

A Dichromium(II) Bis(η^8 -pentalene) Double-Sandwich Complex with a Spin Equilibrium: Synthetic, Structural, Magnetic, and Theoretical Studies

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Received November 15, 2007

The new bis(pentalene) complex $\text{Cr}_2(\eta^5:\eta^5\text{-C}_8\text{H}_4^{1,4\text{-Si}^i\text{Pr}_3})_2$ has been synthesized and characterized; it is found to exhibit paramagnetism at room temperature, and solid-state magnetic studies show that the dimer is best modeled as containing a pair of antiferromagnetically interacting $S = 1/2$ centers with the separation between the singlet ground state and triplet excited state being 2.23 kJ mol^{-1} . Structural data show a Cr–Cr distance of $2.2514(15) \text{ \AA}$, consistent with a strong metal–metal interaction. The bonding has been further investigated by density functional, hybrid, and CASPT2 methods. The metal–metal interaction is best described by a double bond with each metal having an 18-electron count. Theory predicts the singlet and triplet states to lie close in energy but puts the triplet state at a slightly lower energy than the singlet. The energy difference predicted by CASPT2 is closest to the experimental value.

Introduction

The pentalene dianion $\text{C}_8\text{H}_6^{2-}$, an eight-membered 10π -aromatic, has been shown to be a ligand of high versatility in organometallic chemistry, with its bicyclic multihaptic framework stabilizing both *syn*- and *anti*-bimetallics and monometallic compounds via a bent η^8 -coordination mode.¹ The planar π -system is of great interest for the design of conducting “nanowires”.^{2,3} However, its ability to promote strong metal–metal bonding in compounds such as $\text{Mo}(\eta^5:\eta^5\text{-C}_8\text{H}_4^{1,4\text{-Si}^i\text{Pr}_3})_2$ and $[\text{V}(\text{Cp})]_2[\eta^5:\eta^5\text{-C}_8\text{H}_6]$ is also of great interest^{4,5} and has not yet been comprehensively investigated. The subject of metal–metal bonding has fascinated inorganic chemists for decades, and recent findings, such as a 5-fold bonding interaction found between two chromium(I) centers, clearly demonstrate that there are still important discoveries to be made in this area.⁶

Katz et al. first synthesized double-sandwich compounds of the type $\text{M}_2\text{bis}(\text{pentalene})$ for $\text{M} = \text{Co}$ and Ni , for which they proposed a twin metallocene-type environment ($\eta^5:\eta^5$), although

this could not be confirmed by single-crystal X-ray methods.^{7,8} Further work in our laboratory using the 1,4-bis(tri-isopropylsilyl) pentalene derivative has allowed synthesis and structural characterization of the corresponding compounds of Mo, Rh, Pd, and Mn.^{4,9,10} Symmetrical $\eta^5:\eta^5$ -bonding is found for the Mo, Rh, and Pd bimetallics, supported by a variable metal–metal bond order.^{4,9} Meanwhile, the Mn complex independently adopts an asymmetric structure with a low-spin center bound η^5 - and a high-spin center tending toward an η^1 -mode, with no significant metal–metal bonding.¹⁰

Herein we extend this series to the chromium analogue $\text{Cr}_2(\text{C}_8\text{H}_4^{1,4\text{-Si}^i\text{Pr}_3})_2$ and report its synthesis and characterization. Furthermore, magnetic and theoretical methods have been used in order to elucidate the strength of the metal–metal interaction within the Cr_2^{4+} unit.

Results and Discussion

Following a synthetic route similar to that used to synthesize the molybdenum(II) derivative,⁴ 2 equiv of $(\text{C}_8\text{H}_4^{1,4\text{-Si}^i\text{Pr}_3})[\text{K}]_2$ was added to a THF suspension of $\text{Cr}_2(\text{OAc})_4$. This gave, after workup, the corresponding bis(pentalene) complex $\text{Cr}_2(\text{C}_8\text{H}_4^{1,4\text{-Si}^i\text{Pr}_3})_2$ (**1**) in 21% yield; elemental analysis and mass spectrometry (EI) of this product were consistent with this formulation. The mass spectrum of the crude solids remaining, following isolation of **1**, gave no indication of the identity of the side products. No further products could be isolated.

