only C_2 symmetry, with the S_4 symmetry operation factored out of the parent D_{2d} structure. In the O_h group, the characters for the S_4 operation of the O_h representations are +1 for T_{1g} and −1 for T_{2g}. A perturbation of the symmetry from O_h by removal of the S_4 operation therefore predicts that the low energy manifold transition should generate CD transitions with the same signs for both the **A** and **C** isomers, while the high energy manifold should generate transitions of opposite sign. This is consistent with the observed spectra.

Conclusion

Diastereomeric (**A** and **C**) chromic complexes of the chiral ligand (*S*)-desferriferrithiocin have been synthesized, separated, and fully characterized. Previous studies have shown that for chiral ligands such as enterobactin or ferrichrome the synthesis of the enantiomeric ligand causes the preferred metal ion chirality also to be enantiomeric. For instance, microbial discrimination between natural Δ-ferric enterobactin and the synthetic Λ-ferric enantioenterobactin really involves a response to two changes of chirality: the ligand structure and metal ion coordination geometry. In principle the response to these two changes cannot be separated. The cobaltic and chromic complexes are pairs of two diastereomeric isomers **A** and **C** in which the ligand chirality remains unchanged. With these complexes the effect of only the metal ion coordination chirality for siderophore-related iron transport can be probed.

Acknowledgment. A NATO postdoctoral fellowship (to F.E.H.) is gratefully acknowledged. A.H. thanks the "Stiftung für stipendien auf dem Gebiete der Chemie" for a fellowship. We thank Professor Bodie E. Douglas for helpful discussions regarding the IUPAC conventions for nomenclature of coordination complexes. This research is supported by NIH Grant AI 11744.

Supplementary Material Available: Tables of positional and anisotropic thermal parameters, bond distances and angles, and root-mean-square amplitudes of thermal vibration, and two fully labeled plots of **2** and **3** (21 pages); listing of calculated and observed structure factor amplitudes for **2** and **3** (95 pages). Ordering information is given on any current masthead page.

Main-Group–Organotransition-Metal Chemistry: The Cyclopentadienylchromium Polyiodides Including $[(C_5Me_5)_2Cr_2I_3^+]_2[I_{16}^{2-}]$

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Contribution from the School of Chemical Sciences and the Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801. *Received June 1, 1989*

Abstract: The reaction of $[Cp^*Cr(CO)_2]_2$ ($Cp^* = \eta^5$-C_5Me_5) and I_2 affords a compound of the empirical formula Cp^*CrI_3 (**2**). Single-crystal X-ray diffraction shows **2** to be a polymer, $\{[Cp^*CrI(\mu\text{-}I)]_2\cdot[Cp^*Cr(I_3)(\mu\text{-}I)]_2\}_n$ [monoclinic $P2_1/c$; a = 15.658 (2), b = 8.504 (1), c = 23.242 (4) Å; β = 102.48 (1)°; V = 3021.7 (9) Å^3; Z = 2; ρ_{calc} = 2.497 g cm^{-3}; 3014 observed reflections $I > 2.58\sigma(I)$; R = 0.039, R_w = 0.041]. ^{1}H NMR studies show that in chlorinated solvents **2** dissociates into $[Cp^*CrI(\mu\text{-}I)]_2$ (**1**), the latter of which can be prepared by reduction of **2** with Zn/Hg. Treatment of **2** with high concentrations of I_2 (I/Cr of >6) gives $Cp^*CrI_{5.5}$ (**3**), which is formulated as $[Cp^*{}_2Cr_2(\mu\text{-}I)_3]_2[I_{16}]$ [monoclinic, $P2_1/c$; a = 14.744 (2), b = 22.864 (4), c = 23.267 (5) Å; β = 93.77 (2)°; V = 7827 (4) Å^3, Z = 4; ρ_{calc} = 3.005 g cm^{-3}; 6153 observed reflections $I > 2.58\sigma(I)$; R = 0.054, R_w = 0.063]. The cation exhibits a short Cr–Cr distance of 3.00 (1) Å indicative of Cr(III)–Cr(III) bonding. This cation is imbedded within a three-dimensional polyiodide lattice based upon I_{16}^{2-} subunits. The I_{16}^{2-} cluster is comprised of an I_2-linked pair of roughly planar $(I_2)_3I^-$ subunits.

It is well-known that very few inorganic transition-metal compounds can be dissolved intact in noncoordinating solvents. The solution chemistry of inorganic fragments can, however, be studied by using solubilizing organic coligands. The cyclopentadienyl (Cp = C_5H_5) ligands are particularly ideal in this regard since most Cp complexes are soluble in nonpolar solvents and the Cp–M bond is very robust. The solubility characteristics, as well as the redox properties, can be further modified through the use of alkyl substituents on the Cp ligand.

