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Alkylpyridine Complexes of Tungsten(II) and Chromium(II). First Rotational Isomers of $W_2X_4L_4$ Molecules with D_{2h} and D_2 Symmetries

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Introduction

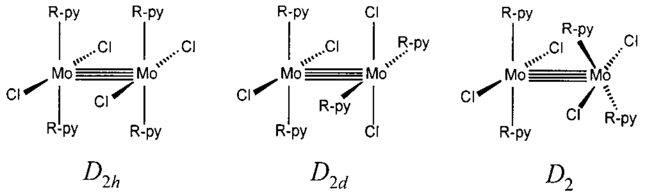
The quadruply bonded dimolybdenum complexes with alkyl-substituted pyridines of the formula $Mo_2Cl_4(R\text{-}py)_4$ have been recently found[1] to exist in several rotameric conformations. Three rotamers have been recognized in the solid state: two eclipsed forms with D_{2h} and D_{2d} virtual symmetries and a range of partially staggered ones, D_2 (Chart 1). The spectroscopic study[2] of these molecules has shown that only two of them, D_{2d} and D_2, are present in solution and that their relative stabilities vary greatly with solvent and temperature. The major conclusion from the research is that the solvation and packing effects profoundly influence the dependence of energy on the angle of internal rotation.

For quadruply bonded ditungsten compounds of the type $W_2X_4L_4$ (X = Cl, CCMe; L = PR_3,[3] NH_2R[4]) the only isomer known was D_{2d}, which is considered to be favorable for steric reasons. Thus, we decided to check on the existence of other rotational conformers for W_2^{4+} complexes with alkyl-substituted pyridines. The synthetic technique was that employed[4] for the isolation of analogous ditungsten complexes with primary amine ligands. We have also tried to extend our efforts to the other group VIB element, chromium, for which no multiply bonded molecules with monodentate ligands are yet known.

Experimental Section

General Procedures. All manipulations were carried out under an atmosphere of dry oxygen-free argon or nitrogen with standard Schlenk techniques. Solvents were dried and deoxygenated by refluxing over suitable reagents before use. Compounds 4-*tert*-butylpyridine, 3-*n*-butylpyridine, and $NaBEt_3H$ were provided by Aldrich Inc. Deuterated benzene was obtained from Cambridge Isotope Laboratories, Inc. and used as received. WCl_4[5] and $CrCl_3(THF)_3$[6] were synthesized according to published procedures. Potassium graphite, KC_8,[7] was prepared by heating the two components at 180−200 °C under an N_2 atmosphere for about 2 h.

Chart 1



Synthesis of $W_2Cl_4(4\text{-}Bu^t\text{-}py)_4$ (1). Tetrahydrofuran (50 mL at −70 °C) was transferred by cannula to a flask that contained a mixture of 0.50 g (1.54 mmol) of WCl_4 and 0.50 g (3.70 mmol) of KC_8 at −78 °C. The system was slowly warmed for 4 h to −15 °C. When the color of the solution changed to blue, 0.7 mL (4.7 mmol) of 4-*tert*-butylpyridine was added. The mixture was left overnight to reach room temperature. All volatile components were then removed under vacuum, and the resulting dark-green solid was extracted with 15 mL of hexanes. The yield in different experiments did not exceed 30% (based on the amount of starting WCl_4). The reduction of W^{IV} to W^{II} can also be carried out by using $NaBEt_3H$ as a reducing agent. In a typical reaction, 0.50 g of WCl_4 were reduced by 3.3 mL of a 1 M solution of $NaBEt_3H$ in THF. However, the yield in this case was considerably lower (about 10% based on WCl_4). Anal. Calcd for $W_2Cl_4N_4C_{36}H_{52}$: C, 41.17; H, 4.99; N, 5.33. Found: C, 41.47; H, 5.18; N, 5.15. IR (Nujol, cm^{-1}): 1616 (m), 1596 (w), 1538 (w), 1497 (m), 1422 (m), 1261 (m), 1227 (m), 1200 (w), 1127 (sh), 1094 (s), 1064 (s), 1021 (s), 868 (w), 839 (m), 832 (m), 818 (sh), 801 (vs), 752 (w), 721 (m), 668 (m), 576 (m), 572 (m). ^1H NMR data (C_6D_6, 22 °C): δ 9.81 (m, 8H), 6.89 (m, 8H), 0.91 (s, 36H). UV−vis [λ_{max}, nm (Nujol)]: 690.