Single crystals suitable for X-ray diffraction were obtained by slow cooling concentrated toluene solutions of **1** to $-30 \text{ }^\circ\text{C}$; the molecules crystallized in the monoclinic space group $\text{C}_{2/c}$.

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for **1**^a

Cr–Cr'	2.2514(15)	M(1)–Cr–M(2)	170.7(2)
Cr–M(1)	1.820(5)	C(2)–C(1)–C(4')	101.8(4)
Cr–M(2)	1.822(5)	C(2)–C(1)–Si(1)	121.0(3)
Cr–C(2)	2.136(5)	C(4)–C(1)–Si(1)	132.4(3)
Cr–C(14)	2.138(5)	C(3)–C(2)–C(1)	113.4(4)
Cr–C(1)	2.142(5)	C(2)–C(3)–C(4)	106.0(4)
Cr–C(15)	2.151(5)	C(4)–C(4)–C(3)	107.2(5)
Cr–C(16)	2.182(5)	C(4)–C(4)–C(1)'	111.1(5)
Cr–C(3)	2.186(5)	C(3)–C(4)–C(1)'	141.6(4)
Cr–C(17)'	2.203(5)	C(7)–C(5)–C(6)	110.0(5)
Cr–C(4)'	2.209(5)	C(7)–C(5)–Si(1)	114.9(4)
Cr–C(4)	2.288(5)	C(6)–C(5)–Si(1)	113.2(4)
Cr–C(17)	2.292(5)	C(2)–C(1)–C(4)'	101.8(4)

^a Symmetry transformations used to generate equivalent atoms: $-x, y, -z + 1/2$; M(1) and M(2) are the centroids of the C(1), C(2), C(3), C(4), C(4)', and C(14), C(15), C(16), C(17), C(17)' rings.

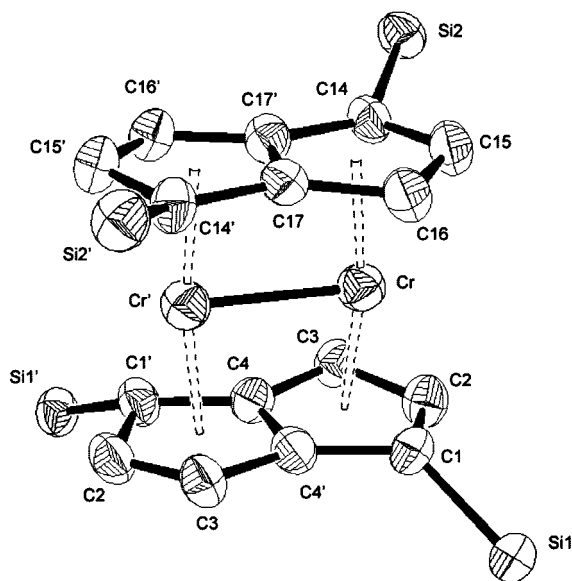


Figure 1. ORTEP view of **1** with thermal ellipsoids at 50% probability and all H atoms and triisopropylsilyl groups omitted for clarity. Primed atoms are generated by symmetry.

Important bond lengths and other structural parameters are given in Table 1, and a view is given in Figure 1.

The molecule is found to be a symmetrical double-sandwich and possesses a center of inversion located at the midpoint between the bridgehead carbons. The parallel arrangement of the planar pentalene ligands, with a staggered conformation of triisopropylsilyl substituents, is identical with the geometry of the Mo(II) analogue.⁴ The ligands are slightly twisted from an ideal eclipsed conformation by 11°; this parameter is similar to that found for the Mo(II) complex (10°).