In exploring the chemistry of such organic-solubilized inorganic fragments, we and others have focused on compounds of the type $[CpME_n]_m$ where E is a main-group atom such as sulfur,[1] oxygen,[2] or phosphorus.[3] This class of CpM–main-group compounds is quite extensive for the chlorides and bromides,[4] but the iodides have received little attention. Iodine and iodides exhibit extensive Lewis acid–base chemistry, and with the large van der Waals radius for iodide (2.15 Å),[5] organometallic iodides might be expected to adopt extended interactions in the solid state. Indeed, "Cp^*IrI_3" ($Cp^* = C_5Me_5$) is a one-dimensional polymer comprised of $[Cp^*Ir(\mu\text{-}I)I]_2$ subunits linked by I_2 molecules that interact with terminal iodo ligands.[6] Likewise, $Pt(I_2)I[C_6H_3(CH_2NMe_2)_2]$ contains an infinite chain of molecules with $I_2\cdots I^-$ (μ-I_3^-) linkages.[7]

The present study of cyclopentadienylchromium iodides grew out our search for organometallic electron *acceptors*.[8] We had

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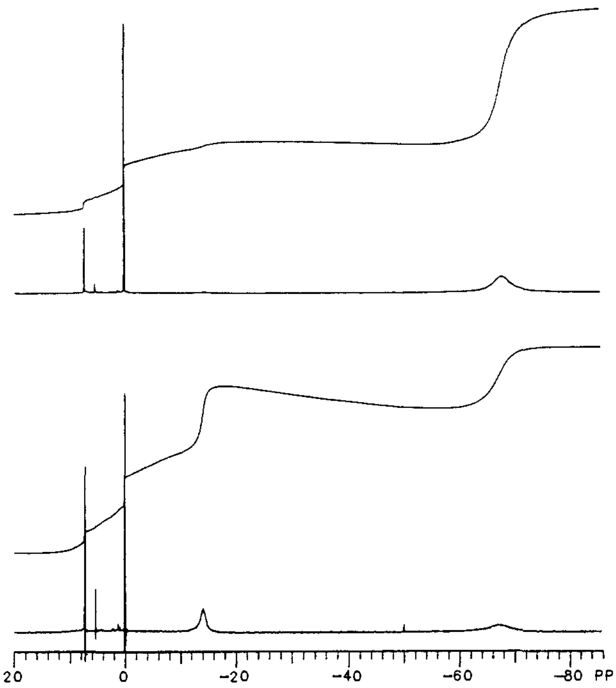

Figure 1. 200-MHz ^{1}H NMR spectra of a saturated $CDCl_3$ solution of Cp^*CrI_3 (top, [Cr] ≈ 15 mM) and of a solution saturated with Cp^*CrI_3 and I_2 (bottom, $[I_2]$ ≈ 50 mM).

previously shown that the acceptor power of the isoleptic $(C_5R_5)MX_3$ series increases by ~700 mV as one proceeds from Ti to V. Furthermore, it was found that $CpVX_3$ becomes more oxidizing when chloride is replaced by bromide. This interesting effect can be attributed to the poorer π-donor abilities of Br.[9] Thus, $CpVBr_3$ is the most oxidizing neutral organometallic compound known. With $E_{1/2}$ = 510 mV (vs Ag/AgCl), $CpVBr_3$ is sufficiently oxidizing that it forms a stable salt with ferrocene ($E_{1/2}$ = 500 mV), i.e., $[Cp_2Fe^+][CpVBr_3^-]$.[10]

It has also been found by us that "Cp^*CrBr_3" is so oxidizing that it is unstable with respect to free bromine. The adduct $\{[Cp^*CrBr(\mu\text{-}Br)]_2\cdot Br_2\}_n$ has in fact been identified crystallographically.[11] Studies on the corresponding Cp^*CrI_x systems identified three phases, one of which also consists of a related halogen adduct. At still higher I/Cr ratios an unprecedented stage in metal polyhalide chemistry is observed. This paper describes the approach to and the realization of this new stage.

Results

Synthesis and Interconversions of Cp^*CrI_x(Cp^* = η^5-C_5Me_5). This study concerns the (pentamethylcyclopentadienyl)chromium iodides: Cp^*CrI_2 (**1**), Cp^*CrI_3 (**2**), and $Cp^*CrI_{5.5}$ (**3**). The reaction of $[Cp^*Cr(CO)_2]_2$ and excess I_2 results in the formation of a material whose empirical formula corresponds to **2**. In addition to **2**, we obtained a small amount of $Cp^*Cr(CO)_3I$.[12] We were unable to convert the tricarbonyl iodide into **2** with further iodine by either thermal or photochemical treatments. Solutions of **2** in $CDCl_3$ (TMS) show a well-resolved ^{1}H NMR resonance at δ −68 (fwhh = 600 Hz). At high concentrations of **2** an additional resonance appears at δ −14 (230 Hz).

Complex **2** can be converted into the other two members of the Cp^*CrI_x series. The reaction of **2** with an excess of Zn/Hg forms Cp^*CrI_2 (**1**). This material is presumed to be dimeric, i.e., $[Cp^*CrI(\mu\text{-}I)]_2$, analogous to the chlorides and bromides.[13] Complex **1** displays a ^{1}H NMR resonance at δ −68 in $CDCl_3$, but no concentration dependent signal at δ −14. In contrast to our results, Köhler, Brunner, and co-workers observe *two* peaks in the ^{1}H NMR spectrum of their sample of $[Cp^*CrI_2]_2$, which they attribute to cis and trans isomers.[14] We are unable to reconcile the discrepancy between our observations. Solutions of **1** react with iodide resulting in an immediate color change of blue to the green color characteristic of **2**. Unlike $[Cp^*CrBr(\mu\text{-}Br)]_2$,[15] **1** does not react cleanly with 0.5 equiv of O_2; instead free I_2 is formed, as are a variety of organometallic products.

