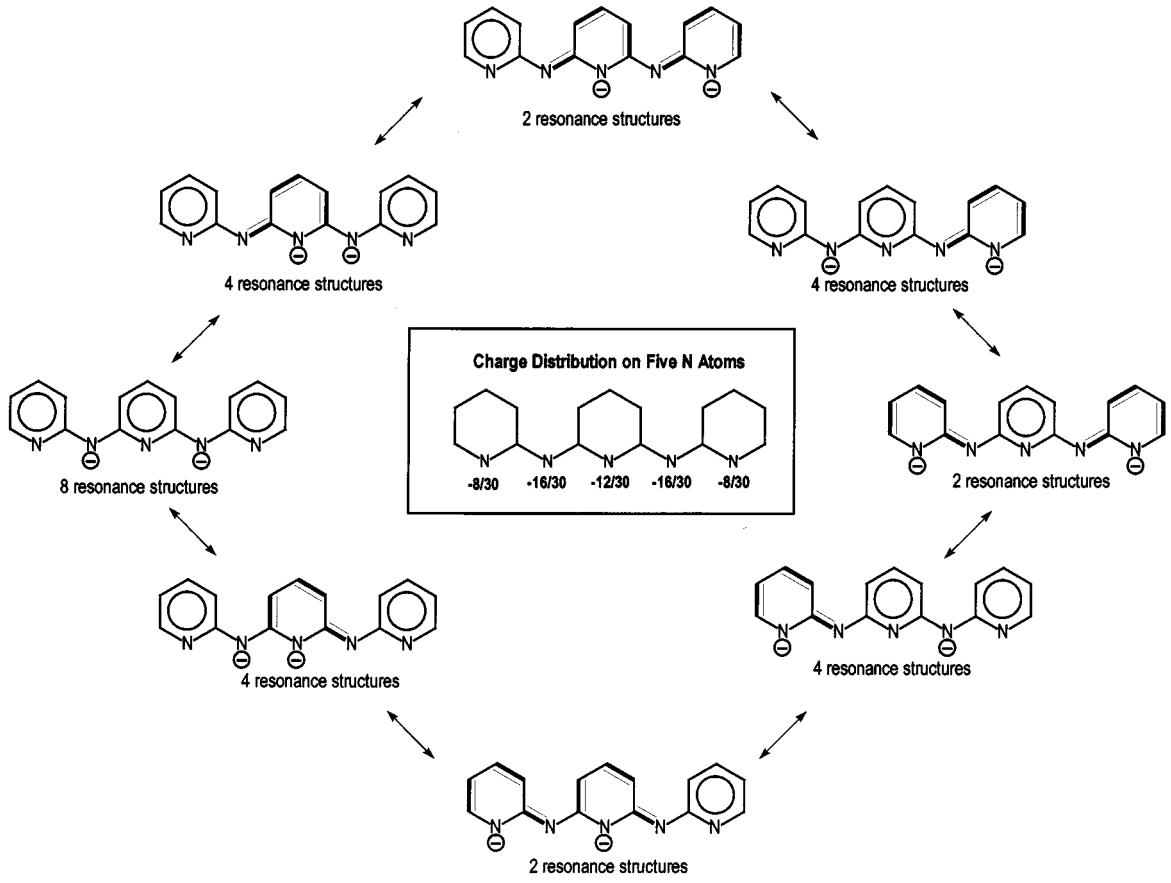
Table 3. The averaged Cr−N distances [Å] for compounds **1**, **2**, **3**, and **4**



Compound	Cr(1)−N	Cr(2)−N	Cr(3)−N	Cr(4)−N	Cr(5)−N
1	2.119(3)	2.021(3)	2.050(3)	2.021(3)	2.119(3)
2	2.086(3)	2.019(5)	2.055(3)	2.019(5)	2.086(3)
3	2.070(7)	2.004(6)	2.034(6)	1.992(6)	2.079(6)
4	2.081(6)	2.014(5)	2.053(5)	2.031(5)	2.095(5)

[a] Charges on the nitrogen atoms according to 30 resonance structures.