Dark-violet, block-shaped crystals of **1a** were obtained by keeping a purple diethyl ether solution of the compound at −30 °C for 1 week. Dark-brown needles of **1a**·C_7H_8 were grown from a saturated toluene solution at −30 °C in a few days. Dark, almost black, needles of **1a**·C_6H_6 were formed in 2 days by layering a concentrated benzene solution with hexanes at room temperature. Small dark-violet blocks of **1b**·4-Bu^t-py were deposited from hexane solution of the compound in the presence of free ligand. Dark blocks of **1b**·C_6H_{14} were immediately crystallized when a concentrated toluene solution was layered with hexanes at room temperature. Dark-green crystals of **1c**·$(CH_3)_2CO$ were quickly isolated from saturated acetone solution that was placed in a freezer (−30 °C).

Synthesis of $W_2Cl_4(3\text{-}Bu^n\text{-}py)_4$ (2). This compound was prepared following the same procedure with KC_8 as described for $W_2Cl_4(4\text{-}Bu^t\text{-}py)_4$ (**1**) using 0.8 mL (5.28 mmol) of 3-*n*-butylpyridine and 40 mL of THF. Yield: 0.090 g (11% based on the amount of WCl_4). Anal. Calcd for $W_2Cl_4N_4C_{36}H_{52}$: C, 41.17; H, 4.99; N, 5.33. Found: C, 41.58; H, 5.31; N, 5.08. ^1H NMR data (C_6D_6, 22 °C): δ 9.74 (s, 4H), 9.67 (t, 4H), 6.74 (d, 4H), 6.73 (d, 4H), 2.30 (t, 8H), 1.43 (m, 8H), 1.20 (m, 8H), 0.82(t, 12H).

Dark-green crystals of **2** were obtained by layering hexanes over benzene or toluene solutions or by keeping of a concentrated solution of the compound in acetone at −30 °C.

Synthesis of $Cr_3Cl_6(4\text{-}Bu^t\text{-}py)_6$ (3). To the blue solution of 0.23 g (0.61 mmol) of $CrCl_3(THF)_3$ in 30 mL of toluene at −70 °C 0.7 mL of 1 M toluene solution of $NaBEt_3H$ (0.70 mmol) was added dropwise. The system was slowly warmed to −30 °C, and 0.4 mL (3.70 mmol) of 4-Bu^t-py was added to the solution, which changed its color to green. The mixture was allowed to reach room temperature and was vigorously stirred for another 2 h, resulting in a fluorescent, greenish-yellow solution. All volatile components were removed under reduced pressure, and the residue was washed with diethyl ether (15 mL). The product appeared as a mixture with NaCl and was separated from the latter by several extractions with benzene. Yield: 0.10 g, 41%. IR (Nujol, cm^{-1}):

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10.1021/ic000555v CCC: $19.00

Table 1. Crystallographic Data for Different Rotational Isomers of $W_2Cl_4(4\text{-}Bu^t\text{-}py)_4$ (**1**) and $Cr_3Cl_6(4\text{-}Bu^t\text{-}py)_6$ (**3**)