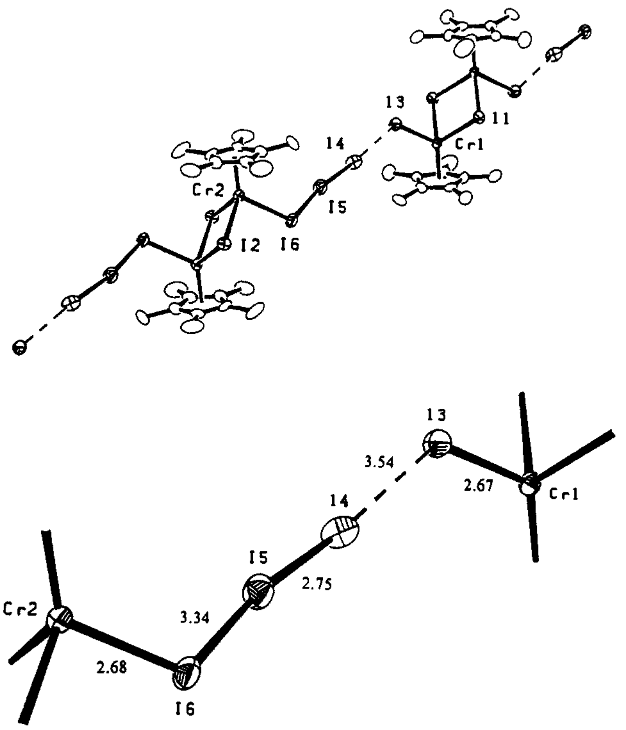

Figure 2. Structure of $\{[Cp^*Cr(I_3)(\mu\text{-}I)]_2\cdot[Cp^*CrI(\mu\text{-}I)]_2\}_n$ (top) and the interdimer triiodide–iodide linkage (bottom).

The addition of iodine to $CDCl_3$ solutions of **2** results in the appearance of the δ −14 signal observed for concentrated solutions of **2** alone (Figure 1). The maximum ratio of integrated δ −14 to −68 signals occurs when the solution also becomes saturated with I_2 (I/Cr of ca. 15:1). The δ −14 peak is attributed to $[Cp^*_2Cr_2(\mu\text{-}I)_3]^+$ since the same peak slowly appears upon the addition of $AgBF_4$ to a solution of **1**. Slow cooling of concentrated CH_2Cl_2 solutions at I/Cr ratios of >6 gives black crystalline plates, which analyze as $Cp^*CrI_{5\pm0.1}$ and evolve iodine when broken or upon standing at room temperature. Structural characterization of this material showed that the true I/Cr ratio is 5.5:1 (vide infra).

Structure of Cp^*CrI_3 (2). In the solid state, **2** is viewed as the copolymer $\{[Cp^*CrI(\mu\text{-}I)]_2\cdot[Cp^*Cr(I_3)(\mu\text{-}I)]_2\}_n$ (Figure 2). Each of the two chromium dimers have crystallographically imposed inversion symmetry. The "$[Cp^*CrI(\mu\text{-}I)]_2$" subunits are linked to the "$[Cp^*Cr(I_3)(\mu\text{-}I)]_2$" subunits by I···I contacts of 3.542 (1) Å, while the (bridging) triiodide is unsymmetrical [2.754 (1), 3.339 (1) Å] and bent [166.88 (5)°]. The asymmetry in,the interdimer I···I contacts and angles resembles that for $Cd(NH_3)_4(I\cdot I_2)_2$,[16] $Cu(NH_3)_4I_2\cdot I_2$,[17] Pt(1,10-phenanthroline)$I_{5,6}$,[18] and in particular the iridium analogue of **2**, $[Cp^*Ir(\mu\text{-}I)]_2\cdot I_2$.

The Cr–Cr distances in the two subunits are nonbonding, 3.654 (3) Å for "$[Cp^*Cr(I_3)(\mu\text{-}I)]_2$" and 3.771 (3) Å for "$[Cp^*CrI(\mu\text{-}I)]_2$". In contrast, the Ir–Ir distances in $[Cp^*IrI(\mu\text{-}I)]_2\cdot I_2$ are 4.011 (1) and 4.068 (1) Å.[19] The Cr–I distances remain about the same

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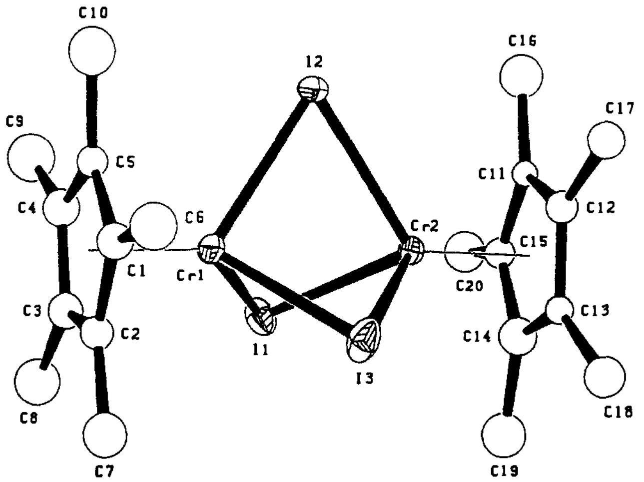

Figure 3. Structure of the $[Cp^*_2Cr_2(\mu\text{-}I)_3]^+$ subunits of Cp*CrI$_{5.5}$.