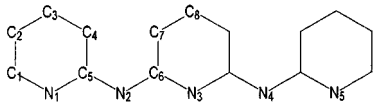
According to the structural analyses listed in Table 3, the Cr−N distances are in the order $Cr-N_{amido}$ [Cr(2)−N] < the central $Cr-N_{py}$ [Cr(3)−N] < the terminal $Cr-N_{py}$ [Cr(1)−N] for compounds **1**, **2**, **3**, and **4**. This result could be due to the charge distribution on the $tpda^{2-}$ ligand. The resonance structures of the $tpda^{2-}$ ligand is described in Scheme 2. The probability of two negative charges distri-



Scheme 2. Resonance structures of $tpda^{2-}$ ligand

buting on the terminal N_{py}, the N_{amido}, and the central N_{py} atoms are 8:30, 16:30, and 12:30, respectively. From this negative charge distribution, the bond interaction between Cr and N atoms should be in the sequence of the Cr−N_{amido} > the central Cr−N_{py} > the terminal Cr−N_{py} bond. Such a result will reflect directly on the Cr−N distance giving the order Cr−N_{amido} < the central Cr−N_{py} < the terminal Cr−N_{py}. The Cr−N distance predicted from the resonance structures of the $tpda^{2-}$ ligand is in a good agreement with those obtained from structural analyses. No matter what the oxidation state of terminal Cr ion is (2+ or 3+), or what the axial ligand is, the averaged terminal Cr−N_{py} distances are always the longest and the averaged Cr−N_{amido} bond lengths are the shortest. This result is also found in $[Ni_5(\mu_5\text{-tpda})_4X_2]$ and $[Co_5(\mu_5\text{-tpda})_4X_2]$ complexes.[8][9] Beside the Cr−N bond lengths, the π bond orders of C−N and C−C bonds obtained from the resonance structures shown in Scheme 2 are also consistent with those observed for the $tpda^{2-}$ ligands in compounds **1**, **3**, and **4** (Table 4).

Table 4. The averaged N−C and C−C distances [Å] for compounds **1**, **3**, and **4**



Bond type	π-Bond order[a]	1	3	4
N1−C1	11/30	1.356(5)	1.357(10)	1.359(9)
N1−C5	11/30	1.363(5)	1.357(10)	1.359(9)
N2−C5	8/30	1.373(4)	1.384(10)	1.373(8)
N2−C6	6/30	1.379(5)	1.387(10)	1.385(8)
N3−C6	9/30	1.366(4)	1.369(9)	1.361(8)
C1−C2	19/30	1.361(6)	1.370(13)	1.356(11)
C2−C3	11/30	1.385(7)	1.383(14)	1.378(12)
C3−C4	19/30	1.374(6)	1.372(13)	1.363(11)
C4−C5	11/30	1.404(5)	1.401(12)	1.406(10)
C6−C7	15/30	1.396(5)	1.386(11)	1.394(9)
C7−C8	15/30	1.379(6)	1.374(13)	1.373(10)

[a] π bond order was calculated according to 30 resonance structures.

Conclusions

In summary, a five-centred multiple bonding scheme has been successfully demonstrated for both late transition metal ions (M = Ni, Co)[8][9] and an early transition metal ion (M = Cr) (compounds **1** and **2**). According to the structural analyses two types of Cr−Cr−Cr−Cr−Cr unit are observed in the $[Cr_5(tpda)_4]$ fragments. One is a delocalized Cr^{II}_5 system (compounds **1** and **2**) with four nearly equal Cr−Cr distances, the other is a localized $[C^{III}\cdots C^{II}_4]$ system (compounds **3** and **4**) with four asymmetric Cr−Cr distances. Two short quadruple bonds are found. The magnetic behaviors of these two systems are in accordance with the structural analysis and qualitative theoretical predictions.