	1a	**1a**·C_7H_8	**1b**·4-Bu^t-py	**1c**·$(CH_3)_2CO$	**3**
formula	$W_2Cl_4N_4C_{36}H_{52}$	$W_2Cl_4N_4C_{43}H_{60}$	$W_2Cl_4N_5C_{45}H_{65}$	$W_2Cl_4N_4OC_{39}H_{58}$	$Cr_3Cl_6N_6C_{54}H_{78}$
fw	1050.32	1142.45	1185.52	1108.39	1179.92
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$C2/c$	$P\bar{1}$
a, Å	8.455(2)	8.556(1)	15.264(3)	32.970(5)	7.884(2)
b, Å	10.004(1)	11.809(2)	15.155(3)	10.227(1)	13.966(4)
c, Å	13.412(2)	12.696(3)	22.186(4)	28.962(2)	14.180(5)
α, deg	68.53(2)	107.88(3)			77.765(8)
β, deg	72.74(1)	105.68(1)	105.01(2)	103.21(1)	86.868(9)
γ, deg	85.90(1)	99.16(2)			73.96(2)
V, Å^3	1007.3(3)	1133.6(4)	4957(2)	9507(2)	1466.5(8)
Z	1	1	4	8	1
ρ_{calcd}, g cm^{-3}	1.731	1.674	1.589	1.549	1.336
μ, mm^{-1}	6.000	5.339	4.887	5.092	0.859
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
temp, °C	−60	−60	−60	−60	−100
R1,^{a} wR2^b [$I > 2\sigma(I)$]	0.037, 0.093	0.037, 0.085	0.090, 0.194	0.046, 0.114	0.056, 0.121
R1,^{a} wR2^b (all data)	0.038, 0.095	0.042, 0.089	0.135, 0.233	0.053, 0.124	0.078, 0.139

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^2$.

Table 2. Selected Bond Distances (Å), Angles (deg), and Torsion Angles (deg) for $W_2Cl_4(4\text{-}Bu^t\text{-}py)_4$ (**1a**−**1c**)

	1a	**1a**·C_7H_8	**1b**·4-Bu^t-py		**1c**·$(CH_3)_2CO$	
W−W	2.2631(6)	2.2602(8)	2.259(1)		2.2605(6)	
W−N	2.193(6)	2.202(7)	2.18(2)	2.15(2)	2.196(9)	2.176(9)
	2.199(6)	2.207(7)	2.21(2)	2.16(2)	2.185(9)	2.193(9)
W−Cl	2.410(2)	2.410(2)	2.403(6)	2.412(7)	2.397(3)	2.401(3)
	2.393(2)	2.394(2)	2.404(6)	2.406(7)	2.383(3)	2.392(3)
N−W−N	156.6(2)	157.7(3)	155.9(7)	159.1(8)	157.4(3)	158.6(3)
Cl−W−Cl	148.46(6)	150.47(8)	151.0(2)	149.3(2)	150.3(1)	151.0(1)
N−W−Cl	82.7(2)	84.9(2)	83.6(5)	86.1(6)	86.4(2)	83.8(3)
	88.8(2)	89.7(2)	87.9(5)	89.1(5)	89.8(2)	89.2(2)
	85.0(2)	84.3(2)	86.5(5)	83.6(5)	82.2(2)	85.7(3)
	91.3(2)	90.2(2)	90.0(5)	90.0(6)	90.2(2)	90.7(3)
W−W−N	102.4(2)	101.1(2)	103.5(5)	100.9(5)	101.0(2)	102.5(2)
	100.4(2)	100.7(2)	100.6(5)	99.9(6)	101.4(2)	98.9(2)
W−W−Cl	109.01(5)	107.61(6)	104.1(2)	105.8(2)	105.73(7)	104.56(7)
	102.47(5)	101.92(6)	104.8(2)	104.8(2)	103.95(7)	104.39(8)
N−W−W−N$_{av}$	0.0(2)	0.0(3)	10.3(7)		19.8(3)	
Cl−W−W−Cl$_{av}$	0.00(7)	0.00(8)	5.8(2)		14.2(1)	

1618 (vs), 1557 (sh), 1544 (m), 1502 (m), 1421 (s), 1398 (w), 1370 (sh), 1261 (vs), 1230 (m), 1203 (w), 1098 (vs), 1071 (vs), 1031 (vs), 1023 (vs), 862 (w), 845 (m), 827 (vs), 804 (vs), 730 (m), 668 (w), 575 (vs), 550 (m), 467 (w).