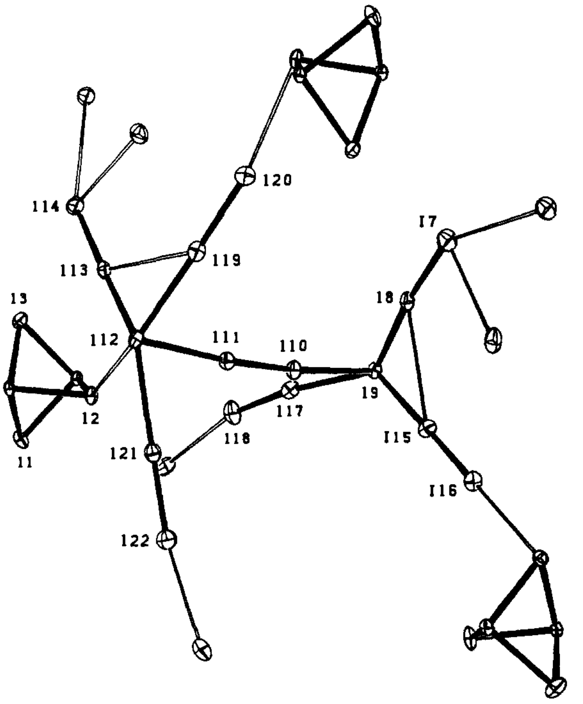

Figure 4. Structure and coordination environment of the I_{16}^{2-} subunit of Cp*CrI$_{5.5}$ (Cp* groups omitted for clarity).

in both the subunits of 2 (2.71 Å). The strands of the polymer fit together such that an "I$_3$···I" component lies directly above a Cp* ligand of an adjoining strand.

Structure of Cp*CrI$_{5.5}$ (3). On the basis of the crystallographic study this complex is formulated as $[Cp^*_2Cr_2(\mu\text{-}I)_3]_2[I_{16}]$ (Figure 3). The Cr–I distances [2.69 (1) Å] are nearly identical with those in 2. The cations display quite short Cr–Cr distances [3.00 (1) Å], which can be compared to the Cr–Cr distances in $Cr_2(\mu\text{-}Br)_3Br_6^{3-}$ (3.31 Å)[20] and $Cr_2(\mu\text{-}Cl)_3Cl_6^{3-}$ (3.12 Å).[21] The short Cr–Cr distance in 3 implies metal–metal bonding, unprecedented for a $[Cr^{III}]_2$ species.[22] The μ-I···μ-I distances within cations fall in the range 3.790 (2)–3.909 (3) Å, within the sum of van der Waals distances for iodine. This suggests the possibility that the bond between the Cr(III) centers is influenced by iodine–iodine repulsions. A trigonometric calculation (for r_{Cr-I} = 2.70 Å) shows that the μ-I···μ-I distances would contract to 3.55 Å if the Cr–Cr distance were nonbonding at 3.50 Å. In the case of $[Ti_2Cl_6(\mu\text{-}Cl)_3]^-$,[23] the bridging Ti–Cl distances average 2.50 (3) Å and the nonbonding Ti(IV) centers are separated by ≥3.420 (7) Å resulting in very short μ-Cl···μ-Cl contacts of 3.115 (10)–3.182 (8) Å.[24] The organometallic cation in 3 is surrounded by the unique polyiodide anion I_{16}^{2-} (Figure 4). These dianions are built up of two roughly planar $(I_2)_3I^-$ subunits bridged by an I$_2$, i.e., $\{(\mu\text{-}I_2)[(I_2)_3I]_2\}^{2-}$. The I–I distances within this cluster dianion are all ≤3.502 (3) Å.

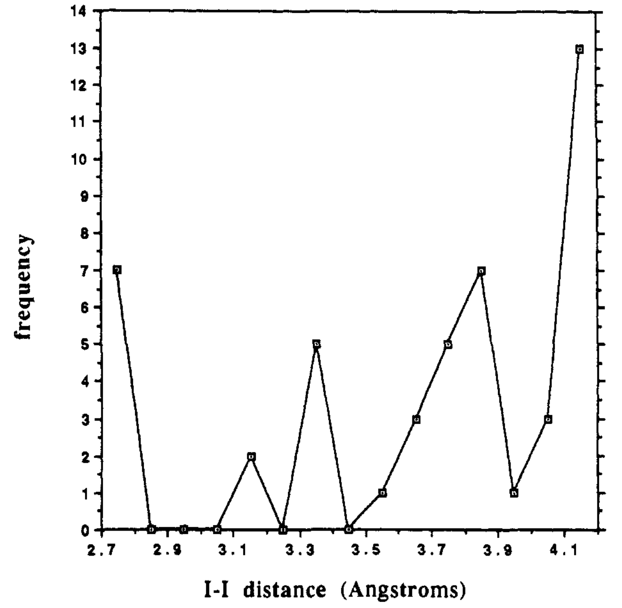

Figure 5. Histogram of I···I distances in Cp*CrI$_{5.5}$ per formula unit.

