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Precursors for Assembly of Supramolecules Containing Quadruply Bonded Cr_2^{4+} Units: Systematic Preparation of $Cr_2(formamidinate)_n(acetate)_{4-n}$ (n = 2–4)

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Four quadruply bonded dichromium complexes with mixed-ligand sets, $Cr_2(formamidinate)_n(acetate)_{4-n}$ (n = 2–4), were synthesized from reactions of anhydrous $Cr_2(O_2CCH_3)_4$ and formamidinate anions. The Cr–Cr bond lengths fall in the range for "supershort" Cr–Cr bonds as they vary from 1.8897(5) Å to 2.012(1) Å. The distance variation depends on the presence or absence of weak axial interactions. Because formamidinate ligands are less labile than acetate groups, these compounds may be useful building blocks for the construction of neutral supramolecules having dichromium units linked by polydentate dianions.

Introduction

There is emerging interest in the use of metal atoms (or ions) as key elements in the self-assembly of metal-organic supramolecular arrays.[1] Most of these studies have focused on systems with single-metal building blocks of the type ML_2, where the L ligands are usually diamine, diphosphane or dicarboxylate and the metal atoms are Pt, Pd, Zn or Cd.[2] These species usually have ions with large charges. The introduction of metal–metal bonded dinuclear units into this field have enriched the diversity of the geometry and properties of the supramolecular systems and allowed the syntheses of neutral molecules.[3] Appropriate selection of the metal containing units and suitable linkers have led to the formation of a variety architectures, including dimers of dimers, loops, triangles, squares, complex polygons and extended 2D and 3D materials.[4]

One of the best strategies for construction of large molecules containing metal–metal bonds has been the use of precursors having subunits containing paddlewheel species with mixed ligands in which some of the paddles are nonlabile formamidinate groups, while the remaining coordination sites are occupied by easily displaceable ligands, such as acetonitrile molecules or carboxylate groups. The labile ligands are then replaced by polydentate linkers to assemble the target supramolecules whose structures depend on the dimensions of the linkers and shape of the corner piece precursors. On the basis of the appropriate choice of subunits and linkers, three basic assembly schemes have been generally employed: (1) Two metal–metal bonded units supported by three formamidinate groups are linked to give dimers of dimers as shown in Scheme 1. Examples are the dimers of dimolybdenum compounds that have been obtained by reactions of $Mo_2(DAniF)_3(CH_3CN_{eq})_2^+$ species (DAniF = *N*,*N′*-di-*p*-anisylformamidinate) with tetraalkylammonium salts of various dicarboxylates.[5] When $Mo_2(DAniF)_3(O_2CCH_3)$ was used as starting material, even the more basic diamidate or the all-nitrogen-donor linker fluoflavinate may be used as linkers and these ligands enable very high intramolecular electronic communication.[6] Compounds having two $Ru_2(DAniF)_3$ units linked by terephthalate anions have also been made by reaction of $(NBu_4)_2O_2CC_6H_4CO_2$ with the building block $Ru_2(DAniF)_3(O_2CCH_3)Cl$[7] and analogous Ru_2 compounds with diphenylformamidinate have also been made.[8] (2) Dimetal units with two *cisoid* formamidinate groups with rigid dianions allow the formation of squares, triangles (Scheme 2) and, under some circumstances, loops. Examples are the series of molecular squares assembled by reactions of [*cis*-$M_2(DAniF)_2(CH_3CN_{eq})_4]^{2+}$ (M = Mo, Rh) and dicarboxylate linkers.[9] Sometimes equilibria between triangles and the corresponding squares exist in solution because of entropy-dominated processes.[10] (3) Precursors with structures having *transoid* nonlabile formamidinate groups are expected to give one-dimensional polymers (Scheme 3). Current work in our laboratory involves the synthesis of ladder structures from *trans*-$M_2(DAniF)_2(O_2CCH_3)_2$ compounds. In addition, by utilizing the axial coordination and a combination of these linkage modes, more complex architectures can be made.[11] What is clear from this discussion is that building blocks with mixed-ligand sets of different