Light-green needle-shaped crystals of **3** were obtained by layering a benzene solution of the compound with hexanes at room temperature.

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer 16PC FTIR spectrometer using suspensions of the compounds in Nujol. ^{1}H NMR spectra were obtained on a Varian XL-200E spectrometer; the internal standard resonance was C_6D_5H, 7.15 ppm. Electronic spectral data were acquired on a Cary-17D UV−vis spectrophotometer. Elemental analyses were done by Canadian Microanalytical Services, Ltd.

X-ray Crystallographic Procedures. Single crystals of compounds **1**−**3** were obtained as described above. The X-ray diffraction experiments were carried out on a Nonius FAST diffractometer with an area detector using Mo Kα radiation. In each case, a crystal of suitable quality was affixed to the end of a quartz fiber with grease in a cold nitrogen stream (−60 °C; −100 °C for **3**). Unit cell determination and data collection followed routine procedures and practices of this laboratory.[8] Oscillation photographs about principal axes were taken to confirm the Laue class and axial lengths. All data were corrected for Lorentz and polarization effects. The intensities for **1a**, **1b**·4-Bu^t-py, and **1c**·$(CH_3)_2CO$ were also corrected for absorption anisotropy effects using a local adaptation of the program SORTAV.[9] The structures were solved and refined using the SHELXTL direct methods[10] and the SHELXL-93 programs[11] on a DEC Alpha running VMS. In each model the hydrogen atoms were included in the structure factor calculations at idealized positions. Relevant crystallographic data for complexes **1** and **3** are summarized in Table 1.

Orientation disorder was encountered in several cases. Many Bu^t groups were disordered over two or three rotational orientations. A severe disorder of 4-Bu^t-py ligands and interstitial solvent molecules was found in the crystal structures of **1b**·C_6H_{14} and **1b**·4-Bu^t-py, but the core structure (similar for both crystals) was well refined and we are using here the data for 4-*tert*-butylpyridine solvate for comparison purposes. All crystals of **2** appeared to be racemic twins, and we do not report on their refinement details.

Results and Discussion

Synthesis and Crystal Growth. The dimolybdenum(II,II) chloride/alkylpyridine complexes have been obtained in our previous work[1] either by substitution of secondary amine ligands in $Mo_2Cl_4(NHEt_2)_4$ with R-py or by reduction of an Mo_2^{6+} complex with Na/Hg in the presence of pyridine ligands. In view of the unavailability of the corresponding starting materials in the case of tungsten we used a two-electron reduction of WCl_4 by KC_8 followed by the addition of the alkylpyridine ligand to get $W_2Cl_4(R\text{-}py)_4$ (R = Bu^t (**1**) and Bu^n (**2**)). This method has already been successfully employed by us[4] in obtaining analogous ditungsten(II,II) complexes with primary amines, W_2Cl_4-

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$(NH_2R)_4$ (R = Et, Pr^n, Bu^n, Bu^s, Cy). The relatively low yields in these reactions can probably be explained by the fact that the reduction of the W^{IV} compound does not lead exclusively to one form of W^{II} species,[12] and therefore, some parallel reactions are taking place. Nevertheless, the title compounds **1** and **2** can be effectively separated from the reaction mixture by the extraction with hexanes and characterized in pure form.

The ditungsten(II,II) complexes $W_2Cl_4(R\text{-py})_4$ are significantly less stable than the analogous dimolybdenum species, both in the solid state and in solution. This instability, which is probably caused by the ease of oxidation of the W_2^{4+} core, substantially limited the study of the compounds. First, we were unable to use such "oxidizing" solvents as alkyl halides (CH_2Cl_2 and $CHCl_3$); therefore, we could not employ the small alkylpyridines (picoline and lutidine) as we did in the case of molybdenum[1] because these are the only solvents in which they are amply soluble. Second, we could neither explore a wide range of solvents nor employ long time periods in the crystal growth of different rotamers. These may well be the reasons for not obtaining the D_{2d} conformation for tungsten.