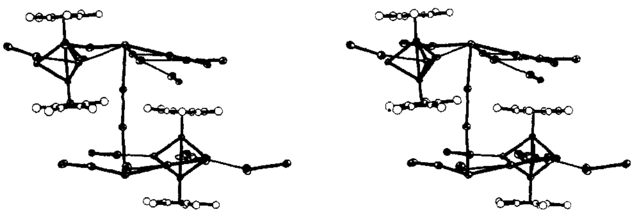

Figure 6. Stereoscopic packing diagram for Cp*CrI$_{5.5}$.

Perhaps the most striking structural aspect of 3 though is the inorganic latticework. Between the I_{16}^{2-} "spindles" there are many significant I···I contacts in the range of 3.643 (3)–3.824 (3) Å. The range of I···I contacts in 3 is shown in a histogram of the crystallographic data (Figure 5). The distances for the "I$_2$" subunits appear as a grouping of contacts around 2.75 Å, while the I$_2$···I$^-$ distances are grouped around 3.3 Å. Interionic contacts range from ~3.6 to 3.9 Å, just below the van der Waals radius of iodine at 4 Å. The I···I contacts define a ruffled layer structure in the *b*–*c* plane (Figure 6). The $[Cp_2^*Cr_2(\mu\text{-}I)_3]^+$ cations are incorporated into the polyiodide sheets through a sereis of Cr$_2$I$_3$···I contacts in the range of 3.700 (3)–3.85 (3) Å. Thus, 20 of the 22 iodine atoms in the formula unit comprise these ruffled sheets. The central I$_2$ moieties of the I_{16}^{2-} spindles interconnect the sheets, and the bulky Cp*Cr fragments fill the galleries between the I$_2$ pillars.

Discussion

At the outset of this project we had predicted that Cp*CrI$_3$, if it could be prepared, would not be a chromium(IV) complex.

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(19) The Ir–Ir distance for $[Cp^*IrI_2]_2$ is 4.072 (1) Å: Churchill, M. R.; Julis, S. A. *Inorg. Chem.* **1979**, *18*, 1215.

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(22) Cr(III)–Cr(III) bonds are very rare; see: Cotton, F. A.; Walton, R. A. *Multiple Bonds between Metal Atoms*; John Wiley and Sons: New York, 1982; p 235. Note that Cp$_4$Cr$_4$S$_4$ has a diamagnetic ground state: Eremenko, I. L.; Nefedov, S. E.; Pasynskii, A. A.; Orazsakhatov, B.; Ellert, O. G.; Struchkov, Yu. T.; Yanovsky, A. I.; Zagorevsky, D. V. *J. Organomet. Chem.* **1989**, *368*, 185, and references therein.

(23) Kistenmacher, T. J.; Stucky, G. D. *Inorg. Chem.* **1971**, *10*, 122.

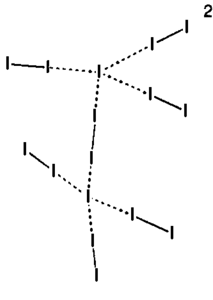
(24) Another example is $[\{Ir(I)_2(PR_3)_2\}_2(\mu\text{-}I)_3]^+$ wherein the Ir centers are separated by more than 3.5 Å: Nolte, M. J.; Singleton, E.; van der Stok, E. *Acta Crystallogr.* **1978**, *34B*, 1684.

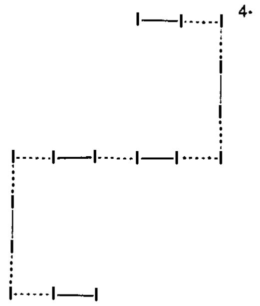
We discovered, however, that the addition of very large excesses of iodine leads to the abstraction of I^- (eq 1).

$$7I_2 + 2[Cp^*CrI(\mu\text{-}I)]_2 \rightleftarrows 2Cp^*_2Cr_2(\mu\text{-}I)_3^+ + I_{16}^{2-} \quad (1)$$

The structure of **2** shows how the added iodine can interact with the coordinated iodide in **1** leading eventually to $Cp^*_2Cr_2(\mu\text{-}I)_3^+$. In the final product, the I^- is sequestered by the formation of a stable, weakly basic polyiodide anion. The Cr–Cr distance in **3** is contracted by ca. 0.5 Å compared to those in **2**. The reduced ^1H NMR chemical shift and the narrowed line width of the signal also indicates significant pairing of the d electrons. The NMR and crystallographic data point to a Cr···Cr bonding interaction in $Cp^*_2Cr_2(\mu\text{-}I)_3^+$, but this cation merits further characterization[25] since **3** itself is thermal sensitive.