The most noteworthy feature of **1** is the internuclear distance of the chromium atoms of 2.2514(15) Å; this is sufficiently close to imply significant metal–metal bonding and is found to be closer for chromium than for the molybdenum analogue (2.340(1) Å), in which a Mo=Mo double bond has been determined.⁴ Although this shorter distance may imply stronger bonding, it is to be expected from the smaller ionic radius of Cr²⁺ vs Mo²⁺. Shannon, in his comprehensive study of atomic radii, has not given parameters for Mo²⁺;¹¹ however, the trivalent ions reflect the increase in ionic radius for a first- vs a second-row transition metal: the ionic radii are reported for Cr³⁺ as 0.69 Å and for Mo³⁺ as 0.73 Å, respectively. In the bulk metal state, the interatomic distances vary from 2.498 Å

for Cr⁰ to 2.725 Å for Mo⁰. Therefore, comparatively, the increase in M–M distance in M₂(C₈H₄SiPr₃)₂ for M = Cr to Mo is rather small at 0.0886 Å. The variation in M–M distances for chromium tetracarboxylates is substantial and depends on carboxylate substituents and other co-ligands and, therefore, do not make a meaningful comparison with those for the molybdenum tetracarboxylates.¹²

Comparison with the Mo(II) reaction shows two immediate differences. First, water is found to be a necessary reagent in the synthesis of Mo₂(η⁵:η⁵-C₈H₄SiPr₃)₂, in order to selectively destroy an alternative (and, as yet, uncharacterised) isomer. This is not found to be necessary in the preparation of **1** either because the species is not present in the chromium reaction or because **1** crystallizes from the mixture cleanly. In fact, addition of water causes rapid decomposition of **1**, while the Mo(II) analogue is water-stable. **1** is also found to be paramagnetic in solution, to the extent that it could not be characterized by NMR methods, unlike the diamagnetic molybdenum compound. These initial findings suggest that the metal–metal interaction is changed in the progression from Mo to Cr in M₂(C₈H₄SiPr₃)₂. The related π-ligand-bridged Cr(II) species [(η-Cp)Cr]₂(μ-η⁵:η⁵-COT) has been described by Heck et al. as containing a formal Cr=Cr doubly bonded fragment and is found to be rigorously diamagnetic; crystallographic data are unfortunately lacking.¹³

The majority of Cr–Cr bonds in Cr₂⁴⁺ units are best treated theoretically by multiconfigurational methods.^{14–16} These dimers are often formulated as having a quadruple bond, with one σ, two π, and one δ interaction. In fact, the proportion of this configuration varies widely and can be as small as 12%. Cr–Cr distances vary considerably irrespective of bond order and have been found in tetracarboxylates from 1.83 Å to as much as 2.60 Å.^{12,17} The diamagnetism of these compounds is indicative of this bond order (although does not rule out a Cr=Cr double bond or strong antiferromagnetic coupling between the centers); however several of the carboxylates show weak paramagnetism at higher temperatures (also found in analogous molybdenum and tungsten tetracarboxylates).¹⁷ This is consistent with a singlet ground state and a low-lying excited triplet state (formed from a depopulation of an MO of δ-symmetry). The electronic configuration of Mo₂bis(pentalene) is meanwhile best described as (σ)²(π)²(δ)²(δ*)², leading to a formal double bond.¹⁸

Thus, the observed room-temperature paramagnetism of **1** is not consistent with a simple quadruple bond, and therefore it represents an unusual example of Cr–Cr bonding, which has been further investigated by magnetometry and theoretical methods.

The magnetism of **1** in the solid state was investigated by variable-temperature SQUID magnetometry from $T = 1.8$ to 300 K. Plots of molar susceptibility (χ) and effective magnetic moment (μ_{eff}) versus temperature are shown in Figure 2. The molar susceptibility plot χ vs T has been expanded for $T > 35$ K in Figure 3. Corrections for diamagnetism were incorporated by using Pascal's constants and by subtracting the measurements made for the empty sample holder.

