of Cu^{II}(OEiBC), Bocian and co-workers[47] report an intense 1403-cm^{-1} RR band that is assigned as a C_α–N mode. The frequency of this band of Cu^{II}(OEiBC) is unusually high relative to frequencies typical for Cu^{II}(chlorins).[8,15,21] Han et al.[48] also noted that bands in this region were high in frequency for the extracted siroheme of *Escherichia coli* sulfite reductase. Thus, the high frequency of the dominant band in the ~1340–1410 cm^{-1} RR spectra of iBC's, relative to those of porphyrins or chlorins, appears to be characteristic of the isobacteriochlorin macrocycle.

Conclusions. The data presented herein provide unexpectedly clear-cut examples of the utility of symmetry analysis in the study of complex systems. They also provide the first resonance Raman and Fourier transform infrared spectra for a set of tetrapyrrolic macrocycles that are sequentially reduced from porphyrin to chlorin to isobacteriochlorin.

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Contribution from the Laboratorium voor Anorganische Chemie, Rijksuniversiteit Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands, Chemistry Department, University of Ottawa, Ottawa, Ont. K1N 6N5, Canada, and Laboratorium voor Kristal- en Structuurchemie, Rijksuniversiteit Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands

The Unpredictable Structural Features of Chromium(II) Pyrrolyls: Synthesis and X-ray Structures of Monomeric Square-Planar $(\eta^1\text{-}2,5\text{-}Me_2C_4H_2N)_2Cr(py)_2$, Square-Pyramidal $(\eta^1\text{-}C_4H_4N)_2Cr(py)_3$, Dimeric $[(7\text{-azaindolyl})_2Cr(DMF)]_2$, and Polymeric $[(\eta^1\text{-}2,5\text{-}Me_2C_4N_2)_4CrNa_2(THF)_2(Et_2O)]_n$. An Aborted Cr–Cr Quadruple Bond Formation?

Jilles J. H. Edema,[†] Sandro Gambarotta,[*,§] Auke Meetsma,[†] Frê van Bolhuis,[†] Anthony L. Spek,[‡] and Wilberth J. J. Smeets[‡]

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Reaction of $CrCl_2THF_2$ with 2 equiv of C_4H_4NM or $2,5\text{-}Me_2C_4H_2NM$ (M = Li, Na) leads to the formation of monomeric $(\eta^1\text{-}C_4H_4N)_2Cr(L)_3$ [L = THF (**1**), py (**2**)] and $(\eta^1\text{-}2,5\text{-}Me_2C_4H_2N)_2\,Cr(L)_2$ [L = THF (**4**), py (**5**)], respectively. The crystal structures of **2** and **5** were solved by X-ray diffraction analyses. In spite of the similarity between the ligands, the two monomeric complexes possess remarkably different structures: **2** has an unusual square-pyramidal geometry, while **5** is square-planar with low- and high-spin electronic configurations of the metal, respectively. Crystal data are as follows (T = 130 K, Mo K$\bar{\alpha}$, λ = 0.71073 Å): **2**, triclinic, space group $P\bar{1}$, a = 9.153 (4) Å, b = 10.659 (2) Å, c = 13.707 (3) Å, α = 86.01 (1)°, β = 82.93 (3)°, γ = 88.65 (2)°, Z = 2. **5**, triclinic, space group $P\bar{1}$, a = 6.986 (2) Å, b = 8.812 (2) Å, c = 9.018 (3) Å, α = 87.09 (2)°, β = 68.95 (2)°, γ = 83.18 (2)°, Z = 1. Dimerization was observed when a donor atom, attached to one of the two α positions of the pyrrolyl ligands, restored the unique geometry of the three-center chelating ligands. The dimeric structure of $[(7\text{-azaindolyl})_2Cr(DMF)]_2\cdot 2DMF$ (**7**) (DMF = *N*,*N*-dimethylformamide) was demonstrated by X-ray diffraction analysis. Crystal data for **7**: monoclinic, space group $P2_1/a$, a = 9.458 (1) Å, b = 19.085 (2) Å, c = 11.850 (1) Å, β = 109.92 (1)°, Z = 2 Magnetic properties and structural features [Cr–Cr = 2.604 (2) Å] suggest the absence of a Cr–Cr quadruple bond. Reaction of **1** and **4** with 2 equiv of C_4H_4NNa and $2,5\text{-}Me_2C_4H_2NNa$ leads respectively to the formation of stable polymeric chromates $[(C_4H_4N)_4CrNa_2L_3]_n$ (**3**) and $[(2,5\text{-}Me_2C_4H_2N)_4CrNa_2L_3]_n$ (**6**). [L = Et_2O, dioxane, THF]. The polymeric aggregation, demonstrated in the case of **6** by an X-ray structure determination, is achieved via a π interaction of the pyrrolyl ligands with the Na cations from two different $[(\eta^1\text{-pyrrolyl})_4Cr]^{2-}$ fragments. Crystal data for **6** (T = 130 K, Mo K$\bar{\alpha}$ λ = 0.71073 Å) are as follows: monoclinic, space group $P2_1$, a = 9.045 (1) Å, b = 15.285 (1) Å, c = 13.621 (1) Å, β = 97.42 (1)°, Z = 2.

Introduction

The chemistry of transition-metal complexes containing heterocyclopentadienyl ligands has experienced a steady growth of interest during the last two decades.[1]

The possibility of those ligands being involved in $\eta^5 \rightarrow \eta^3 \rightarrow \eta^1$ ring slippage processes is especially relevant in view of the role played in homogeneous catalysis. In the case of pyrrolyl ligands, the presence of a donor atom such as nitrogen in the heterocycle enhances this possibility.[2] For pyrrole, in fact, both the π-[3-10] and σ-bonding fashion[11-15] have been widely documented. In this second case the Lewis acidity of the metal determines the extent of nitrogen to metal π-interaction.

In spite of the electronic and steric flexibility of this ligand, the chemistry of pyrrolyl transition-metal compounds is rather limited to date. Following our interest in the chemistry of divalent chromium,[16] we were interested in studying the structural features

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[†] Rijksuniversiteit Groningen.

[‡] Rijksuniversiteit Utrecht.

[§] University of Ottawa.

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of chromium(II) pyrrolyls, especially in view of the well-known ability of Cr(II) species to form Cr–Cr multiple bonds.[17] In fact in a previous report, a monomeric structure has been suggested for some chromium(II) and chromium(III) pyrrolyls on the basis of the magnetic properties, although no structural data have been reported.[18] In this paper we describe the synthesis and structures of four novel chromium(II) pyrrolyls.

Experimental Section

All operations were performed under inert atmosphere (N_2 or Ar) with use of standard Schlenk techniques or in a nitrogen-filled drybox (BRAUN-MB 200). $CrCl_2(THF)_2$ was prepared according to published procedures.[19] Infrared spectra were recorded on a Unicam SP3-300 instrument; Nujol mulls were prepared in the drybox. Elemental analyses were carried out at the Microanalytical Department of the Rijksuniversiteit Groningen. Samples for magnetic measurements were weighed in a drybox with a microanalytical balance and sealed in a calibrated Teflon capsule. Magnetic measurements were performed with a Faraday balance (Oxford Instruments) and corrected for the underlying diamagnetism.[20]

$(\eta^1\text{-}C_4H_4N)_2Cr(py)_3\cdot$tol (2). $CrCl_2(THF)_2$ (2.2 g, 8.2 mmol) was added to a solution of C_4H_4NLi in THF (30 mL) prepared by reacting pyrrole (1.18 g, 17.6 mmol) with stoichiometric amounts of MeLi. The resulting reddish-purple solution was stirred for 3 h. After solvent removal in vacuo, the residual solid was recrystallized from boiling toluene (15 mL), containing 5 mL of pyridine. Moderately air-sensitive, brown-red crystals were obtained when the mixture was allowed to stand at room temperature (2.94 g, 5.73 mmol, 70% yield).