The chromium(II) compound, $Cr_3Cl_6(4\text{-Bu}^t\text{-py})_6$ (**3**), has been obtained by reduction of a Cr^{III} complex followed by addition of the 4-Bu^t-py ligand. Compound **3** is very unstable, even in its crystalline form. From a chemical point of view, the stoichiometry of **3** is exactly what was desired to create an analogue of complexes **1** and **2**. On a structural level (vide infra), however, we are dealing again with the characteristic resistance of chromium atoms to form a quadruple Cr−Cr bond unless they are coordinated entirely by bridging ligands.

Molecular Structures. The crystal structures the several solvates of the ditungsten compound $W_2Cl_4(4\text{-Bu}^t\text{-py})_4$ (**1a**−**1c**) all consist of two trans WCl_2L_2 units united by a W−W bond. The bond lengths (2.259−2.263 Å) fall within the range established[13] for tungsten−tungsten quadruple bonds. In the crystals obtained from different solvents we have found molecules that have similar dimensions (Table 2) except for the angle of internal rotation about the W−W axis (Figure 1). Molecule **1a** (Figure 2) has an eclipsed centrosymmetric D_{2h} structure where pyridine groups are facing each other across the dimetal unit. Two other molecules **1b** and **1c** (Figure 3) display deviations from eclipsed geometry and have N−W−W−N torsion angles of 10° and 20°, respectively, which reduce their symmetries to D_2.

Both isomers, D_{2h} and D_2, represent the first examples for ditungsten compounds of the type $W_2X_4L_4$ with monodentate ligands. All other complexes of that kind known to date[3,4] possess a noncentrosymmetric $W_2X_4L_4$ (X = Cl, CCMe; L = PR_3, NH_2R) core with D_{2d} virtual symmetry and eclipsed geometry. At the same time there are several examples of ditungsten (II,II) complexes with bridging diphosphines, $W_2X_4(P{-}P)_2$, which display the rotational conformations similar to those in alkylpyridine compounds: D_{2h} (X = Br, P−P = dppm[14]) and D_2 (X = Cl, P−P = dppm,[15] dppe,[16] dippp[17]).

Comparing rotational isomers for $W_2Cl_4(4\text{-Bu}^t\text{-py})_4$ (**1a**−**1c**) with analogous dimolybdenum molecules,[1] we note that they are very similar. In fact, some of them (**1b**·4-Bu^t-py and **1c**·$(CH_3)_2CO$) even form isomorphous crystals. The only real differences in geometric characteristics are found in the metal−metal bond, which is about 0.12 Å shorter for Mo−Mo, and in

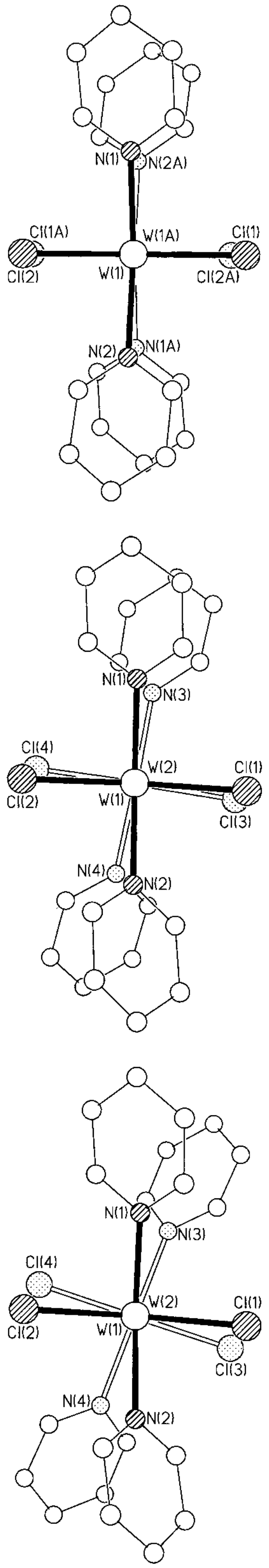

Figure 1. Views of the central part of the molecules $W_2Cl_4(4\text{-Bu}^t\text{-py})_4$, **1a** (top), **1b** (middle), and **1c** (bottom), directly down the W−W axis. Atoms are represented as spheres of arbitrary radii, and the *tert*-butyl groups of pyridine ligands and all hydrogen atoms are omitted. For individual angles, see Table 2.