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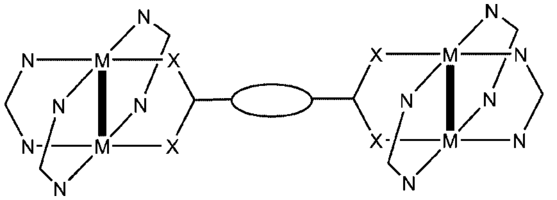
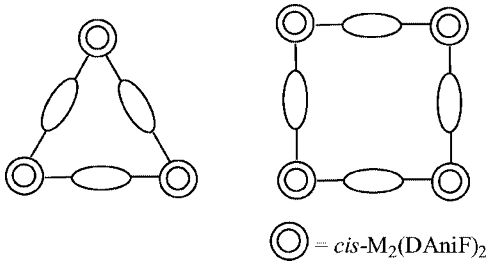
labilities allow selective substitution of the more labile ligands, and preparation of such species is critical for the successful assembly of large molecules.



Scheme 1.



Scheme 2.

An additional advantage of using M–M bonded units in building supramolecules is that a wide selection of transition metal atoms are available and their electronic structures are generally well understood, which allow the introduction of internal spectroscopic probes. Thus far, most of the studies have been limited to dimolybdenum compounds and a handful of molecules containing W_2, Ru_2 and Rh_2 units. Even though the first-row transition metal, chromium, is prone to support metal–metal bonds, and hundreds of compounds with Cr_2^{4+} core have been studied no efforts have been devoted to the methodical construction of appropriate corner pieces.[12] It should be noted that generally chromium compounds are useful in a variety of applications such as catalysts in organic synthetic applications[13] and are also found to be of importance in biosystems.[14] Recently an interesting compound with a Cr-to-Cr bond of order 5 has been reported, in a work that should encourage further exploration of the chemistry of this element.[15]

As a first step in the syntheses of large molecules containing Cr_2^{4+} units, here we report the systematic syntheses of dichromium compounds of the type Cr_2(formamidinate)$_n$(acetate)$_{4-n}$ (n = 2–4). The compounds are a pair of isomers, namely *cis*-$Cr_2(DPh^{Cl}F)_2(O_2CCH_3)_2$, **1**, [$DPh^{Cl}F$ = (o-$ClC_6H_4N)_2CH$], and *trans*-$Cr_2(DPh^{Cl}F)_2(O_2CCH_3)_2$ (**2**), as well as $Cr_2(DAniF)_3(O_2CCH_3)$ (**3**) and the parent compound $Cr_2(DAniF)_4$ (**4**). All of these compounds have been characterized structurally and by various spectroscopic techniques.

Results and Discussion

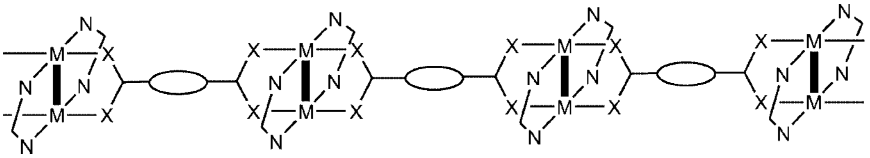
Syntheses

Reaction of 2 equiv. of $LiDPh^{Cl}F$ with 1 equiv. of anhydrous $Cr_2(O_2CCH_3)_4$ in THF at –70 °C affords **1** and **2** as shown by the isolation of two types of crystals when a benzene solution of the isomer mixture was layered with isomeric hexanes: red acicular crystals of *cis*-$Cr_2(DPh^{Cl}F)_2(O_2CCH_3)_2$ (**1**) and yellow-orange block crystals of *trans*-$Cr_2(DPh^{Cl}F)_2(O_2CCH_3)_2$ (**2**). Because of their distinctive shape and color, these isomers can be manually separated in a relatively easy manner and isolated in reasonable yields. It should be mentioned that the appropriate selection of the formamidinate ligands is important as earlier studies had shown that an analogous reaction of $Cr_2(O_2CCH_3)_4$ with 2 equiv. of $LiDPh^{OMe}F$ [$DPh^{OMe}F$ = (o-$CH_3OC_6H_4N)_2CH$] gave only the *cis* product,[16] while reaction of the heavier congener $Mo_2(O_2CCH_3)_4$ and 2 equiv. of HDAniF in the presence of $NaOCH_3$ exclusively produced the *trans* species, namely *trans*-$Mo_2(DAniF)_2(O_2CCH_3)$.[17] In the latter study, the *cis* isomer, *cis*-$Mo_2(DAniF)_2(O_2CCH_3)_2$, was obtained from a two-step reaction in which first $Mo_2(DAniF)_4$ and $(Et_3O)BF_4$ in CH_3CN reacted to produce *cis*-$Mo_2(DAniF)_2(CH_3CN_{eq})_4^{2+}$. This reaction was followed by addition of acetate anions which replaced the acetonitrile molecules in the intermediate.