Anal. Calcd for $C_{30}H_{31}N_5Cr$ (found): C, 70.17 (69.60); H, 6.04 (6.06); N, 13.66 (13.70); Cr, 10.14 (10.03). IR (Nujol mull, KBr, cm^{-1}): 1600 (m), 1595 (m), 1575 (w), 1530 (w), 1475 (s), 1440 (s), 1290 (w), 1220 (s), 1215 (m), 1160 (s), 1080 (s), 1065 (m), 1030 (m), 1020 (s), 995 (s), 910 (w), 760 (s), 725 (s), 710 (m), 695 (s), 665 (s), 620 (w), 610 (w), 475 (m), 430 (m), 360 (m).

$(\eta^1\text{-}C_4H_4N)_4CrNa_2$(dioxane)$_3$ (3). Neat pyrrole (1.20 mL, 17.2 mmol) was added dropwise to a suspension of NaH (0.46 g, 16.7 mmol) in THF (40 mL). The mixture was stirred for 40 min until gas evolution had ceased. After addition of $CrCl_2(THF)_2$ (1.12 g, 4.2 mmol), the color turned deep red. The resulting mixture was stirred for 20 h. After solvent removal in vacuo, the residual solid was redissolved in 25 mL of toluene. After filtration and addition of 5 mL of dioxane, the solution separated large-size, air-sensitive, red crystals (1.69 g, 2.70 mmol, 64% yield) after standing at room temperature overnight.

Anal. Calcd for $C_{28}H_{40}N_4O_6Na_2Cr$ (found): C, 54.38 (53.69); H, 6.53 (6.40); N, 9.09 (8.95); Cr, 8.48 (8.31); Na, 7.33 (7.35) IR (Nujol mull, KBr, cm^{-1}): 1950 (m), 1930 (m), 1700 (m), 1690 (m), 1550 (m), 1520 (m), 1280 (s), 1260 (s), 1210 (w), 1195 (w), 1130 (s), 1100 (s), 1080 (s), 1070 (s), 1040 (s), 1020 (s), 925 (m), 885 (w), 870 (s), 815 (w), 800 (s), 725 (s), 670 (w), 660 (m), 600 (s), 350 (m).

$(\eta^1\text{-}2,5\text{-}Me_2C_4H_2N)_2Cr(THF)_2$ (4). Neat 2,5-dimethylpyrrole (1.12 mL, 1.05 g, 10.9 mmol) was added to a suspension of NaH (0.26 g, 10.8 mmol) in THF (50 mL). The mixture was stirred and boiled for 20 min. After addition of $CrCl_2(THF)_2$ (1.45 g, 5.4 mmol), the color turned reddish purple. The stirring was continued for 24 h. After filtration, the volume was reduced to 10 mL and an equal amount of pentane was added. The resulting solution was cooled overnight at 0 °C upon which air-sensitive, purple crystals separated (1.78 g, 4.6 mmol, 85% yield).

Anal. Calcd for $C_{20}H_{32}O_2N_2Cr$ (found): C, 62.45 (62.55); H, 8.47 (8.33); Cr, 13.52 (13.54); N, 7.22 (7.20). IR (Nujol mull, KBr, cm^{-1}) 1580 (m), 1535 (w), 1485 (m), 1395 (w), 1375 (s), 1305 (w), 1295 (w), 1255 (s), 1190 (m), 1080 (s), 1040 (w), 1025 (s), 985 (w), 965 (m), 910 (s), 855 (s), 795 (w), 750 (s), 700 (w), 695 (w), 605 (w), 410 (w), 385 (s).

$(\eta^1\text{-}2,5\text{-}Me_2C_4H_2N)_2Cr(py)_2$ (5). Neat 2,5-dimethylpyrrole (1.25 g, 13.1 mmol) was added to suspension of NaH (0.31 g, 12.9 mmol) in THF (30 mL). The resulting mixture was stirred and gently heated for 30 min until gas evolution was complete. After addition of $CrCl_2(THF)_2$ (1.70 g, 6.4 mmol), the stirring was continued for 20 h. The solvent was removed in vacuo, and the residual air-sensitive, purple solid was recrystallized from 15 mL of toluene containing 3 mL of pyridine (1.68 g, 4.22 mmol, 66% yield).

Anal. Calcd for $C_{22}H_{26}N_4Cr$ (found): C, 66.33 (66.43); H, 6.53 (6.72); N, 14.07 (14.07); Cr, 13.06 (12.88). IR (Nujol mull, KBr, cm^{-1}): 1620 (w), 1595 (s), 1590 (s), 1480 (4), 1400 (m), 1380 (s), 1320 (s), 1265 (s), 1220 (s), 1195 (w), 1165 (s), 1100 (w), 1070 (s), 1060 (s), 1010 (s), 1000 (w), 960 (s), 790 (s), 760 (s), 740 (s), 695 (s), 635 (s), 430 (s).

$[(\eta^1\text{-}2,5\text{-}Me_2C_4H_2N)_4CrNa_2(THF)_2(Et_2O)]_n$ (6). Method A. Neat 2,5-dimethylpyrrole (1.25 g, 13.1 mmol) was added dropwise to a suspension of NaH (0.31 g, 12.9 mmol) in THF (50 mL). The mixture was stirred for 30 min at 50 °C, and $CrCl_2(THF)_2$ (0.85 g, 3.2 mmol) was added. The color slowly turned red and the stirring was continued for 24 h. After the solvent was removed in vacuo, the residual solids were recrystallized from 15 mL of Et_2O at −80 °C, yielding pyrophoric, orange-red crystals (1.63 g, 2.3 mmol, yield 74%).

Anal. Calcd for $C_{36}H_{58}N_4O_3Na_2Cr$ (found): C, 62.44 (62.19); H, 8.38 (8.36); N, 8.09 (8.11); Na, 6.64 (6.84); Cr, 7.68 (7.51). IR (Nujol mull, KBr, cm^{-1}): 2760 (m), 1720 (w), 1574 (m), 1385 (m), 1305 (w), 1295 (m), 1265 (s), 1195 (m), 1050 (s), 1000 (w), 920 (m), 905 (s), 770 (s), 750 (m), 745 (s), 660 (w), 460 (m), 390 (m).

Method B. Neat 2,5-dimethylpyrrole (0.83 g, 8.70 mmol) was added dropwise to a suspension of NaH (0.20 g, 8.33 mmol) in 20 mL of THF. After the mixture was stirred for 20 min at 50 °C, solid $(2,5\text{-}Me_2C_4H_2N)_2Cr(THF)_2$ (**5**) (1.54 g, 4.01 mmol) was added. The stirring was continued for 24 h. The solvent was removed in vacuo and the solid recrystallized from 10 mL of ether at −80° (1.97 g, 2.85 mmol, yield 71%).

[(7-Azaindolyl)$_2$Cr(DMF)]$_2$ (DMF = *N,N*-Dimethylformamide) (7). A solution of 7-azaindole (0.44 g, 3.7 mmol) was added to a solution of $Mes_2Cr(THF)_3$ (0.92 g, 1.8 mmol) in pyridine (50 mL). The air-sensitive yellow crystalline material, which separated when the mixture was left standing at room temperature for 3 days, was recrystallized from DMF–pyridine mixed solvent (yield 0.34 g, 0.96 mmol, 53%).