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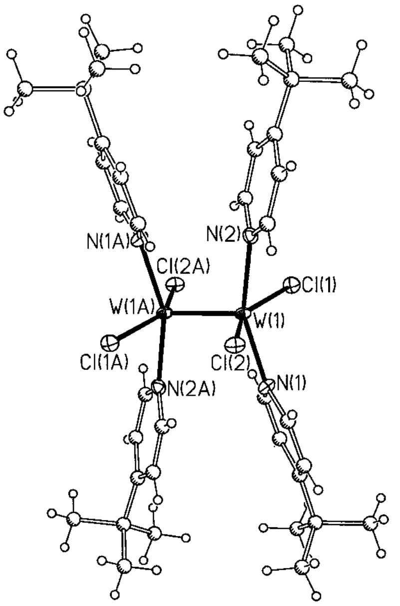

Figure 2. Perspective drawing of the D_{2h} isomer of $W_2Cl_4(4\text{-}Bu^t\text{-}py)_4$ (**1a**). Atoms are represented by thermal ellipsoids at the 40% probability level. For clarity carbon and hydrogen atoms are shown as spheres of arbitrary radii and are not labeled. Only one orientation of disordered *tert*-butyl groups is displayed.

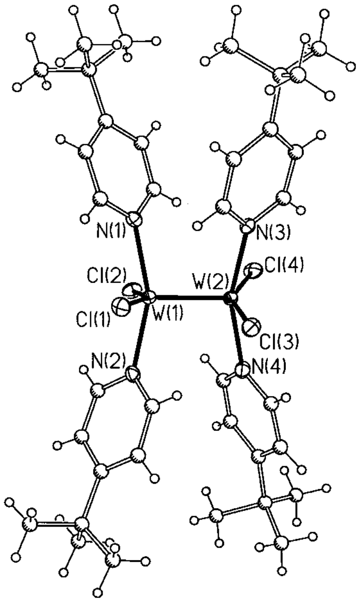

Figure 3. Perspective drawing of the D_2 isomer of $W_2Cl_4(4\text{-}Bu^t\text{-}py)_4$ (**1c**). Atoms are represented by thermal ellipsoids at the 40% probability level. For clarity carbon and hydrogen atoms are shown as spheres of arbitrary radii and are not labeled. Only one orientation of disordered *tert*-butyl groups is displayed.

the metal−nitrogen bonds, which are 0.06 Å shorter, on average, in the tungsten case.

Compound **3** crystallizes in the triclinic space group $P\bar{1}$ with one trinuclear molecule $Cr_3Cl_6(4\text{-}Bu^t\text{-}py)_6$ (Figure 4) in the unit cell. Chromium atoms are arranged linearly, and Cr···Cr separations of 3.622(1) Å indicate that no metal−metal bonds are present. The central metal atom Cr(1) lies on an inversion center and is bridged by chlorine atoms to each terminal Cr(2) atom. All bridging is unsymmetrical (Table 3) with differences in the chlorine−chromium distances of ca. 0.2 and 0.5 Å for Cl(1) and Cl(2), respectively. In the latter case the Cr(1)−Cl(2) separation of 2.900(2) Å can be hardly considered as bonding interaction. Each chromium atom also has two 4-*tert*-butylpyridine ligands that are located above and below the $[Cr_3Cl_6]$ plane in an almost eclipsed fashion. As in the case of the dinuclear structure **1a**, the opposite aromatic rings in **3** are not parallel, with the angles between the planes being about 30°. Also, the alkylpyridine ligands of the terminal Cr(2) atoms are bent away from the metal−metal axis, which probably prevents the condensation of other $CrCl_2L_2$ units leading to a one-dimensional polymeric structure $[CrCl_2(4\text{-}Bu^t\text{-}py)_2]_\infty$.