Once **1** and **2** are formed and isolated, these isomers are stable as the ^1H NMR spectra of these isomers in $CDCl_3$, which are significantly different from each other, do not change over a period of many hours. The spectra are thus consistent with retention of the geometry in solution.

An analogous reaction between $Cr_2(O_2CCH_3)_4$ but with 3 equiv. of LiDAniF gave complex **3** which has three DAniF groups and one acetate ligand. It should be noted that even when only 2 equiv. of LiDAniF were used, the isolated product was $Cr_2(DAniF)_3(O_2CCH_3)$ and under such conditions no species having the formula $Cr_2(DAniF)_2(O_2CCH_3)_2$ was observed. Furthermore, when traces of water were present in the reaction mixture or whenever an excess of LiDAniF was used, compound **4** was the only isolated species.[18] This compound can also be prepared conveniently and in better yield by reaction of LiDAniF and $CrCl_2$. Compounds **1**–**4** are soluble in common solvents such as THF, dichloromethane, toluene and benzene.

The CVs of **1**–**4** were recorded in CH_2Cl_2 using scan rates of 100 mV/s and 0.1 M Bu_4NPF_6 as electrolyte. The oxidation processes are irreversible and the potentials ranged from 0.62 V to 1.00 V. This is not unusual for Cr_2^{4+} species which usually decompose upon oxidation. The only Cr_2^{5+} product known so far was produced by oxidation of



Scheme 3.

$Cr_2(DPPC)_4$ (DPPC is the guanidinate-type species *N*,*N′*-diphenyl-1-pyrrolidine carbodiimidate). For $Cr_2(DPPC)_4$ two quasi-reversible waves were observed in the CV having $E_{1/2}$ values of 0.02 and 1.10 V.

Structural Results

Compounds **1**–**4** have been structurally characterized by single crystal X-ray diffraction and their structures are shown in Figure 1. Compound **1** crystallized in the space group $P2_1/n$ with the molecule residing on a general position. The Cr–Cr bond length of 2.0010(6) Å (Table 1) falls in the range of 1.83–2.60 Å found for Cr–Cr distances in paddlewheel species.[12] For such compounds, the metal–metal distances are affected not only by the identity of the supporting ligand but are very sensitive to the presence or absence of axial interactions. For example, the Cr–Cr distance for the $Cr_2(O_2CCH_3)_4$ molecule in gas phase is 1.97 Å, but this distance increases to 2.369(2) Å when two pyridine molecules coordinate to the axial sites.[19] In **1**, there is no direct axial coordination, however, there are weak axial interactions because the two *cis* formamidinate ligands provide one chlorine atom each at distances of 2.817 and 2.864 Å for Cr(1)···Cl(1) and Cr(2)···Cl(4), respectively. For comparison, in the paddlewheel compound of $Cr_2(DPh^{Cl}F)_4$, [Cr–Cr 2.208(2) Å] the distances between the chlorine and chromium atoms (2.766 Å) are shorter than those in **1**.[20] As a consequence, the Cr–Cr bond length in $Cr_2(DPh^{Cl}F)_4$ [2.208(2) Å] is considerably longer than that in **1** [2.0010(6) Å]. The effect of weak axial interactions on dichromium units has also been documented in compounds with ligands such as 2,6-bis(phenylimino)piperidine, 2,2′-dipyridylamine.[21]