The complexation of I^- by four I_2 ligands is unprecedented but represents an extension of the "T"-bonding motif observed in I_9^-.[26] It is interesting to note that our I_{16}^{2-} cluster is of the same nuclearity but considerably different structure as that of I_{16}^{4-}:





Conclusion

The dianion I_{16}^{2-} is a new and structurally unusual polyiodide cluster. It was prepared by the abstraction of coordinated iodide using iodine as a Lewis acid. The abstraction of coordinated main-group (anionic) ligands with iodine may be a useful synthetic procedure applicable to other systems.[27] We have also shown that iodine-rich phases such as **3** can form unusual supramolecular inorganic matrices. This network is intermediate in character between traditional molecular crystals and covalently "cross-linked" solids. Organometallic polyiodides are structurally and electronically novel compounds that merit further systematic study.[28] Lastly, $[Cp_2^*Cr_2(\mu\text{-}I)_3]^+$ features an unusual example of bonding between Cr(III) centers.[29]

Experimental Section

Synthesis. All manipulations were carried out under a nitrogen atmosphere utilizing standard Schlenk-like and drybox techniques. Solvents were distilled under nitrogen from appropriate drying agents (hexanes, Na/K; CH_2Cl_2, P_4O_{10}; CH_3CN, CaH_2; Et_2O, Na/benzophenone). Iodine (Mallinckrodt), zinc (Aldrich), and mercury (Bethlehem) were used as received, and $[Cp^*Cr(CO)_2]_2$ was prepared according to the literature procedure.[30] Solvents for NMR spectra were vacuum distilled from P_4O_{10} ($CDCl_3$; Aldrich) and stored over 4-Å molecular sieves.

Table I. Selected Distances and Angles[a] for $\{[Cp^*Cr(I_3)(\mu\text{-}I)]_2\cdot[Cp^*CrI(\mu\text{-}I)]_2\}_n$

	Distances, Å		
I3–I4	3.542 (1)	I4–I5	2.754 (1)
I5–I6	3.339 (1)	I1–Cr1	2.712 (2)
I3–Cr1	2.672 (2)	I1–Cr1[b]	2.723 (2)
I2–Cr2	2.718 (2)	I6–Cr2	2.680 (2)
I2–Cr2[c]	2.712 (2)	Cr1–Cp1	1.89 (1)
Cr2–Cp2	1.89 (1)	Cr1–Cr1[b]	3.771 (3)
Cr2–Cr2[c]	3.654 (3)		
	Angles, deg		
Cr1–I1–Cr1[b]	87.86 (6)	Cr2–I2–Cr2[c]	84.58 (5)
I4–I3–Cr1	129.71 (5)	I3–I4–I5	173.85 (4)
I4–I5–I6	166.88 (5)	I5–I6–Cr2	111.10 (5)
I1–Cr1–I3	95.35 (6)	I1–Cr1–I1[b]	92.14 (6)
I1–Cr1–Cp1	122.5 (4)	I3–Cr1–I[b]	93.52 (6)
I3–Cr1–Cp1	123.4 (4)	Cp1–Cr1–I1[b]	121.9 (3)
I2–Cr2–I6	92.33 (6)	I2–Cr2–I2[c]	95.42 (6)
I2–Cr2–Cp2	122.0 (4)	I6–Cr2–I2[c]	93.75 (5)
I6–Cr2–Cp2	123.9 (4)	Cp2–Cr2–I2[c]	121.6 (4)

[a] Cp1,2 represents the cyclopentadienyl centroid for Cr1,2. [b] Equivalent position (−*x*, −*y*, 1 − *z*). [c] Equivalent position (1 − *x*, −*y*, −*z*).

$\{Cp^*CrI_3\}_n$ (2). A solution of iodine (324 mg, 1.3 mmol) in 20 mL of CH_2Cl_2 was added to $[Cp^*Cr(CO)_2]_2$ (200 mg, 0.4 mmol) in 20 mL of CH_2Cl_2, venting the evolved CO through an oil bubbler. The green reaction mixture was allowed to stir 1 h and then the solvent removed by evaporation in vacuo. The resulting solid was extracted with 20 mL of CH_2Cl_2, the filtrate was reduced to 1 mL, and precipitation was induced by adding 30 mL of Et_2O. The red supernatant containing $Cp^*Cr(CO)_3I$ was removed and the resulting microcrystalline solid washed twice more with 1 mL of CH_2Cl_2 followed by 30 mL of Et_2O. The yield was 54% (250 mg). Anal. Calcd for $C_{10}H_{15}CrI_3$: C, 21.15; H, 2.66; I, 67.03. Found: C, 21.11; H, 2.66; I, 67.35. Variations in reaction concentrations and time did not increase the yield of **2**. The monoiodide decomposes in solution at room temperature within a day.

$[Cp^*CrI_2]_2$ (1). An excess of Zn granules (140 mg, 2 mmol) was amalgamated in ca. 5 g of Hg under 10 mL of CH_2Cl_2. To this was added a solution of Cp^*CrI_3 (200 mg, 0.4 mmol) in 20 mL of CH_2Cl_2. the initially green solution turned blue within 30 min. After 2 h, the reaction solution was filtered through a fine fritted-glass Schlenk filter. The solvent was removed in vacuo and the resulting solid extracted with 35 mL of toluene. The toluene was removed in vacuo and the solid washed with three 5-mL portions of Et_2O. Yield was 84% (130 mg). Anal. Calcd for $C_{10}H_{15}CrI_2$: C, 27.23; H, 3.43; Cr, 11.79. Found: C, 27.25; H, 3.45; Cr, 11.72. When a 5 mM solution of **1** in CH_2Cl_2 was exposed to 1 equiv of O_2, the initial blue color immediately turned green and then over ca. 10 min turned to the final color of yellow-brown. Removal of the solvent at room temperature in vacuo resulted in iodine in the liquid nitrogen trap. Extraction of the solids with toluene and then CH_2Cl_2, and subsequent examination of the products by ^1H NMR, indicated **2** along with unknown products.