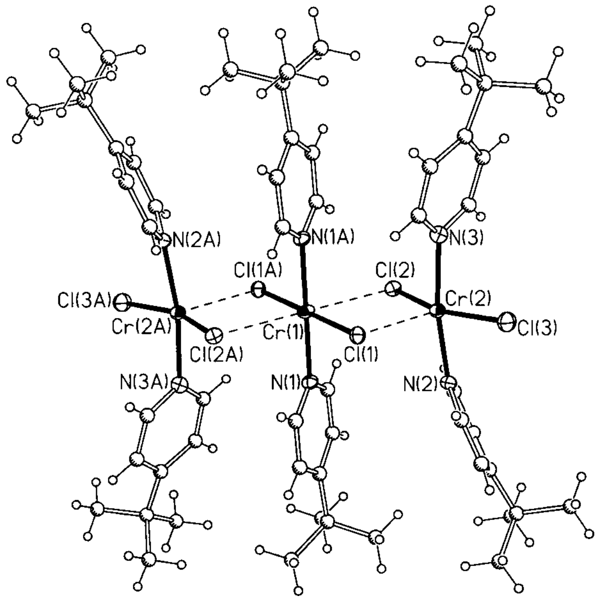

Figure 4. Perspective drawing of $Cr_3Cl_6(4\text{-}Bu^t\text{-}py)_6$ (**3**). Atoms are represented by thermal ellipsoids at the 40% probability level. For clarity carbon and hydrogen atoms are shown as spheres of arbitrary radii and are not labeled. Only one orientation of disordered *tert*-butyl groups is displayed. Long Cr−Cl contacts are drawn by dashed lines.

The coordination of the central Cr(1) atom, with inclusion of the weak contacts to Cl(2), can be considered as tetragonally elongated octahedral, while the terminal Cr(2) centers adopt angularly distorted square-pyramidal geometry. Although the structure of **3** is unique, some of its features are well-known. Five-coordinated chromium(II) atoms have been found in dinuclear complexes $Cr_2Cl_4(L{-}L)_2$ (L−L = μ-dmpm,[18] η-dippe,[19] and η-TMEDA[20]) with bidentate phosphine and amine ligands. These molecules also display long Cr···Cr separations (3.24−3.83 Å) and unsymmetrical (0.21−0.37 Å) chloride bridging. The linear array of three Cr(II) atoms has been described[21] in the isolated $[Cr_3Cl_{12}]^{6-}$ anion which, however, exhibits slightly different overall geometry.

With the unique and curious exception of $Cr_2(tmtaa)_2$[22] no compound having a Cr−Cr quadruple bond has ever been made except when there are four bridging groups that tie the pair of chromium atoms together. In almost all of these cases the four bridging groups are of the three-atom type, and there is an enormous number of such groups. The only two exceptions to the rule of having four such groups (not necessarily all identical[23]) were reported only recently. In these there are three amidinate ligands and a μ-Cl atom.[24] It was found

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Table 3. Selected Bond Distances (Å), Angles (deg), Torsion Angles (deg), and Nonbonding Distances (Å) for $Cr_3Cl_6(4\text{-}Bu^t\text{-py})_6$ (**3**)