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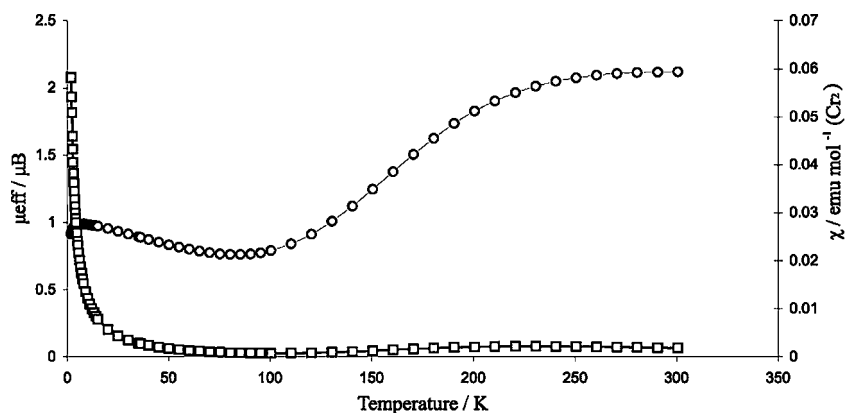


Figure 2. Plots of χ (blue squares) and μ_{eff} (green circles) vs T per dimer for **1** in the solid state from 1.8 to 300 K.

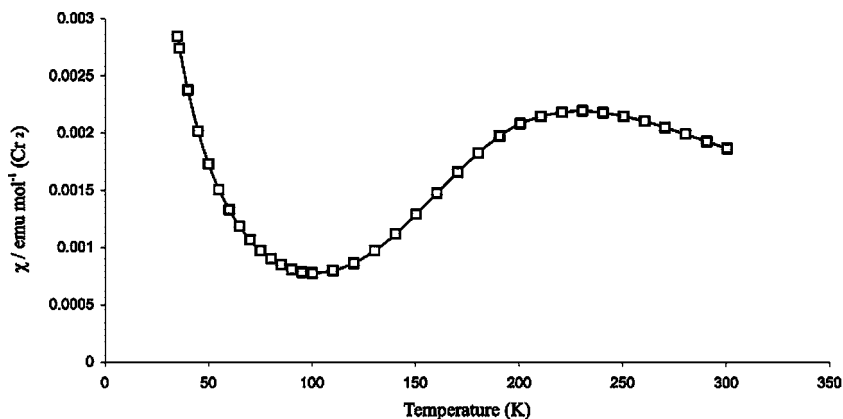


Figure 3. Expansion of high- T region of Figure 2: plot of molar susceptibility (χ) vs T per dimer for **1** from 35 to 300 K.

The values of μ_{eff} demonstrate that **1** does not obey the Curie–Weiss law in the temperature range studied and indicate a thermal population of an excited state from one of lower multiplicity with increasing temperature. The absolute values of μ_{eff} suggest this thermal equilibrium to be between a singlet ground state and a triplet excited state (for the dimer, i.e., one unpaired electron per Cr(II) center), as $\mu_{\text{spin-only}} = 2.83 \mu_{\text{B}}$ for a triplet state ($\mu_{\text{spin-only}} = 2\sqrt{S(S+1)}$); the room-temperature moment for **1** is $2.12 \mu_{\text{B}}$.

The shape of the χ vs T curve is also consistent with that expected for two $S = 1/2$ centers interacting antiferromagnetically in a dimeric compound, with a negative J parameter (J is defined as the isotropic interaction parameter).

The tail that occurs at very low temperatures is due to the presence of some noncoupled paramagnetic impurity (e.g., a mononuclear $S = 1$ Cr(IV) product such as CrO_2). Although the paramagnetic tail gives the appearance of indicating a large amount of impurity, this is not the case (*vide infra*).

Quantitative analysis of the data was achieved using the Bleaney–Bowers expression incorporating a fractional Curie–Weiss term representing an $S = 1$ paramagnetic impurity (eq 1).¹⁹ This equation was fitted to the data using least-squares analysis to give a good fit, with values of $J = -186.2 \text{ cm}^{-1}$, $g_1 = 2.02$, $g_2 = 2.08$, $\rho = 0.0514$, $\theta = -0.56 \text{ K}$, and TIP = $0.0005 \text{ cm}^3 \text{ mol}^{-1}$. The Weiss constant θ is small and negative, representing some antiferromagnetic interaction between the

impurity ions. The molar fraction of this impurity is shown to be very small ($\rho = 0.0514$).