Anal. Calcd for $C_{34}H_{34}N_{10}O_2Cr_2\cdot 2C_3H_7NO$ (found): C, 55.55 (55.03); H, 5.59 (5.32); N, 19.44 (18.84); Cr, 12.03 (12.14). IR (Nujol mull, KBr, cm^{-1}): 1575 (s), 1530 (m), 1400 (s), 1320 (m), 1272 (s), 1250 (s), 1190 (m), 1130 (s), 1095 (w), 1045 (m), 1015 (s), 960 (w), 920 (m), 910 (m), 880 (s), 775 (s), 740 (s), 710 (w), 690 (s), 620 (m), 600 (w), 570 (w), 460 (s).

Reaction of $[(\eta^1\text{-}2,5\text{-}Me_2C_4H_2N)_4CrNa_2(THF)_2(Et_2O)]_n$ with 18-Crown-6. A solution of **6** (1.42 g, 2.05 mmol) in THF (10 mL) was treated with 18-crown-6 (1.10 g, 4.37 mmol). The resulting mixture was stirred for 30 min. After evaporation of the solvent in vacuo, the residual solids were recrystallized from 10 mL of boiling toluene containing 3 mL of pyridine. The product, which separated as green crystals, was identified as **5** (elemental analysis, IR) (0.48 g, 1.21 mmol, yield 58%).

Reaction of $(C_4H_4N)_4CrNa_2$(dioxane)$_3$ with 18-Crown-6. A solution of **3** (0.72 g, 1.15 mmol) in THF (15 mL) was treated with 18-crown-6 (0.64 g, 2.00 mmol). The resulting mixture was stirred for 30 min. The solvent was removed in vacuo, and the residual solid was redissolved in toluene (10 mL) containing 2 mL of pyridine. After the resulting solution was filtered and cooled at −30 °C, brown-red crystals separated. The product was isolated and identified as **2** (elemental analysis, IR) (0.33 g, 0.64 mmol, yield 56%).

X-ray Crystallography. The crystals used for this study were selected in a drybox equipped with a locally modified microscope. Suitable crystals were either sealed in thin-walled Lindemann glass capillaries or glued on the top of a glass fiber covered with a thin layer of paraffin oil and mounted on the diffractometer (CAD-4F) equipped with a locally modified cooling device. The net intensities of the data were corrected for the scale variation and Lorentz and polarization effects, but not for absorption. Details on the structure determination and refinement are given in Table I. Tables of hydrogen atom positions and thermal parameters, extensive lists of bond distances and angles, and tables of F_o, F_c, and $\sigma(F)$ are available as supplementary material. Scattering factors were obtained from Cromer and Mann,[21] and anomalous dispersion factors, from Cromer and Liberman.[22]

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Table I. Crystal Data and Structural Analysis Results

	2	**5**	**6**	**7**
formula	$C_{30}H_{31}N_5Cr$	$C_{22}H_{26}N_4Cr$	$C_{36}H_{58}N_4Na_2O_3Cr$	$C_{34}H_{34}N_{10}O_2Cr_2 \cdot 2C_3H_7ON$
space group	$P\bar{1}$	$P\bar{1}$	$P2_1$	$P2_1/a$
Z	2	1	2	2
a, Å	9.153 (4)	6.986 (2)	9.045 (1)	9.458 (1)
b, Å	10.659 (2)	8.812 (2)	15.285 (1)	19.085 (2)
c, Å	13.707 (3)	9.018 (3)	13.621 (1)	11.850 (1)
α, deg	86.01 (1)	87.09 (2)		
β, deg	82.93 (3)	68.95 (2)	97.42 (1)	109.92 (1)
γ, deg	88.65 (2)	83.18 (2)		
V, Å^3	1323.7 (5)	514.4 (3)	1867.4 (3)	2011.0 (4)
D_{calcd}, g cm^{-3}	1.289	1.286	1.232	1.428
μ_{calcd}, cm^{-1}	4.47	5.5	3.6	5.8
radiation (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
T, K	130	130	130	100
R_F	0.044	0.035	0.042	0.063
R_{wF}	0.049	0.044	0.042	0.059

Table II. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for **2**

atom	x	y	z	B, Å^2
Cr	0.20337 (9)	0.01966 (8)	0.73858 (6)	1.43 (2)
N(1)	0.2108 (4)	0.1469 (4)	0.8443 (3)	1.66 (9)
N(2)	0.2414 (5)	−0.1058 (4)	0.6300 (3)	2.0 (1)
N(3)	0.2053 (4)	0.1752 (4)	0.6271 (3)	1.9 (1)
N(4)	0.2417 (4)	−0.1328 (4)	0.8455 (3)	1.67 (9)
N(5)	−0.0541 (4)	0.0017 (4)	0.7588 (3)	1.70 (9)
C(1)	0.0961 (6)	0.1985 (5)	0.9034 (4)	1.9 (1)
C(2)	0.1442 (6)	0.2952 (5)	0.9531 (4)	2.3 (1)
C(3)	0.2980 (6)	0.3022 (5)	0.9244 (4)	2.1 (1)
C(4)	0.3348 (6)	0.2120 (5)	0.8575 (4)	1.9 (1)
C(5)	0.1416 (6)	−0.1712 (5)	0.5879 (4)	1.9 (1)
C(6)	0.2127 (6)	−0.2510 (5)	0.5217 (4)	2.3 (1)
C(7)	0.3652 (6)	−0.2332 (5)	0.5209 (4)	2.5 (1)
C(8)	0.3780 (6)	−0.1442 (5)	0.5886 (4)	2.1 (1)
C(9)	0.1681 (6)	0.2928 (5)	0.6526 (4)	2.5 (1)
C(10)	0.1587 (7)	0.3934 (5)	0.5821 (4)	2.9 (1)
C(11)	0.1871 (6)	0.3732 (5)	0.4839 (4)	2.7 (1)
C(12)	0.2240 (6)	0.2531 (5)	0.4580 (4)	2.6 (1)
C(13)	0.2308 (6)	0.1561 (5)	0.5306 (4)	2.1 (1)
C(14)	0.2924 (6)	−0.1133 (5)	0.9317 (4)	2.1 (1)
C(15)	0.3227 (6)	−0.2094 (5)	0.9991 (4)	2.6 (1)
C(16)	0.3007 (6)	−0.3324 (5)	0.9795 (4)	2.6 (1)
C(17)	0.2456 (7)	−0.3540 (5)	0.8926 (4)	2.9 (1)
C(18)	0.2182 (6)	−0.2532 (5)	0.8273 (4)	2.3 (1)
C(19)	−0.1356 (6)	0.0460 (5)	0.6883 (4)	1.8 (1)
C(20)	−0.2864 (5)	0.0306 (5)	0.6941 (4)	1.9 (1)
C(21)	−0.3570 (6)	−0.0334 (5)	0.7779 (4)	2.3 (1)
C(22)	−0.2766 (6)	−0.0780 (5)	0.8523 (4)	2.1 (1)
C(23)	−0.1258 (6)	−0.0585 (5)	0.8400 (4)	2.0 (1)
C(24)	0.5974 (6)	0.4920 (5)	0.7303 (4)	2.5 (1)
C(25)	0.6521 (7)	0.5960 (5	0.7727 (4)	2.6 (1)
C(26)	0.7883 (7)	0.5889 (5)	0.8063 (4)	2.8 (1)
C(27)	0.8728 (7)	0.4786 (6)	0.8012 (4)	3.1 (1)
C(28)	0.8184 (6)	0.3756 (5)	0.7630 (4)	2.6 (1)
C(29)	0.6833 (7)	0.3820 (5)	0.7274 (4)	2.5 (1)
C(30)	0.4559 (7)	0.4992 (6)	0.6866 (5)	3.8 (2)