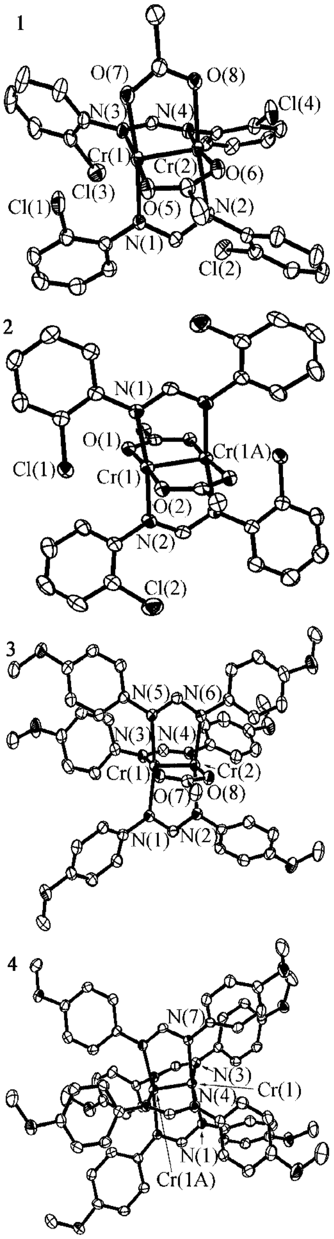


Figure 1. Structures of **1**–**4** with displacement ellipsoids drawn at the 40% probability level. Note the presence of weak Cr···Cl axial interactions in **1** and **2** and the absence of axial interactions in **3** and **4**. The Cr–Cr distances [2.0010(6) and 2.012(1) Å] for **1** and **2**, respectively, are longer than for **3** and **4** [1.8897(5) and 1.924(1) Å, respectively].

Table 1. Selected bond lengths [Å] for **1**–**4**.

	1	**2**·C_6H_6	**3**	**4**
Cr(1)–Cr(2)	2.0010(6)		1.8897(5)	
Cr(1)–Cr(1a)		2.012(1)		1.924(1)
Cr(1)–N(1)	2.051(2)	2.068(3)	2.049(2)	2.067(2)
Cr(1)–O(1)		2.004(3)		
Cr(1)–N(3)	2.051(2)		2.019(2)	2.049(2)
Cr(1)–O(3)				
Cr(1)–N(5)			2.044(2)	
Cr(1)–O(5)	2.018(2)			
Cr(1)–N(7)				2.050(2)
Cr(1)–O(7)	2.001(2)		2.027(2)	
Cr(2)–N(2)	2.055(2)	2.049(3)	2.027(2)	
Cr(2)–O(2)		2.017(3)		
Cr(2)–N(4)	2.043(2)		2.048(2)	2.054(2)
Cr(2)–N(6)			2.033(2)	
Cr(2)–O(6)	1.992(2)			
Cr(2)–O(8)	2.015(2)		2.025(2)	

Compound **2**, an isomer of **1**, crystallized in the space group $P\bar{1}$ with the molecule residing on an inversion center. The Cr–Cr bond length of 2.012(1) Å is very similar to that in **1**. Again the two *trans* formamidinate ligands provide one chlorine donor atom capable of interacting with a chromium atom at a distance of 2.793 Å.

For **3**, which crystallized in the space group $P2_1/c$ with $Z = 4$, the Cr–Cr bond length of 1.8897(5) Å is within the range found in *super-short* quadruply bonded compounds. This is due to the lack of axial coordination by either solvent or other donor atoms in the formamidinate ligand. The bulky formamidinate groups also prevent intermolecular interactions between Cr and O atoms which tend to lengthen the Cr–Cr distances such in the structure of anhydrous $Cr_2(O_2CR)_4$, in which weak intermolecular Cr···O interactions allow the association of $Cr_2(O_2CR)_4$ molecules to form a polymer.[12]

In compound **4**, which crystallized in the space group *C*2/*c* with *Z* = 4, the molecule is located on a general position. The Cr–Cr bond length of 1.924(1) Å resembles that of 1.9178(11) Å in the $Cr_2(DPh^{m-OMe}F)_4$ analogue[22] and it is consistent for a species without axial interactions. It should be noted that the Cr–Cr distance in the $Cr_2(DPho^{-OMe}F)_4$ isomer, which has *o*-methoxy groups providing axial interactions, is 2.140(2) Å.[20] This distance is about 0.22 Å longer than that in **4**.

Concluding Remarks

Systematic syntheses and characterization are reported for a series of dichromium compounds with mixed ligand sets of formamidinate and acetate groups, $Cr_2(formamidinate)_n(acetate)_{4-n}$ (*n* = 2–4). The Cr–Cr bond lengths are strongly influenced by the presence or absence of axial interactions. These compounds are expected to serve as precursors for the preparation of supramolecules with different architectures utilizing selective ligand substitution based on the fact that acetate groups are generally more labile than formamidinate groups.