$Cp^*CrI_{5.5}$ (3). Samples were obtained via two methods:

(A) A solution of Cp^*CrI_3 with a slight excess of I_2 (ca. 1.5 equiv of I_2) in CH_2Cl_2 was prepared. Solvent evaporation at room temperature resulted in thermally unstable product, which slowly lost varying amounts of I_2 unless stored at −25 °C.

(B) Preparation of a solution as in (A) followed by slow crystallization afforded the complex in thermally stable platy crystals. These could be stored at room temperature if collected unbroken or otherwise stored at −25 °C. Anal. Calcd for $C_{10}H_{15}CrI_{5.5}$: C, 13.57; H, 1.71. Found for two determinations: C, 14.79/14.65; H, 1.88/1.84.

Physical Measurements. Proton NMR spectra were recorded at ca. 20 mM sample concentrations (unless otherwise indicated) at 20 °C on a 200-MHz Varian XL-200 FT-NMR spectrometer. Microanalyses were carried out by the School of Chemical Sciences (SCS) Microanalytical Laboratory. Structural determinations were perforemd by the SCS X-ray Crystallography Center.

Structural Determination of Cp^*CrI_3. The structure was determined from a crystal obtained by slow cooling to −25 °C of a CH_2Cl_2 solution. The dark opaque platy crystal selected (0.2 × 0.5 × 0.6 mm) was mounted under an inert atmosphere inside a 0.5-mm thin-walled, tapered

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Table II. Selected Intramolecular Distances and Angles for $[Cp^*_2Cr_2(\mu\text{-}I)_3]_2[I_{16}]$

Distances, Å			
I7–I8	2.771 (3)	I8–I9	3.124 (3)
I9–I10	3.399 (2)	I10–I11	2.732 (2)
I11–I12	3.380 (2)	I12–I13	3.107 (3)
I13–I14	2.786 (3)	I9–I15	3.336 (3)
I15–I16	2.735 (3)	I9–I17	3.388 (3)
I17–I18	2.725 (3)	I12–I19	3.319 (3)
I19–I20	2.739 (3)	I12–I21	3.502 (3)
I21–I2	2.719 (3	I1–Cr1	2.700 (4)
I2–Cr1	2.699 (4)	I3–Cr1	2.684 (4)
I1–Cr2	2.690 (4)	I2–Cr2	2.707 (4)
I3–Cr2	2.673 (4)	Cr1–Cr2	3.012 (5)
I4–Cr3	2.694 (4)	I5–Cr3	2.684 (4)
I6–Cr3	2.702 (4)	I4–Cr4	2.701 (4)
I5–Cr4	2.672 (4)	I6–Cr4	2.690 (4)
Cr3–Cr4	3.001 (5)	Cr1–Cp1[a]	1.85 (2)
Cr2–Cp2	1.86 (2)	Cr3–Cp3	1.87 (2)
Cr4–Cp4	1.86 (2)		
Angles, deg			
Cr1–I1–Cr2	67.9 (1)	Cr1–I2–Cr2	67.7 (1)
Cr1–I3–Cr2	68.4 (1)	Cr3–I4–Cr4	67.6 (1)
Cr3–I5–Cr4	68.2 (1)	Cr3–I6–Cr4	67.6 (1)
I7–I8–I9	173.94 (9)	I8–I9–I10	80.02 (6)
I8–I9–I15	77.72 (6)	I8–I9–I17	138.30 (7)
I10–I9–I15	85.84 (6)	I10–I9–I17	75.59 (6)
I15–I9–I17	132.47 (7)	I9–I10–I11	174.68 (9)
I10–I11–I12	172.05 (9)	I11–I12–I13	94.48 (6)
I11–I12–I19	79.57 (6)	I11–I12–I21	73.62 (6)
I13–I12–I19	77.38 (6)	I13–I12–I21	141.50 (7)
I19–I12–I21	133.06 (7)	I12–I13–I14	176.34 (8)
I9–I15–I16	177.36 (8)	I9–I17–I18	170.87 (9)
I12–I19–I20	177.81 (9)	I12–I21–I22	169.74 (9)
I1–Cr1–I2	89.2 (1)	I1–Cr1–I3	92.6 (1)
I1–Cr1–Cr2	55.9 (1)	I1–Cr1–Cp1	124.9 (8)
I2–Cr1–I3	93.1 (1)	I2–Cr1–Cr2	56.3 (1)
I2–Cr1–Cp1	124.8 (9)	I3–Cr1–Cr2	55.6 (1)
I3–Cr1–Cp1	122.7 (8)	Cr2–Cr1–Cp1	178.3 (8)
I1–Cr2–I2	89.2 (1)	I1–Cr2–I3	93.0 (1)
I1–Cr2–Cr1	56.2 (1)	I1–Cr2–Cp2	124.3 (7)
I2–Cr2–I3	93.2 (1)	I2–Cr2–Cr1	56.0 (1)
I2–Cr2–Cp2	125.8 (7)	I3–Cr2–Cr1	56.0 (1)
I3–Cr2–Cp2	121.9 (7)	Cr1–Cr2–Cp2	177.7 (7)
I4–Cr3–I5	92.4 (1)	I4–Cr3–I6	90.5 (1)
I4–Cr3–Cr4	56.3 (1)	I4–Cr3–Cp3	124.0 (7)
I5–Cr3–I6	92.5 (1)	I5–Cr3–Cr4	55.7 (1)
I5–Cr3–Cp3	122.7 (8)	I6–Cr3–Cr4	56.0 (1)
I6–Cr3–Cp3	125.3 (8)	Cr4–Cr3–Cp3	178.3 (8)
I4–Cr4–I5	92.5 (1)	I4–Cr4–I6	90.6 (1)
I4–Cr4–Cr3	56.1 (1)	I4–Cr4–Cp4	122.6 (8)
I5–Cr4–I6	93.0 (1)	I5–Cr4–Cr3	56.1 (1)
I5–Cr4–Cp4	123.4 (8)	I6–Cr4–Cr3	56.4 (1)
I6–Cr4–Cp4	125.4 (8)	Cr3–Cr4–Cp4	178.2 (8)