Table III. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for **5**

atom	x	y	z	U(eq),[a] Å^2
Cr(1)	0	0	0	0.0131 (1)
N(1)	−0.2577 (3)	0.1432 (2)	0.1537 (2)	0.0169 (5)
N(2)	0.0091 (3)	0.1508 (1)	−0.1805 (2)	0.0148 (5)
C(1)	−0.3645 (3)	0.2533 (2)	0.0952 (2)	0.0189 (6)
C(2)	−0.5319 (3)	0.3467 (2)	0.1921 (3)	0.0215 (6)
C(3)	−0.5940 (4)	0.3291 (3)	0.3549 (3)	0.0236 (6)
C(4)	−0.4851 (4)	0.2175 (3)	0.4168 (3)	0.0242 (6)
C(5)	−0.3207 (3)	0.1266 (2)	0.3130 (3)	0.0210 (6)
C(6)	0.0724 (3)	0.2943 (2)	−0.1901 (2)	0.0180 (5)
C(7)	−0.0047 (4)	0.3863 (2)	−0.2887 (3)	0.0226 (6)
C(8)	−0.1195 (4)	0.2964 (3)	−0.3439 (3)	0.0225 (6)
C(9)	−0.1077 (3)	0.1531 (2)	−0.2758 (2)	0.0181 (6)
C(10)	0.2026 (4)	0.3304 (3)	−0.0987 (3)	0.0287 (7)
C(11)	−0.2071 (4)	0.0150 (3)	−0.2878 (3)	0.0266 (7)

[a] $U_{eq} = {}^1/_3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$.

For Complex 2. Final lattice parameters were determined by least-squares treatment using the setting angles of 25 reflections in the range 12.3° $\leq \theta \leq$ 16.9°. From a total of 3902 reflections in the range 1° $\leq \theta \leq$ 23.5°, 2308 were used in the refinement. The structure was solved by direct methods using the SDP/PDP (Enraf-Nonius) program system.[23] Block-diagonal least-squares of F with unit weights converged to a final value of $R_F = 0.044$ and $R_{wF} = 0.049$ with anisotropic temperature factors used for the non-hydrogen atoms and fixed isotropic temperature factors used for the hydrogen atoms. The hydrogen atoms were located from difference Fourier maps and introduced in the refinement. Final atomic coordinates are listed in Table II.

For Complex 5. Unit cell dimensions and their standard deviations were determined from the setting angles of 23 reflections in the range 6.64° $< \theta <$ 18.41°. The triclinic unit cell was checked for the presence of higher lattice symmetry; reduced cell calculations did not indicate any higher lattice symmetry.[24] A 360° ψ-scan for a close to axial reflection $(\bar{3}\bar{1}\bar{1})$ showed a variation in intensity of less than 5% about the mean value. Standard deviations in the intensities, based on counting statistics, were increased on the basis of an analysis of the excess variance[25] of the three reference reflections: $\sigma^2(I) = \sigma_{cs}^2(I) + (0.025I)^2$. A total of 2199 reflections satisfied the $I \geq 2.5\sigma(I)$ criterion of observability. The structure was solved by Patterson methods and subsequent partial structure expansion (SHELXS86).[26] Refinement on F was carried out by block-diagonal least-squares techniques with anisotropic thermal parameters for the non-hydrogen atoms. A subsequent difference Fourier synthesis gave all the hydrogen atoms, which were refined with isotropic thermal parameters. Final refinement on F by block-diagonal least-squares techniques with anisotropic thermal parameters for the non-hydrogen atoms and isotropic thermal parameters for the hydrogen atoms converged at $R_F = 0.035$ ($R_{wF} = 0.044$). Final fractional atomic coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms are given in Table III. Calculations were carried out on the CDC-Cyber 170/760 computer of the University of Groningen with the program packages XTAL,[27] EUCLID[28] (calculation of geometric data), and a locally modified version of the program ORTEP[29] (preparation of illustrations).

For Complex 6. Unit cell parameters were determined from a least-squares treatment of the setting angles of 25 reflections in the range 8° $< \theta <$ 12°. Data were collected in the range 1.3 ° $< \theta <$ 24.0° on a crystal of 0.30 × 0.30 × 0.37 mm. Two reference reflections indicated

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(28) Spek, A. L. The EUCLID package. In *Computational Crystallography*; Sayre, D., Ed. Clarendon Press: Oxford, England, p 528.

(29) Johnson, C. K. ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA 1965.

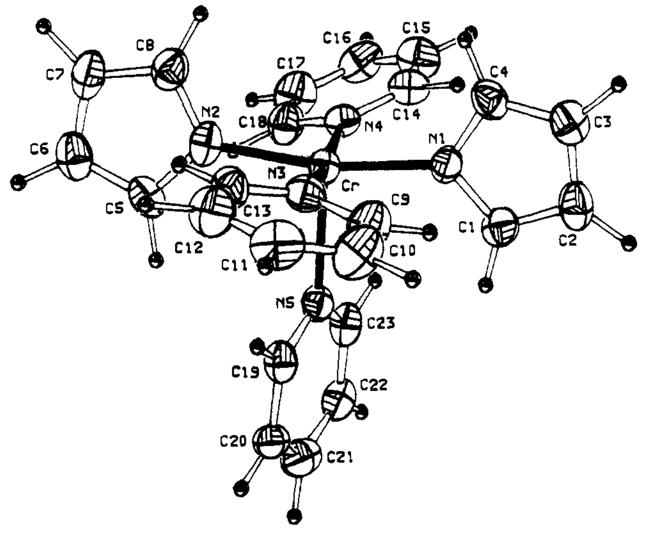


Figure 1. ORTEP plot of **2**. Thermal ellipsoids are drawn at the 50% probability level.

no decay. The structure was solved by direct methods[26] (SHELXS86) and refined on F by full-matrix least-squares techniques. Hydrogen atoms were introduced at calculated positions (C–H = 0.98 Å) and included in the final refinement riding on their carrier atoms. Non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms with common isotropic thermal parameters. Convergence was reached at $R_F = 0.042$ [$w = 1/\sigma^2(F)$]. The absolute structure was checked with refinement of an inverted model resulting in a slightly higher R_F value ($R_F = 0.043$). Final refined positional parameters are given in Table IV. All calculations were performed with SHELX76[30] and the EUCLID package[28] (geometrical calculations and illustration) on a Microvax-II computer.

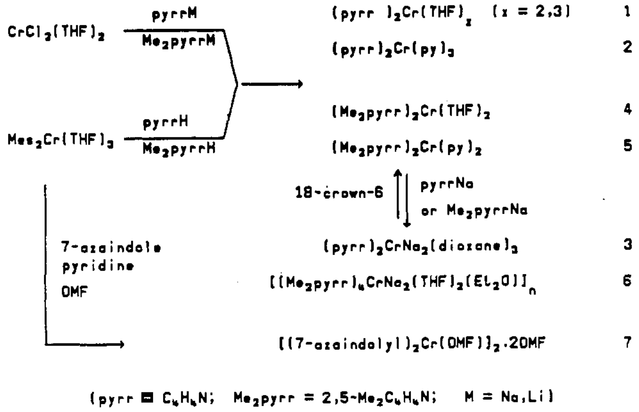
For Complex 7. Unit cell parameters were determined from a least-squares treatment of the setting angles of 25 reflections in the range 2.5° < θ < 10.6°. Data were collected in the range 1.1° < θ < 25.4° on a crystal of size 0.25 × 0.13 × 0.35 mm, corrected for a linear decay of 4.4% as indicated by three reference reflections and merged into a unique set (R_i = 3.7%). The structure was solved by Patterson methods (SHELXS86)[26] and subsequent difference Fourier syntheses and refined on F by full-matrix least-squares techniques. Three atoms of the coordinated DMF molecule were found disordered over two positions with gof = 0.76 (1) and 0.24 (1), respectively. H atoms were introduced at calculated positions (C–H = 0.98 Å) and included in the refinement riding on their carrier atoms. All non-H atoms, except the minor disordered atoms, were refined with anisotropic thermal parameters whereas H atoms were refined with two common isotropic thermal parameters. Convergence was reached at $R_F = 0.063$ [$w = 1/\sigma^2(F)$]. Final refined positional parameters are given in Table V. All calculations were performed with SHELX76[30] and the EUCLID package[28] (geometrical calculations and illustrations) on a MicroVax-II computer.