Experimental Section

Materials and Methods: All reactions and manipulations were performed under nitrogen, using either a dry box or standard Schlenk line techniques. Solvents were purified under argon using a Glass Contour solvent purification system or distilled under nitrogen over appropriate drying agents. Anhydrous $Cr_2(O_2CCH_3)_4$[23] and the formamidinate precursors[24] were synthesized following reported procedures; other commercially available chemicals were used as received.

Analytical and Physical Measurements: Elemental analyses were performed by Robertson Microlit Laboratories, Madison, New Jersey. Electronic spectra were measured on a Shimadzu UV–2501PC spectrometer in CH_2Cl_2 solution. ^1H NMR spectra were recorded on a Inova–300 NMR spectrometer with chemical shifts (δ, ppm) referenced to residual $CHCl_3$ in $CDCl_3$. Cyclic voltammograms (CVs) were collected on a CH Instruments electrochemical analyzer with Pt working and auxiliary electrodes, Ag/AgCl reference electrode, scan rate of 100 mV/s, and 0.10 M Bu_4NPF_6 (in CH_2Cl_2) as electrolyte.

Preparation of *cis*-$Cr_2(DPh^{Cl}F)_2(O_2CCH_3)_2$ (1) and *trans*-$Cr_2(DPh^{Cl}F)_2(O_2CCH_3)_2$ (2): To a solution of $HDPh^{Cl}F$ (265 mg, 1.00 mmol) in THF (20 mL) at –70 °C, methyllithium in diethyl ether (0.32 mL, 1.6 M) was added slowly with stirring. The yellow solution was warmed to 0 °C and then transferred to a suspension of anhydrous chromium acetate (170 mg, 0.500 mmol) in THF (20 mL). The color of the brown suspension turned gradually to orange. After 4 h, the solvent was removed under reduced pressure and the solid residue was extracted with benzene (15 mL). The benzene solution was filtered through a Celite-packed frit, and the filtrate was layered with isomeric hexanes. Two types of crystals formed within 7 d: red acicular crystals of *cis*-$Cr_2(DPh^{Cl}F)_2(O_2CCH_3)_2$ (**1**) and yellow-orange block crystals of *trans*-$Cr_2(DPh^{Cl}F)_2(O_2CCH_3)_2$ (**2**). These were manually separated.

For 1: Yield: 138 mg (37%). ^1H NMR (C_6D_6): 8.62 (s, 2 H, –NC*H*N–), 7.18 (d, 4 H, aromatic C–*H*), 6.80 (m, 8 H, aromatic C–*H*), 6.48 (t, 4 H, aromatic C–*H*), 2.33 (s, 6 H, –CH_3). UV-vis: λ_{max} (ε, $M^{-1} mol^{-1}$) = 400 (1.5×10^3) nm. **1**·$2H_2O$: $C_{30}H_{26}Cl_4Cr_2N_4O_5$ (786): calcd. C 45.82, H 3.58, N 7.12; found C 46.02, H 3.96, N 6.92.

For 2: Yield: 104 mg (28%). ^1H NMR (C_6D_6): 8.67 (s, 2 H, –NC*H*N–), 7.03 (d, 4 H, aromatic C–*H*), 6.80 (m, 8 H, aromatic C–*H*), 6.55 (t, 4 H, aromatic C–*H*), 2.25 (s, 6 H, –CH_3). UV-vis: λ_{max} (ε, $M^{-1} mol^{-1}$) = 450 (1.1×10^3) nm. **2**·H_2O: $C_{30}H_{24}Cl_4Cr_2N_4O_4$ (768): calcd. C 46.89, H 3.43, N 7.26; found C 47.08, H 4.07, N 6.87.