Experimental Section

Spectroscopic Measurements: IR: Nicolet Fourier-Transform IR, MAGNA-IR 500 spectrometer in the range of 500−4000 cm^{-1}, KBr discs. − UV/Vis: Hewlett Packard (HP) 8453 spectrophotometer. − Temperature dependent magnetic susceptibility: SQUID system with 10,000 Gauss external magnetic field. − Molar magnetic susceptibility: recorded every 5 K in the range of 5−300 K. The H_2tpda ligand was synthesized according to the literature.[1,8a]

Preparation and Characterization of $[Cr_5(\mu_5\text{-tpda})_4Cl_2]$ (1): Anhydrous $CrCl_2$ (0.369 g, 3 mmol), H_2tpda (0.526 g, 2 mmol) and potassium *tert*-butoxide (0.44 g, 4 mmol) were placed in an Erlenmeyer flask, and naphthalene (10 g) added under nitrogen in the glove box. The mixture was refluxed under nitrogen and heated to 180−200°C for 6 h. After the mixture had cooled, *n*-hexane was added to wash out the naphthalene. The remaining solid was extracted with CH_2Cl_2 and re-crystallized from a $CHCl_3$/ether solution. Deep brown crystals were obtained (yield: 30%). − IR (KBr): $\tilde{\nu}$ = 1602 cm^{-1}, 1578, 1547 (C=C). − MS (FAB); *m/z* (%): 1376 (7) $[M]^+$. − UV/Vis (CH_2Cl_2): λ_{max} (ε) = 283 nm ($7.56\cdot10^4$ M^{-1} cm^{-1}), 326 ($5.58\cdot10^4$ M^{-1} cm^{-1}), 390 ($4.20\cdot10^4$ M^{-1} cm^{-1}), 710 ($8.15\cdot10^3$ M^{-1} cm^{-1}). − $\mathbf{1}\cdot CHCl_3\cdot O(C_2H_5)_2$: calcd. C 49.74, H 3.53, N, 17.85; found C 49.66, H 3.66, N 17.84.

Preparation and Characterization of $[Cr_5(\mu_5\text{-tpda})_4(NCS)_2]$ (2): $[Cr_5(\mu_5\text{-tpda})_4(Cl)_2]$ (0.05 g, 0.036 mmol) was placed in an Erlenmeyer flask in THF (40 mL). The brown solution was stirred for 5 min and filtered off. NaSCN (0.06 g, 0.72 mmol) was added to the filtrate and stirring continued for 2 d. Then water (50 mL) was added to dissolve unchanged NaSCN. The solution was extracted with CH_2Cl_2 (3× 60 mL) and Na_2SO_4 added to remove water. The remaining solvent was removed by rotary evaporator and recrystallized from a CH_2Cl_2/ether solution. Deep brown crystals were obtained (yield: 30%). − IR (KBr): $\tilde{\nu}$ = 1604 cm^{-1}, 1577, 1546 (C=C), 2033 (C≡N). − MS (FAB); *m/z* (%): 1421 (1) $[M]^+$. − UV/Vis (CH_2Cl_2): λ_{max} (ε) = 288 nm ($1.19\cdot10^5$ M^{-1} cm^{-1}), 332 ($7.84\cdot10^4$ M^{-1} cm^{-1}), 392 ($7.52\cdot10^4$ M^{-1} cm^{-1}), 721 ($9.02\cdot10^3$ M^{-1} cm^{-1}). − $\mathbf{2}\cdot CH_2Cl_2\cdot 6\,H_2O$: calcd. C 46.86, H 3.62, N 19.08; found C 47.70, H 3.71, N 19.08.

Preparation and Characterization of $[Cr^{III}Cr^{II}_4(\mu_5\text{-tpda})_4F_2]BF_4$ (3): $[Cr_5(\mu_5\text{-tpda})_4(Cl)_2]$ (0.1 g, 0.072 mmol) and silver tetrafluoroborate ($AgBF_4$, 0.028 g, 0.14 mmol) were placed in a 50 mL flask containing THF (20 mL). After 1 h of stirring, the solution was filtered to remove AgCl and Ag solid, leaving a clear dark brown solution. The solution was concentrated and a brown powder obtained. The powder was recrystallized from CH_3CN/ether solution. Deep brown crystals were obtained (yield: 35%). − IR (KBr): $\tilde{\nu}$ = 1606 cm^{-1}, 1581, 1547 (C=C). − UV/Vis (CH_2Cl_2): λ_{max} (ε) = 290 nm ($9.03\cdot10^4$ M^{-1} cm^{-1}), 396 ($6.00\cdot10^4$ M^{-1} cm^{-1}), 716 ($5.38\cdot10^3$ M^{-1} cm^{-1}). − MS (FAB): *m/z* (%): 1343 (60) $[M]^+$. − $\mathbf{3}\cdot 2\,CH_2Cl_2\cdot 3\,H_2O$: calcd. C 43.07, H 3.32, N 15.95; found: C 43.27, H 3.23, N 15.95.