Cr(1)···Cr(2)	3.622(2)	Cr(2)−Cl(2)	2.388(2)
Cr(1)−Cl(1)	2.414(1)	Cr(2)−Cl(3)	2.365(2)
Cr(1)···Cl(2)	2.900(2)	Cr(2)−N(2)	2.144(4)
Cr(1)−N(1)	2.108(4)	Cr(2)−N(3)	2.129(4)
Cr(2)−Cl(1)	2.626(2)		
N(1)−Cr(1)−N(1A)	180.0	N(2)−Cr(2)−Cl(1)	93.6(1)
N(1)−Cr(1)−Cl(1)	89.6(1)	N(2)−Cr(2)−Cl(2)	92.1(1)
N(1)−Cr(1)−Cl(2)	90.2(1)	N(2)−Cr(2)−Cl(3)	89.6(1)
Cl(1)−Cr(1)−Cl(2)	87.53(5)	N(3)−Cr(2)−Cl(1)	95.9(1)
N(2)−Cr(2)−N(3)	170.2(2)	N(3)−Cr(2)−Cl(2)	89.6(1)
Cl(1)−Cr(2)−Cl(2)	94.73(6)	N(3)−Cr(2)−Cl(3)	85.7(1)
Cl(1)−Cr(2)−Cl(3)	104.25(6)	Cr(1)−Cl(1)−Cr(2)	91.79(5)
Cl(2)−Cr(2)−Cl(3)	160.80(6)	Cr(1)−Cl(2)−Cr(2)	85.90(5)
N(1)−Cr(1)−Cr(2)−N(2)	0.8(2)	Cl(1)−Cr(1)−Cr(2)−Cl(3)	−8.03(9)
N(1A)−Cr(1)−Cr(2)−N(3)	−3.7(2)	Cl(1A)−Cr(1)−Cr(2)−Cl(2)	−2.26(6)

Table 4. Position of the Absorptions in the Visible Spectra Associated with $\delta \rightarrow \delta^*$ Transitions (nm) for Complexes of the Type $W_2X_4L_4$ (X = Cl, Br, CCR; L_2 = Two Amines, Two Phosphines, Diphosphine)

compound	Nujol	THF	toluene	other
$W_2Cl_4(4\text{-}Bu^t\text{-py})_4$	690 (D_{2h}) 645 (D_2)	680, 720	680, 720	
$W_2Cl_4(NH_2Pr)_4$[a]		573		
$W_2Cl_4(NH_2Bu^t)_4$[a]		581		
$W_2Cl_4(NH_2Cy)_4$[a]		575		
$W_2Cl_4(PMe_3)_4$[b]	658			659
$W_2Cl_2(CCMe)_2(PMe_3)_4$[b]				726
$W_2(CCMe)_4(PMe_3)_4$[b]				773
$W_2Cl_4(PMe_2Ph)_4$[c]	674			
$W_2Br_4(PMe_2Ph)_4$[c]	682			
$W_2Cl_4(PMePh_2)_4$[c]	683			
$W_2Br_4(PMePh_2)_4$[c]	689			
$W_2Cl_4(dppm)_2$[d]	726			737
$W_2Br_4(dppm)_2$[c]	720			

[a] See ref 4. [b] In *n*-hexane, see ref 26. [c] See ref 14. [d] In benzene, see ref 15.

recently[25] that having only two bridging groups of the three-atom type and two μ-Cl atoms again fails to produce a Cr−Cr bond.

UV−Vis Spectra. The UV−vis spectrum of the solid D_{2h} rotamer **1a** displays a moderately intense absorption band at 690 nm. This peak is consisted with the data on $\delta \rightarrow \delta^*$ transitions for quadruply bonded $W_2X_4L_4$ molecules (Table 4). At the same time, for the THF or toluene solution we observed two bands in the $\delta \rightarrow \delta^*$ transition region at 680 and 720 nm, respectively, which might suggest the presence of more than one rotational conformation in these media. Any further interpretation of the spectroscopic data is problematic. The lack of a crystalline compound in which there is a D_{2d} molecule is unfortunate. It would be tempting to assign the two bands observed in solution to D_{2d} (680 nm) and D_2 (720 nm) isomers as in the analogous molybdenum case,[2] but we cannot confirm either of these assignments by citing data on crystals. One might suppose (and this receives support from preliminary DFT calculations) that the $\delta \rightarrow \delta^*$ separations in the D_{2h} and D_{2d} conformers should be about the same. Thus, by using the observed band position (690 nm) for the D_{2h} isomer in the crystal, it could be argued that the 680 nm band in solution is in the expected position for the D_{2d} isomer, and it is reasonable that the D_2 isomer should have its band at longer wavelength.

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Supporting Information Available: Five X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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