Preparation of $Cr_2(DAniF)_3(O_2CCH_3)$ (3): A procedure analogous to that described above for **1** and **2** but using HDAniF (383 mg, 1.50 mmol) and $Cr_2(O_2CCH_3)_4$ (170 mg, 0.500 mmol) in THF gave an orange product. Crystals were obtained by layering a benzene solution of **3** with hexanes. Yield: 315 mg (68%). ^1H NMR (C_6D_6): 8.94 (s, 2 H, –NC*H*N–), 8.76 (s, 1 H, –NC*H*N–), 6.68 (d, 16 H, aromatic C–*H*), 6.40 (d, 8 H, aromatic C–*H*), 6.24 (d, 8 H, aromatic C–*H*), 3.22 (s, 12 H, –OCH_3), 3.10 (s, 6 H, –CH_3 in DAniF). UV-vis: λ_{max} (ε, $M^{-1} mol^{-1}$) = 410 (1.3×10^3) nm. $Cr_2C_{47}H_{48}N_6O_8$ (929): calcd. C 60.77, H 4.62, N 9.05; found C 60.88, H 4.36, N 9.14.

Preparation of $Cr_2(DAniF)_4$ (4): To a suspension of anhydrous $CrCl_2$ (130 mg, 1.00 mmol) and HDAniF (510 mg, 2.00 mmol) in THF (30 mL) at –78 °C, a solution of methyllithium in diethyl ether

Table 2. X-ray crystallographic data for **1**–**4**.

	1	2·C_6H_6	3	4·$2C_6H_6$
Empirical formula	$C_{30}H_{24}Cl_4Cr_2N_4O_4$	$C_{36}H_{30}Cl_4Cr_2N_4O_4$	$C_{47}H_{48}Cr_2N_6O_8$	$C_{72}H_{72}Cr_2N_8O_8$
Fw	750.33	828.44	928.91	1281.38
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$C2/c$
a [Å]	19.062(3)	8.342(4)	21.648(5)	33.293(10)
b [Å]	7.662(1)	10.701(5)	10.750(3)	10.002(3)
c [Å]	22.258(3)	10.967(5)	18.945(5)	20.914(6)
α [°]	90	102.929(8)	90	90
β [°]	102.687(2)	91.142(8)	92.235(4)	111.888(6)
γ [°]	90	111.594(7)	90	90
Volume [Å^3]	3171.6(7)	881.6(7)	4405.(4)	6462(3)
Z	4	1	4	4
T [K]	213	213	213	213
λ [Å]	0.71073	0.71073	0.71073	0.71073
$d_{calcd.}$ [g/cm^3]	1.571	1.560	1.401	1.317
μ [mm^{-1}]	1.064	0.966	0.555	0.399
R_1,[a] wR_2[b]	0.0392, 0.0874	0.0569, 0.1453	0.0431, 0.1045	0.0831, 0.1087

[a] $R_1 = \Sigma|F_o| - |F_c|/\Sigma|F_o|$. [b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

(0.65 mL, 1.6 M) was added slowly with stirring. The gray suspension changed gradually to a turbid orange dispersion. After 3 h, the solvent was removed under reduced pressure and the residue washed with hexanes (3 × 15 mL). The dry solid was dissolved in benzene (15 mL) and filtered through a Celite-packed frit, and then the filtrate was layered with hexanes. Yield: 420 mg (75%). ^{1}H NMR (δ, ppm in C_6D_6): 8.69 (s, 4 H, –NC*H*N–), 6.62 (d, 16 H, aromatic C–*H*), 6.38 (d, 16 H, aromatic C–*H*), 3.19 (s, 24 H, –C*H*$_3$ in DAniF). UV-vis: λ_{max} (ε, $M^{-1} mol^{-1}$) = 502 (1.2×10^3) nm. $Cr_2C_{60}H_{60}N_8O_8$ (1125.17): calcd. C 64.05, H 5.37, N 9.96; found C 63.89, H 4.86, N 9.64.

X-ray Structural Determinations: Single crystals suitable for X-ray analysis were mounted on the tips of cryoloops attached to a goniometer head. Data for **1**, **2**·C_6H_6, **3** and **4** were collected at –60 °C with a Bruker SMART 1000 CCD area detector system. Cell parameters were determined using the program SMART.[25] Data reduction and integration were performed with the software SAINT,[26] while the absorption corrections were applied by using the program SADABS.[27] The structures were solved by direct methods and refined using the SHELXS–97 program.[28] Non-hydrogen atoms, except for those of disordered solvent molecules, were refined with anisotropic displacement parameters. Hydrogen atoms were added in calculated positions. Crystallographic data are given in Table 2 and selected bond lengths in Table 1.

CCDC-641377 to -641380 (for **1**–**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

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