Results

The synthetic procedures used for the preparation of chromium(II) pyrrolyls are essentially those previously used for the synthesis of Cr(II) alkoxides and amides.[16] Reaction of $CrCl_2(THF)_2$ with 2 equiv of C_4H_4NM (M = Li, Na) or of $Mes_2Cr(THF)_3$[31] (Mes = 2,4,6-mesityl) with 2 equiv of C_4H_4NH, affords purple solutions from which purple $(C_4H_4N)_2Cr(THF)_x$ (**1**) was isolated in good yield and crystalline form. Unfortunately, the high tendency of **1** to lose coordinated solvent precluded reproducible analytical characterization. However stable, red-brown crystals of $(C_4H_4N)_2Cr(py)_3$ (**2**) were obtained upon treatment of **1** with pyridine in toluene (Scheme I).

A structure study was undertaken for complexes **2**, **5**, **6**, and **7**, whose results are presented in Tables I–VI and Figures 1–4. Finally the magnetic properties of all the compounds were measured. These results are reported at appropriate places in the Discussion section.

Scheme I



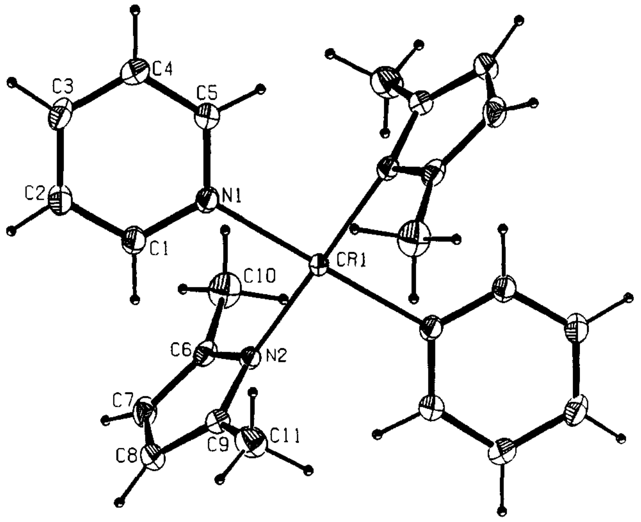


Figure 2. ORTEP plot of **5**. Thermal ellipsoids are drawn at the 50% probability level.

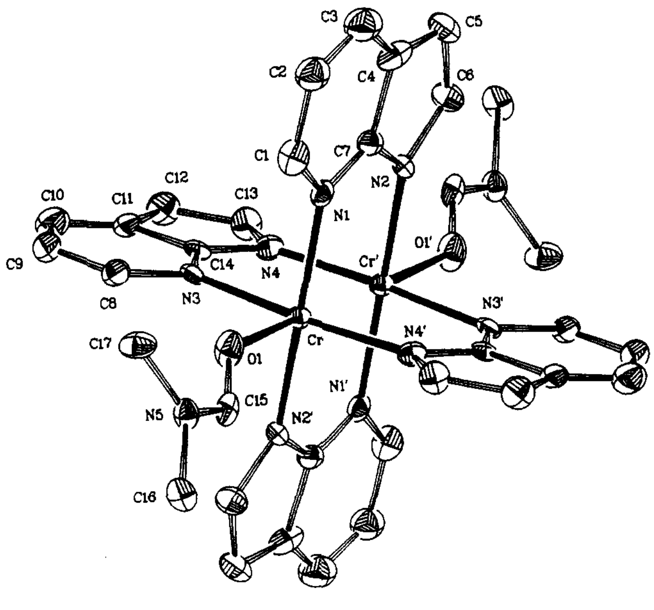


Figure 3. Thermal motion ellipsoid plot of **7** (50% probability level).

Discussion

An X-ray structure determination carried out on a single crystal of **2** showed the monomeric molecule to possess an unusual square-based pyramidal coordination geometry (Figure 1). The two pyrrolyl and pyridine ligands, which are trans to one other, define the basal plane. The chromium atom is only slightly above

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Table IV. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for **6**

atom	*x*	*y*	*z*	*U*(eq),[a] Å^2
Cr	0.10015 (9)	0.5268	0.19312 (6)	0.0261 (2)
N(10)	0.1382 (5)	0.4003 (3)	0.1474 (3)	0.030 (2)
N(20)	0.1152 (5)	0.6608 (3)	0.2203 (3)	0.033 (2)
N(30)	0.2007 (5)	0.4980 (3)	0.3360 (3)	0.028 (2)
N(40)	−0.0576 (4)	0.5444 (3)	0.0689 (3)	0.029 (1)
C(11)	0.2772 (6)	0.3671 (4)	0.1329 (4)	0.032 (2)
C(12)	0.2617 (7)	0.2823 (4)	0.1023 (4)	0.038 (2)
C(13)	0.1092 (6)	0.2610 (4)	0.0968 (4)	0.036 (2)
C(14)	0.0367 (6)	0.3344 (4)	0.1221 (3)	0.029 (2)
C(15)	−0.1263 (6)	0.3479 (4)	0.1203 (4)	0.034 (2)
C(16)	0.4147 (6)	0.4214 (4)	0.1486 (5)	0.042 (2)
C(21)	0.1727 (7)	0.7167 (4)	0.1553 (4)	0.039 (2)
C(22)	0.1519 (7)	0.8030 (4)	0.1840 (5)	0.046 (2)
C(23)	0.0842 (7)	0.7995 (4)	0.2702 (5)	0.046 (2)
C(24)	0.0647 (7)	0.7122 (4)	0.2918 (4)	0.038 (2)
C(25)	0.0104 (8)	0.6731 (5)	0.3817 (5)	0.048 (3)
C(26)	0.2507 (7)	0.6846 (4)	0.0734 (5)	0.044 (2)
C(31)	0.3346 (5)	0.5264 (5)	0.3843 (3)	0.031 (2)
C(32)	0.3582 (7)	0.4927 (4)	0.4778 (4)	0.042 (2)
C(33)	0.2349 (7)	0.4386 (4)	0.4885 (4)	0.042 (2)
C(34)	0.1406 (6)	0.4454 (3)	0.4027 (4)	0.030 (2)
C(35)	−0.0113 (7)	0.4046 (4)	0.3787 (5)	0.039 (2)
C(36)	0.4290 (6)	0.5921 (4)	0.3395 (4)	0.038 (2)
C(41)	−0.0543 (5)	0.5249 (4)	−0.0291 (3)	0.029 (2)
C(42)	−0.1939 (5)	0.5340 (4)	−0.0813 (4)	0.032 (2)
C(43)	−0.2905 (6)	0.5585 (3)	−0.0133 (4)	0.038 (2)
C(44)	−0.2048 (6)	0.5653 (3)	0.0774 (4)	0.033 (2)
C(45)	−0.2580 (6)	0.5780 (4)	0.1754 (4)	0.039 (2)
C(46)	0.0841 (6)	0.4959 (4)	−0.0693 (4)	0.038 (2)
Na(1)	0.1179 (3)	0.2397 (2)	−0.0981 (2)	0.0403 (8)
O(50)	0.3206 (5)	0.2982 (3)	−0.1626 (3)	0.050 (2)
C(51)	0.4185 (7)	0.3639 (6)	−0.1165 (5)	0.065 (3)
C(52)	0.4491 (9)	0.4203 (6)	−0.2033 (7)	0.077 (4)
C(53)	0.4626 (9)	0.3546 (6)	−0.2839 (6)	0.071 (3)
C(54)	0.3425 (9)	0.2935 (5)	−0.2676 (5)	0.071 (3)
Na(2)	0.2850 (3)	0.3181 (2)	0.3187 (2)	0.0461 (9)
O(60)	0.1840 (4)	0.1897 (3)	0.3694 (3)	0.041 (2)
O(70)	0.5152 (5)	0.2413 (4)	0.3336 (3)	0.068 (2)
C(61)	0.0482 (7)	0.1481 (5)	0.3267 (6)	0.062 (3)
C(62)	0.0455 (8)	0.0578 (4)	0.3653 (5)	0.060 (3)
C(63)	0.2040 (8)	0.0414 (5)	0.4071 (6)	0.071 (3)
C(64)	0.2603 (8)	0.1310 (5)	0.4400 (5)	0.058 (3)
C(71)	0.6484 (9)	0.2437 (6)	0.4014 (6)	0.089 (4)
C(72)	0.623 (1)	0.3076 (6)	0.4757 (7)	0.100 (4)
C(73)	0.5208 (9)	0.1606 (6)	0.2707 (5)	0.066 (3)
C(74)	0.6237 (8)	0.1650 (6)	0.1979 (6)	0.077 (3)