Preparation and Characterization of $[Cr^{III}Cr^{II}_4(\mu_5\text{-tpda})_4F(CF_3SO_3)](CF_3SO_3)$ (4): $[Cr_5(\mu_5\text{-tpda})_4(Cl)_2]$ (0.05 g, 0.036 mmol) and $AgCF_3SO_3$ (0.019 g, 0.072 mmol) were placed in 50 mL flask containing THF (20 mL). After 1 h of stirring, the solution was filtered to remove AgCl and Ag solid, leaving a clear dark brown solution. The solution was concentrated and a brown powder obtained. The powder was recrystallized from $CHCl_3$/ether solution. Deep brown crystals were obtained (yield: 30%). − IR (KBr): $\tilde{\nu}$ = 1604 cm^{-1}, 1581, 1547 (C=C). − MS (FAB); *m/z* (%): 1454 (21) $[M]^+$.

Crystal Structure Determinations: Data collection was carried out on a Siemens SMART diffractometer with a CCD detector with

Table 5. Crystal data for compounds **1**, **2**, **3**, and **4**

Compound	**1**·2 $O(C_2H_5)_2$·4 $CHCl_3$	**2**	**3**·1.5 CH_3CN·2 H_2O·THF	**4**·SO_3CF_3·2 $CHCl_3$
Formula	$C_{72}H_{68}Cl_{14}Cr_5N_{20}O_2$	$C_{62}H_{44}Cr_5N_{20}S_2$	$C_{67}H_{52.5}BCr_5N_{21.5}O_3$	$C_{64}H_{46}Cl_6Cr_5F_7N_{20}O_6S_2$
Molecular weight	2001.76	1417.28	1591.61	1861.03
Crystal system	Monoclinic	Tetragonal	Monoclinic	Monoclinic
Space group	*C*2/*c*	*I*4/*m*	$P2_1/n$	$P2_1/c$
Color of crystal	Brown	Brown	Brown	Brown
a [Å]	28.5053(3)	10.8142(2)	16.7514(1)	13.7588(1)
b [Å]	14.0725(2)		17.5659(2)	17.8995(1)
c [Å]	25.1033(1)	26.1892(7)	23.1206(3)	31.0298(2)
β [°]	122.87		100.882(1)	93.620(1)
V [Å^3]	8457.9(2)	3062.8(1)	6681.0(1)	7626.64(9)
Z	4	2	4	4
R_F, $R_w(F^2)$ (all data)	0.1004, 0.1669	0.0696, 0.1729	0.1448, 0.2462	0.1361, 0.2092
R_F, $R_w(F^2)$ [$I > 2\sigma(I)$]	0.0672, 0.1419	0.0543, 0.1575	0.0899, 0.2163	0.0758, 0.1750
GOF	1.114	1.067	1.078	1.033

[a] $R_F = \Sigma|F_o - F_c|/\Sigma|F_o|$; $R_w(F^2) = [\Sigma w|F_o^2 - F_c^2|^2/\Sigma w(F_o^4)]^{1/2}$.

Mo radiation (λ = 0.71073 Å) at room temp. A preliminary orientation matrix and unit cell parameters were determined from 3 runs of 15 frames each, each frame correspond to a 0.3° scan in 20 s, following by spot integration and least-squares refinement. For each structure, data were measured using ω scans of 0.3° per frame for 20 s until a complete hemisphere had been collected. Cell parameters were retrived using SMART[13] software and refined with SAINT on all observed reflections. Data reduction was performed with the SAINT[14] software and corrected for Lorentz and polarization effects. Absorption corrections were applied with the program SADABS.[15] The detail crystal data of compounds **1**, **2**, **3**, and **4** are listed in Table 5.