$$\chi_{\text{m}} = \left(\frac{2N_{\text{A}}g_1^2\mu_{\text{B}}^2}{3k(T-\theta)} \right) (\rho) + \left(\frac{2N_{\text{A}}g_2^2\mu_{\text{B}}^2}{kT} \right) \left(\frac{e^{2J/kT}}{3e^{2J/kT} + 1} \right) (1-\rho) + \text{TIP} \quad (1)$$

The magnitude of the J value for **1** of -186 cm^{-1} (2.23 kJ mol^{-1}) represents an interaction of moderate strength between the unpaired spins on the d^4 centers. For comparison, the Cr(II) dimer-containing compounds $[(\text{Bu}_3\text{SiO})\text{Cr}]_2(\mu\text{-OSi}^t\text{Bu}_3)_2$,²⁰ $[(\text{Cp}^*)\text{Cr}(\mu\text{-Cl})]_2$,²¹ $[\text{Cr}(\text{Cp}^*)](\eta^5\text{-}\eta^2\text{-}\eta^2\text{-C}_8\text{H}_6)[\text{Cr}(\text{Cp}^*)]_2(\mu\text{-OMe})$,²² and $[(\text{Cp}^*)\text{Cr}(\mu\text{-Me})]_2$ ²¹ have interaction parameters of $J = -200$, -212 , -356 , and -471 cm^{-1} , respectively. The most similar

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Table 2. Intermetallic Distances and Room-Temperature Magnetic Moment Values for a Variety of Cr(II) Dimers, for Comparison with 1^a

compound	$d(\text{Cr}-\text{Cr})$ (Å)	μ_{eff} (298 K) (μ_{B})	J (cm^{-1})	ref
$\text{Cr}_2(\mu\text{-C}_8\text{H}_4\{1,4\text{-Si}^i\text{Pr}_3\}_2)_2$ (1)	2.25	2.1	-186	this work
$(\text{Cp}^*\text{Cr})_2(\mu\text{-Me})_2$	2.26	1.2	-471	21
$(\text{Cp}^*\text{Cr})_2(\mu\text{-Et})(\mu\text{-Ph})$	2.29	1.4		21
$[(\mu\text{-PhNSiMe}_2\text{OSiMe}_2\text{NPh})\text{Cr}]_2$	2.38	2.4		23
$\{[(2,6\text{-Me}_2\text{C}_6\text{H}_3)_2\text{nacnac}]\text{Cr}\}_2(\mu\text{-H})(\mu\text{-CH}_2\text{SiMe}_3)$	2.60	2.5		24
$\{[(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)_2\text{nacnac}]\text{Cr}\}_2(\mu\text{-Me})_2$	2.60	2.5		24
$\{[\mu\text{-}(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)_2\text{N}(\text{CH})\text{N}]\text{Cr}\}_2(\mu\text{-Cl})_2(\text{THF})_2$	2.61	3.3		25
$\{[(2,6\text{-Me}_2\text{C}_6\text{H}_3)_2\text{nacnac}]\text{Cr}\}_2(\mu\text{-H})_2$	2.62	1.2		24
$\{[(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)_2\text{nacnac}]\text{Cr}\}_2(\mu\text{-H})(\mu\text{-Ph})$	2.63	2.4		26
$\{[(\text{Ph}_2\text{PCH}_2\text{SiMe}_2)_2\text{N}]\text{Cr}\}_2(\mu\text{-H})_2$	2.64	2.1	-139	27
$(\text{Cp}^*\text{Cr})_2(\mu\text{-Cl})_2$	2.64	2.0	-212	21
$[\text{CpCr}(\mu\text{-OtBu})_2]$	2.65	2.6		28
$[(^i\text{Bu}_3\text{SiO})\text{Cr}]_2(\mu\text{-OSi}^i\text{Bu}_3)_2$	2.65	2.8	-200	20
$\{[(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)_2\text{nacnac}]\text{Cr}\}_2(\mu\text{-H})_2$	2.68	3.5		24
$[(\text{Cy}_2\text{N})\text{Cr}]_2(\mu\text{-NCy}_2)_2$	2.84	2.6		29
$\{[(\text{Ad})(3,5\text{-Me}_2\text{C}_6\text{H}_3)\text{N}]_2\text{Cr}\}_2[\mu\text{-N}(\text{Ad})(3,5\text{-Me}_2\text{C}_6\text{H}_3)]_2$	2.85	2.5		29
$[(^i\text{Pr}_2\text{N})\text{Cr}]_2(\mu\text{-N}^i\text{Pr}_2)_2$	2.87	2.3		30
$[(\mu\text{-}(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{NSiMe}_2\text{N}(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{SiMe}_2\text{O})\text{Cr}]_2$	2.93	3.8		23
$[(\mu\text{-OSiMe}_2\text{NPhSiMe}_2\text{NPh})\text{Cr}]_2(\text{THF})_2$	3.02	2.9		23
$[\text{Li}(\text{THF})_2(\mu\text{-}2,6\text{-Me}_2\text{C}_6\text{H}_3\text{O})_2\text{Cr}]_2(\mu\text{-}2,6\text{-Me}_2\text{C}_6\text{H}_3\text{O})_2$	3.09	3.2		31
$[(\text{THF})(\text{Ph}_2\text{N})\text{Cr}]_2(\mu\text{-NPh}_2)_2$	3.15	3.6		29
$\{[\mu\text{-Me}_2\text{PCH}_2\text{PMe}_2]\text{Cr}\}_2(\mu\text{-Cl})_2(\text{Cl})_2$	3.24	4.5		32
$\{[(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)_2\text{nacnac}]\text{Cr}\}_2(\mu\text{-Cl})_2$	3.43	3.4	-17	33
$\{[(\text{Ph}_2\text{PCH}_2\text{SiMe}_2)_2\text{N}]\text{Cr}\}_2(\mu\text{-Cl})_2$	3.64	6.5	-12	27