[a] *U*(eq) = one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

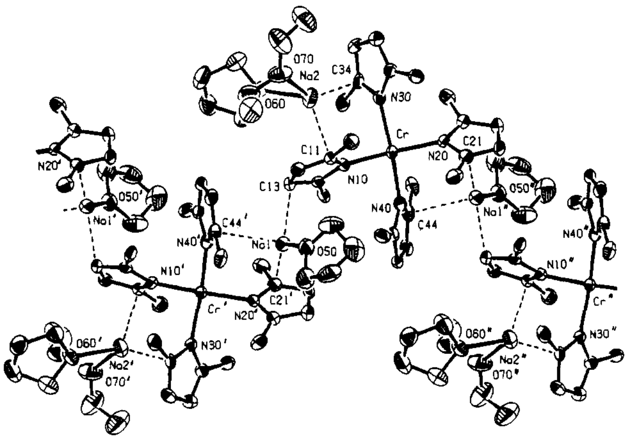

Figure 4. Thermal motion ellipsoid plot of **6** (50% probability level) showing part of the polymeric chain along the 2-fold screw axis.

Table V. Final Coordinates and Equivalent Isotropic Thermal Parameters and Their Esd's in Parentheses for **7**

atom	*x*	*y*	*z*	*U*(eq)[a] or *U*, Å^2
Cr	0.0810 (1)	0.04201 (6)	0.46041 (9)	0.0144 (3)
O(1)	0.2260 (5)	0.1127 (2)	0.3902 (4)	0.029 (2)
N(1)	−0.1041 (5)	0.0556 (3)	0.3036 (4)	0.018 (2)
N(2)	−0.2455 (5)	−0.0261 (3)	0.3749 (5)	0.018 (2)
N(3)	0.0034 (5)	0.1250 (3)	0.5376 (5)	0.016 (2)
N(4)	−0.1371 (5)	0.0469 (3)	0.6142 (4)	0.018 (2)
N(5)	0.4172 (6)	0.1555 (3)	0.3358 (5)	0.020 (2)
C(1)	−0.1119 (8)	0.0980 (4)	0.2111 (6)	0.025 (2)
C(2)	−0.2397 (8)	0.1032 (4)	0.1090 (7)	0.031 (3)
C(3)	−0.3652 (8)	0.0640 (4)	0.0979 (7)	0.037 (3)
C(4)	−0.3666 (8)	0.0199 (4)	0.1862 (6)	0.027 (3)
C(5)	−0.4685 (7)	−0.0271 (4)	0.2150 (6)	0.027 (2)
C(6)	−0.3889 (7)	−0.0533 (4)	0.3260 (6)	0.023 (2)
C(7)	−0.2308 (7)	0.0181 (3)	0.2912 (6)	0.019 (2)
C(8)	0.0427 (7)	0.1927 (3)	0.5367 (6)	0.021 (2)
C(9)	−0.0059 (7)	0.2450 (4)	0.5959 (6)	0.026 (2)
C(10)	−0.0961 (8)	0.2306 (4)	0.6609 (7)	0.032 (3)
C(11)	−0.1373 (7)	0.1635 (4)	0.6679 (6)	0.025 (2)
C(12)	−0.2246 (7)	0.1231 (4)	0.7258 (6)	0.028 (3)
C(13)	−0.2181 (7)	0.0553 (4)	0.6906 (6)	0.025 (2)
C(14)	−0.0862 (6)	0.1116 (3)	0.6021 (5)	0.014 (2)
C(15)[b]	0.354 (1)	0.1107 (5)	0.3898 (7)	0.019 (3)
C(16)[b]	0.5815 (9)	0.1504 (5)	0.3584 (9)	0.027 (3)
C(17)[b]	0.337 (1)	0.2139 (5)	0.2665 (8)	0.027 (3)
		Minor Disorder Atoms [gof = 0.24 (1)]		
C(150)	0.273 (3)	0.151 (2)	0.335 (3)	0.024 (8)
C(160)	0.430 (4)	0.206 (2)	0.242 (3)	0.028 (8)
C(170)	0.538 (3)	0.116 (2)	0.403 (2)	0.019 (7)
		DMF Solvate Molecule		
O(2)	−0.0077 (6)	0.2093 (3)	1.0381 (5)	0.051 (2)
N(6)	0.1442 (6)	0.1543 (3)	0.9532 (5)	0.034 (2)
C(18)	0.0738 (8)	0.2090 (4)	0.9777 (6)	0.031 (3)
C(19)	0.2363 (8)	0.1596 (5)	0.8796 (7)	0.043 (3)
C(20)	0.123 (1)	0.0851 (5)	0.9948 (8)	0.056 (4)

[a] *U*(eq) = one-third of the trace of the orthogonalized **U** matrix. [b] Major disorder atom [gof = 0.76 (1)].

this plane (distance from the plane is 0.195 Å), and a third molecule of pyridine occupies the apical vertex with a remarkably elongated Cr–N distance [Cr–N(5) = 2.350 (4) Å]. The chromium atom is coplanar with each pyrrolyl ring forming Cr–N bond distances [Cr–N(1) = 2.061 Å] that compare well with those of the previously reported Cr(II) amides.[16c,32] The two pyrrolyl groups are only slightly tilted in respect to each other (tilt angle 9.8°), in contrast to the two basal pyridine molecules, which showed a remarkably wider tilt angle (tilt angle 32.6°).