Crystal Data of 1·2 $O(C_2H_5)_2$·4 $CHCl_3$: A brown crystal of approximation dimensions 0.5 × 0.4 × 0.3 mm was mounted on a glass capillary. A total of 27034 reflections in 1650 frames were collected with a final resolution of 0.75 Å. Sadabs absorption correction (T_{min} 0.59 and T_{max} 0.72), 9601 unique reflections (2θ < 55°, R_{int} = 0.058) were used in the refinement. Full-matrix least-square refinement on F^2 converged to R_F = 0.1004 (all data), 0.0672 [$I > 2\sigma(I)$] and $R_w(F^2)$ = 0.1669 (all data), 0.1419 [$I > 2\sigma(I)$].

Crystal Data of 2: A brown crystal of approximation dimensions 0.4 × 0.2 × 0.2 mm was mounted on a glass capillary. A total of 10471 reflections in 1680 frames were collected with a final resolution of 0.75 Å. Sadabs absorption correction (T_{min} 0.58 and T_{max} 0.80), 1614 unique reflections (2θ < 52.7°, R_{int} = 0.040) were used in the refinement. Full-matrix least-square refinement on F^2 converged to R_F = 0.0696 (all data), 0.0543 [$I > 2\sigma(I)$] and $R_w(F^2)$ = 0.1729 (all data), 0.1575 [$I > 2\sigma(I)$].

Crystal Data of 3·1.5 CH_3CN·2 H_2O·THF: A brown crystal of approximation dimensions 0.4 × 0.2 × 0.1 mm was mounted on a glass capillary. A total of 42784 reflections in 1666 frames were collected with a final resolution of 0.75 Å. Sadabs absorption correction (T_{min} 0.51 and T_{max} 0.71), 11400 unique reflections (2θ < 50°, R_{int} = 0.106) were used in the refinement. Full-matrix least-square refinement on F^2 converged to R_F = 0.1448 (all data), 0.0899 [$I > 2\sigma(I)$] and $R_w(F^2)$ = 0.2462 (all data), 0.2163 [$I > 2\sigma(I)$].

Crystal Data of 4·2 $CHCl_3$: A brown crystal of approximation dimensions 0.4 × 0.1 × 0.04 mm was mounted on a glass capillary. A total of 41618 reflections in 1666 frames were collected with a final resolution of 0.75 Å. Sadabs absorption correction (T_{min} 0.65 and T_{max} 0.86), 13463 unique reflections (2θ < 50°, R_{int} = 0.089) were used in the refinement. Full-matrix least-square refinement on F^2 converged to R_F = 0.1361 (all data), 0.0758 [$I > 2\sigma(I)$] and $R_w(F^2)$ = 0.2090 (all data), 0.1750 [$I > 2\sigma(I)$].

The structures of **1**, **2**, **3**, and **4** are solved by direct methods with the SHELX-93[15] program and refined by full-matrix least-squares methods on F^2 with SHELXTL-PC V 5.03.[16] All nonhydrogen atomic positions were located in difference Fourier maps and refined anisotropically. Hydrogen atoms were placed in their geometrically generated positions.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-113116 {$[Cr_5(tpda)_4Cl_2]$}, -113117 {$[Cr_5(tpda)_4(NCS)_2]$}, -113118 {$[Cr_5(tpda)_4F_2](BF_4)$}, -113119 {$[Cr_5(tpda)_4(F)(OTf)](OTf)$}. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Molecular Orbital Calculation: A simple molecular orbital calculation namely Extended Hückel Molecular Orbital method (EHMO) was chosen to apply on such a large system for the purpose of investigating the bonding features of five-centred Cr−Cr−Cr−Cr−Cr bond qualitatively. The EHMO is performed using the program ICON.[17] The atomic coordinates are derived directly from the X-ray diffraction data of $[Cr_5(tpda)_4Cl_2]$ (**1**). The basis functions of Cl, C, N, and H are taken from the default values of the program. The basis functions for Cr is as follows:[18] $H_{ii}(4s) = -8.66$ eV, $\zeta = 1.70$; $H_{ii}(4p) = -5.24$ eV, $\zeta = 1.70$; $H_{ii}(3d) = -11.22$ eV, $\zeta_1 = 4.95$, $C_1 = 0.488$, $\zeta_2 = 1.60$, $C_2 = 0.721$.

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