^a Values for the interaction parameter J given where available. Diamagnetic compounds, including the Cr(II) tetracarboxylates, have not been listed.

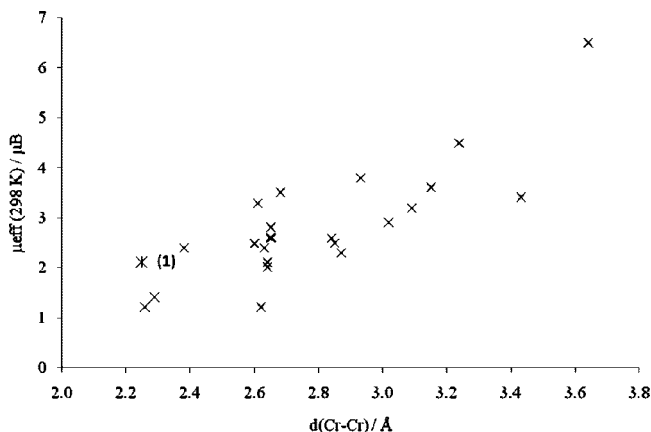


Figure 4. Plot of intermetallic separation $d(\text{Cr}-\text{Cr})$ vs room-temperature magnetic moment μ_{eff} for a variety of Cr(II) dimers listed in Table 2. Data point for compound **1** indicated with a vertical line through the cross.

correlations to **1** on this basis are therefore with $[(^i\text{Bu}_3\text{SiO})\text{Cr}]_2(\mu\text{-OSi}^i\text{Bu}_3)_2$ and $[(\text{Cp}^*)\text{Cr}(\mu\text{-Cl})_2]$; interestingly, we find the Cr–Cr bond distances to be significantly longer in these compounds: 2.658(13) and 2.642(3) Å vs 2.2514(15) Å in **1**.^{20,21}

Only a small number of dimeric chromium compounds have been fully analyzed by variable-temperature magnetic methods, and thus there are relatively few compounds with reported J values with which to compare **1**. More commonly reported is a single room-temperature effective magnetic moment μ_{eff} , and these values, along with the Cr–Cr interatomic distances, are shown in Table 2 for a range of Cr(II) dimers. Interaction parameter J is also given where available. Note that diamagnetic compounds, including the tetracarboxylates, have not been listed.