The pentacoordination of chromium observed in complex **2** is quite unusual for a monomeric Cr(II) derivative. It might be considered a result of a possible ligand-field high stabilization energy, the resulting d^4 low-spin electronic configuration (μ_{eff} = 2.73 μ_B, μ_B/Cr calculated spin only for a low-spin d^4 μ_{eff} = 2.83 μ_B) providing an empty, low-energy d orbital suitable for coordination of an additional ligand. In contrast, the 2,5-dimethylpyrrolyl complex $(\eta^1\text{-}2,5\text{-}Me_2C_4H_2N)_2Cr(py)_2$ (**5**), which has the two axial positions sterically protected, is tetracoordinated, square-planar with the normal high-spin d^4 electronic configuration of chromium (μ_{eff} = 4.87 μ_B).

The geometry of **5** was confirmed by an X-ray diffraction analysis (Figure 2). The chromium atom lies on an inversion center in the plane defined by the four nitrogen atoms [N(1)–Cr–N(2) = 88.62 (7)°]. The two pyrrolyl ligands are almost eclipsed in respect to each other having Cr–N bond lengths comparable to those observed in complex **2** [Cr–N(2) = 2.036 (2) Å]. Different from **2**, however, the chromium atom is outside the plane of each pyrrolyl moiety [distance from the plane is 0.608 (4) Å]. Finally, one of the two methyl groups of each pyrrolyl ligand lies on the axis perpendicular to the plane of the molecular core, reaching a fairly short nonbonding distance with the metal atom [Cr···C(10) = 3.329 (3) Å; calculated Cr···H(102) = 2.980 (4) Å]. Here, the steric protection provided by the two methyl groups on the fifth and sixth coordination sites of chromium might

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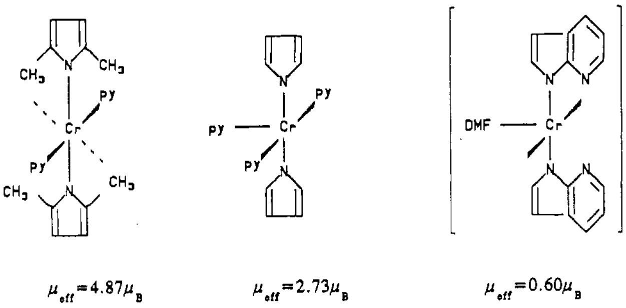
(32) Bradley, D. C.; Hursthouse, M. B.; Newing, C. W.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1972**, 567.

Table VI. Selected Bond Distances (Å) and Angles (deg)

2	5	7	6
Cr-N(1) = 2.061 (4)	Cr-N(1) = 2.145 (2)	Cr-N(1) = 2.090 (5)	Cr-N(10) = 2.074 (5)
Cr-N(3) = 2.174 (4)	Cr-N(2) = 2.036 (1)	Cr-N(2′) = 2.062 (6)	Cr-N(30) = 2.086 (4)
Cr-N(5) = 2.350 (4)	N(1)-Cr-N(2) = 88.62 (7)	Cr-O(1) = 2.274 (5)	Na(2)-C(34) = 2.680 (6)
N(4)-Cr-N(1) = 90.0 (2)		Cr-N(3) = 2.084 (2)	Na(2)-C(11) = 2.631 (6)
N(1)-Cr-N(5) = 96.0 (2)		Cr-N(4′) = 2.064 (6)	Na(1″)-C(44) = 2.783 (5)
		Cr··Cr′ = 2.604 (2)	Na(1″)-C(21) = 2.666 (7)
		N(1)-Cr-N(2) = 173.2 (2)	Na(1)-C(13) = 2.685 (6)
		N(1)-Cr-O(1) = 91.6 (2)	N(30)-Cr-N(20) = 91.8 (2)

Chart I



preclude the achievement of higher coordination numbers.

The coordination of chromium in complex **2** is reminiscent of the geometry of the mononuclear fragments that are the building blocks of the well-known quadruply bonded complexes of dichromium containing three-center bridging ligands.[17] In those units in fact, the coordination geometry of chromium is square pyramidal. An additional donor atom (from either coordinating solvent or the ligand itself) frequently occupies the axial coordination site, playing an important role in determining the value of the intermetallic separation.[17] Questions arise about which factors inhibit the formation of a Cr–Cr quadruple bond in complex **2**. We believe that the lack of dimeric aggregation is just a result of a very poor ability of pyrrolyl ligand to bridge two metal centers. Corresponding with this hypothesis, when the unique geometry of the three-center chelating ligand[17] is restored, just by placing a donor atom in one of the α positions of the pyrrolyl ring, a dichromium complex is formed (Chart I). In fact the reaction of $Mes_2Cr(THF)_3$ with 2 equiv of 7-azaindole in pyridine leads to the formation of the dimeric, almost diamagnetic $[(7\text{-azaindolyl})_2Cr(DMF)]_2{\cdot}2DMF$ (**7**), obtained as light yellow crystals upon treatment with DMF (DMF = *N*,*N*-dimethylformamide).

The temperature dependence of the magnetic susceptibility (4.3–298 K) in agreement with the Curie–Weiss law showed a largely negative value of Θ [Θ = −170 K], which diagnoses the presence of a strong antiferromagnetic exchange[33] as being possibly responsible for the low value of the magnetic moment (μ_{eff} = 0.60 μ_B/Cr).

The structure of **7**, demonstrated by X-ray analysis, shows the usual dimeric arrangement of the well-known quadruply bonded complexes of dichromium (Figure 3). The molecule lies on an inversion center with the four planes of the indolyl ligands perpendicular to each other and two molecules of DMF occupying the two axial coordination sites. The geometry around each chromium atom closely resembles the structure of **2**. The four nitrogen atoms define a plane from which Cr is only slightly outside, protruding from the coordination polyhedron (distance from the plane 0.11 (1) Å), with Cr–N distances [Cr–N(1) = 2.090 (5) Å, Cr–N(2′) = 2.062 (6) Å, Cr–N(3) = 2.084 (6) Å, Cr–N(4′) = 2.064 (6) Å] which compare well with those of **2**. The oxygen atom of the axial DMF molecule coordinates chromium, reaching a distance of 2.274 (5) Å that, although quite short, is still in the range observed for the axial ligation in the quadruply bonded systems.[17] The value of the intermetallic contact [Cr–Cr = 2.604 (2) Å] is to our knowledge the largest yet found in this class of complexes.

Theoretical investigations have pointed out that the basicity of the bridging ligand is an important factor in influencing the Cr–Cr bond length.[34] The implication of this is that one must have a ligand more basic than carboxylate to have "supershort" Cr–Cr bonds. In contrast, the 7-azaindolyl ligand, which is far more basic[37] than CF_3COO^- [the longest Cr–Cr contact (2.541 Å) has been found in the $[(CF_3COO)_2Cr$ dimer]][17] showed further lengthening of the Cr–Cr distance by 0.07 Å. Even the basicity of the axial ligand, the most important factor affecting the Cr–Cr bond distance,[17,35] does not justify here the remarkably long Cr–Cr separation.[38] The high value of the dipole moment of DMF (3.54 D),[39] which is the highest in the series of molecules used for the axial ligation and which is related to the coordinating ability of the ligands, also cannot explain the large Cr–Cr distance of **7**. For these reasons, complex **7** escapes the normal classification scheme for understanding the value of the Cr–Cr bond length.[17,34,40] In addition to that, there is no doubt that the ligands that possess the unique geometry and electronic configuration of the three-center chelating ligands have a special ability to force a short vicinity between the two transition metals.[41] Finally, it seems quite unrealistic to claim the presence of a quadruple bond with a value of the Cr–Cr distance of 2.604 (2) Å. Furthermore, the presence of residual paramagnetism and of a strong antiferromagnetic exchange indicates that the bond order in complex **7** should be definitely less than quadruple, if any bond does exist at all. Therefore we conclude that, rather than a "superlong" Cr–Cr quadruple bond, the intermetallic contact in complex **7** can be better regarded as a pure artefact of the geometry of the 7-azaindolyl ligand.