[a] Cp1,4 represents the cyclopentadienyl centroid for Cr1,4.

glass capillary. Data collection was performed at 26 °C on a Syntex $P2_1$ automated four-circle diffractometer with graphite crystal monochromated molybdenum radiation [λ(K$\bar{\alpha}$) = 0.71073 Å].

The sample had well-developed faces but there were a few attached crystallites that could not be removed without damage to the parent crystal. A unique set of 15 reflections was carefully selected and centered to determine cell parameters [monoclinic $P2_1/c$; a = 15.658 (2), b = 8.504 (1), c = 23.242 (4) Å; β = 102.48 (1)°; V = 3021.7 (9) Å^3; Z = 2; ρ_{calc} = 2.497]. From 4863 measured, 4177 unique intensites were processed resulting in 3014 observed reflections with $I > 2.58\sigma(I)$. Total crystal exposure time was 51.59 h. The data were corrected for anomalous dispersion, Lorentz, and polarization effects and numerically corrected for absorption (transmission factor range, 0.358–0.078). The crystal was larger than ideal (equidimensional, 0.3-mm diameter), but the absorption correction eliminated nonpositive-definite thermal tensors. The only apparent consequence of this large crystal volume was the loss of 56 strong reflections that flooded the counting chain. Correction for crystal decay was also applied (<12%).

The structure was solved by direct methods (SHELXS-86); correct positions for the iodine and chromium atoms were deduced from an E map. Subsequent least-squares difference Fourier calculations gave positions for the remaining non-hydrogen atoms. Hydrogen atoms were included as fixed contributors in idealized positions. Non-hydrogen atoms were refined with anisotropic thermal coefficients and a group isotropic thermal coefficient was varied for the hydrogen atoms. Selected distances and angles are provided in Table I. The highest peaks in the final difference Fourier map (range: +0.86 > e/Å^3 > −0.86) were deemed insignificant. A final analysis of variance between observed and calculated structure factors showed slight dependence upon sin (θ); R = 0.039, R_w = 0.041.

Structural Determination of Cp*CrI$_{5.5}$. The structure was determined from a crystal grown by slow cooling of a CH_2Cl_2 solution of {Cp*CrI$_3$ + 1.5I$_2$}. The dark opaque tabular crystal selected (0.1 × 0.2 × 0.2 mm) was mounted with oil (Paratone-N, Exxon) to a thin glass fiber at −25 °C. Data collection was performed at −75 °C on an Enraf-Nonius CAD4 automated κ-axis diffractometer using graphite monochromated molybdenum radiation [λ(K$\bar{\alpha}$) = 0.71073 Å].

The sample had damaged faces and a few attached crystallites. The determined cell parameters were a = 14.744 (2), b = 22.864 (4), c = 23.267 (5) Å; β = 93.77 (2)°; V = 7827 (4) Å^3; Z = 4; ρ_{calc} = 3.005. From 11 844 measured, 10 854 unique intensities were processed in the monoclinic space group $P2_1/c$ resulting in 6153 observed reflections with $I > 2.58\sigma(I)$. Total crystal exposure time was 88.37 h. The data were corrected for anomalous dispersion, Lorentz, and polarization effects and numerically corrected for absorption (transmission factor range, 0.414–0.154).

The structure was solved by direct methods (SHELX-86); correct positions for the iodine atoms were deduced from an E map. Subsequent least-squares difference Fourier calculations gave positions for the chromium and carbon atoms. Hydrogen atom contributions were not included in structure factor calculations. In the final cycle of least squares, iodine and chromium atoms were refined with anisotropic thermal coefficients and carbon atoms were refined with independent isotropic thermal coefficients. Selected intramolecular distances and angles are provided in Table II. The highest peaks in the final difference Fourier map (range +1.60 > e/Å^3 > −1.51) were in the vicinity of the iodine atoms. No systematic errors were observed; R = 0.054, R_w = 0.063.

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Supplementary Material Available: Tables of thermal parameters (for **2** and **3**), calculated hydrogen atom positions (for **2**), intermolecular distances (for **3**), and positional parameters (for **2** and **3**) (7 pages); final observed and calculated structure factors for **2** and **3** (39 pages). Ordering information is given on any current masthead page.