Further reaction of **2** with 2 equiv of C_4H_4NNa followed by treatment with dioxane led to formation of $(C_4H_4N)_4CrNa_2(dioxane)_3$ (**3**). This compound can also be conveniently prepared in one-pot synthesis from $CrCl_2(THF)_2$ and 4 equiv of C_4H_4NNa (Scheme I). Similarly, $(2{,}5\text{-}Me_2C_4H_2N)_2Cr(THF)_2$ (**4**) reacts quickly with 2 equiv of $2{,}5\text{-}Me_2C_4H_2NNa$ forming the chromate species $[(2{,}5\text{-}Me_2C_4H_2N)_4CrNa_2(THF)_2(Et_2O)]_n$ (**6**) (Scheme I). The solid-state structure of **6** (Figure 4), determined by X-ray diffraction methods, can be regarded as a one-dimensional polymeric chain composed of discrete monomeric units. Each monomeric unit formally contains a $[(\text{pyrrolyl})_4Cr]^{2-}$ dianion bonded to two unequivalent Na cations. The polymeric aggregation is achieved via interaction of Na(1) of one unit with three

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(41) For example $[Cu(OOCCH_3)_2]_2{\cdot}2H_2O$ is isostructural with **7** with a Cu···Cu nonbonding distance of 2.64 Å. Careful reconsiderations of the magnetic properties[33] excluded the presence of a δ bond initially claimed. Figgis, B. N.; Martin, R. L. *J. Chem. Soc. A* **1956**, 3837.

carbon atoms of a pyrrolyl ring bonded to Na(2) of a second unit. The coordination around chromium is distorted square-planar, the dihedral angle between the N(30)–Cr–N(10) and N(20)–Cr–N(40) planes being 23.4 (2)°. The chromium atom is σ-bonded to the four pyrrolyl groups and is coplanar with each ring. The Cr–N bonding distances are normal [Cr–N ranging between 2.074 (5) and 2.086 (5) Å] and compare well with those observed in **2**, **5**, and **7**. In contrast to the previous cases, the pyrrolyl rings are severely tilted in respect to each other [tilt angle = 86.9 (3), 84.9 (3)°] probably to minimize the steric interaction between the ortho methyl groups. However, it cannot be excluded that optimization of the coordination geometry around the Na atoms might be also responsible for this arrangement. The high asymmetry of the monomeric unit is mainly determined by the coordination around the two unequivalent Na atoms. Na(1) is bonded to the [N(20)–C(24)] ring in a rather symmetric η^5-fashion, the Na–C distances ranging between 2.667 and 2.957 Å. Conversely, the interaction of Na(1) with the second pyrrolyl ring (N(40)–C(44)) is limited to only one bond [Na(1)–C(44) = 2.783 (5) Å], the other distances (including from nitrogen) being larger than 3 Å. The bonding of Na(2) with the two rings is quite curious. Each ring is η^3-bonded (allylic-like) to Na(2), the shortest contacts being with C(34) and C(11) [Na(2)–C(34) = 2.680 (6) Å, Na(2)–C(11) = 2.631 (6) Å]. Furthermore, three carbon atoms of the two pyrrolyl rings bonded to Na(2) are engaged in a η^3-bonding with Na(1) of a second molecular unit. The shortest distance [Na(1)–C(13) = 2.685 (6) Å] compares with all the other short intramolecular Na–C contacts. This additional intermolecular interaction is responsible for the probably weak polymeric aggregation and the remarkably large thermal effect. In fact, at room temperature, no X-ray diffraction was observed. However, a standard data set was obtained at 130 K from the same crystal that decreased in size by 30% upon cooling.

The magnetic properties of this one dimensional polymer are very close to those of the monomeric square planar complex **5**. The value of the magnetic moment ($\mu_{eff} = 4.59\ \mu_B$) is consistent with a high-spin d^4 electronic configuration of chromium(II), suggesting that the polymeric aggregation of **6** affects only slightly the magnetic behavior of the central Cr^{2+} ion.

Sodium can be easily abstracted from the molecular core of **3** and **6** by simple treatment with strong coordinating agents (pyridine, crown-ethers), leading to the formation of monomeric **2** and **5**, respectively (Scheme I). This suggests furthermore that the coordination of Na to the pyrrolyl groups is quite labile [sharply in contrast to the case of (Et$_2$N)$_4$CrLi$_2$(THF)$_2$[16d] where the Li cation cannot be abstracted] and that the solid-state structure is probably not preserved in solution.

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Supplementary Material Available: For each complex, tables of crystal data, thermal parameters, hydrogen atom positional parameters, and extensive lists of bond angles and distances (27 pages); lists of observed and calculated structure factors (64 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
Texas A&M University, College Station, Texas 77843

Crystal Structure and Reactivity of [Cu(dmpe)$_2$][Cu(Co(CO)$_4$)$_2$] (dmpe = 1,2-Bis(dimethylphosphino)ethane): Staggered and Eclipsed Conformations of [(CO)$_4$CoCuCo(CO)$_4$]$^-$ Anions

Donald J. Darensbourg,* Chi-Shan Chao, Joseph H. Reibenspies, and Christopher J. Bischoff

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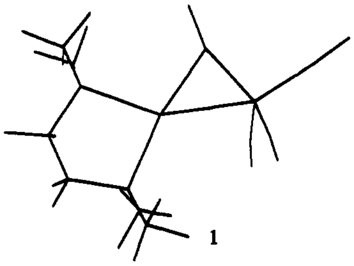
The reaction of NaCo(CO)$_4$ with 1,2-bis(dimethylphosphino)ethane (dmpe) and CuCl in dichloromethane solution gave pale yellow, air-sensitive [Cu(dmpe)$_2$][Cu(Co(CO)$_4$)$_2$], which has been characterized by X-ray crystallography at room temperature. The crystals are monoclinic, space group $C2/c$, with unit cell dimensions a = 18.437 (5) Å, b = 9.880 (2) Å, c = 38.109 (9) Å, β = 102.07 (2)°, V = 6788 (3) Å^3, Z = 8, and R_{wF} = 6.02%. The anions [(CO)$_4$CoCuCo(CO)$_4$]$^-$ are monomers with staggered and eclipsed forms existing simultaneously in the unit cell. The staggered form adopts a linear conformation around copper, whereas in the eclipsed form the Co–Cu–Co bond angle is slightly less than 180°. Reaction of 2 equiv of the ligand dppe (1,2-bis(diphenylphosphino)ethane) with [Cu(Co(CO)$_4$)$_2$]$^-$ at −78 °C instantly affords the Co(CO)$_4^-$ anion and Cu(dppe)$_2^+$, indicative of a highly labile Cu–Co bond.

Introduction

Recently, much attention has been focused on synthetic[1-3] and theoretical[4] studies of heterobimetallic compounds containing copper. It has been reported that the reaction of L$_2$CuCl with the Co(CO)$_4^-$ anion leads to the formation of a binuclear Cu–Co complex (eq 1).[3] A single-crystal structural analysis of

$$L_2CuCl + NaCo(CO)_4 \rightarrow L_2CuCo(CO)_4 + NaCl \quad (1)$$

(tmed)CuCo(CO)$_4$ (tmed = *N,N,N′,N′*-tetramethylethylenediamine) (**1**) showed that one of the carbonyl groups asymmetrically



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bridges the Cu–Co bond.[3] This is consistent with a low-frequency ν(CO) vibration observed at 1820 cm^{-1} in its solid-state infrared spectrum.

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