Wolczanski et al. have previously noted a proportionality between the effective moment μ_{eff} and $d(\text{Cr}-\text{Cr})$ in paramagnetic Cr(II) dimers,²⁰ and therefore we have taken the opportunity to plot these values for the compounds listed in Table 2, as shown in Figure 4. It can be seen that, although there is a relatively wide distribution of data points, there does appear to be an approximate increase in moment with separation of

the spin centers in space; that is, the moment is increasingly quenched the closer the chromium(II) atoms are found to each other. This is consistent with a description of antiferromagnetic coupling in these complexes as being a through-space phenomenon, mediated through orbitals that are pointed toward each other on adjacent centers (rather than, for example, a superexchange mechanism through bridging ligands) and an increased tendency to spin-pair in formal metal–metal bonds at shorter intermetallic distances.

We also find that **1** fits well into this correlation (marked in Figure 4). It can be seen that **1** contains a relatively strong interaction, as evidenced by the short Cr–Cr distance (the shortest plotted in Figure 4) and a relatively low value of μ_{eff} . Several assumptions are made in this hypothesis, however, as the description of the spin equilibria (e.g., considering the ground/excited states to be high-spin or low-spin) and formal metal–metal bonding will doubtless vary from compound to compound, depending on the nature of the ligands, etc. In the case of **1**, we find the spin equilibrium to be between a singlet ground state and a triplet excited state (*vide supra*). Studies on the electronic structure of **1** were consequently undertaken to further investigate the details of the bonding in this novel double-sandwich complex, including the level of metal–metal bonding within the Cr_2 unit.

Electronic Structure

Determining the nature of chromium–chromium bonds theoretically has proved very challenging, even for the “simple” tetracarboxylate chromium dimers, and has prompted Cotton to declare that “the nature of Cr–Cr bonding is an extremely difficult matter to deal with, whether in terms of MO calculations (however sophisticated) or in more empirical terms”.¹² Theoretical calculations using various methods have concluded that, at best, these dimers contain weak single Cr–Cr bonding, as the quadruply bonded configuration $\sigma^2\pi^4\delta^2$ represents such a small part of the wave function, ca. 12% in one study,¹³ dominant

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configurations usually take up >80% of the final wave function at the equilibrium distance. One review has described these compounds as containing little or no metal–metal bonding, but with very strong antiferromagnetic interactions mediated through the ligands to give a diamagnetic complex.³⁴ This is perhaps a little surprising considering the so-called “supershort” bonds with Cr–Cr distances as short as 1.828(2) Å (in Cr₂[2-MeO-5-MeC₆H₃]₄)³⁵ and surely only possible with some direct attractive force stronger than van der Waals interaction. It does indeed bring into question what factors differentiate “antiferromagnetic coupling” from a bone fide metal–metal bond. Very recently, an even shorter Cr–Cr distance of 1.8028(9) Å has been reported in the dimer Cr₂(*N,N'*-bis(2,6-diisopropylphenyl)-1,4-diazadiene), currently the shortest metal–metal bond known.³³ It should be noted that the Cr centers in this complex appear to be best described as monovalent, however, rather than divalent.

The experimental data on **1** raise several questions that lend themselves to computational investigations of the electronic structure and bonding. These include the paramagnetic nature of the compound, the bond order between the Cr atoms, and linked to that the best way of counting electrons in such η^5 : η^5 -pentalene compounds.

The orbital structure of a basic M₂(η^5 : η^5 -C₈H₆)₂ sandwich has been treated before, in particular in the context of the interpretation of the photoelectron spectrum of the Mo analogue of **1**.¹⁸ The orbital structure of Cr₂(η^5 : η^5 -C₈H₆)₂ (**I**), with *D*_{2h} symmetry in the singlet ground state, is shown in Figure 5, and isosurfaces for key orbitals are shown in Figure 6. A fragment calculation gives the principal contributions to the molecular orbitals (MOs) in terms of the MOs of the Cr₂ unit and the pentalene ligand. These are indicated in Figure 5 and quantified in Table 3.

The Cr₂⁴⁺ dimer has eight valence electrons. In the complex **I** they occupy four MOs that are principally metal in character, 10a_g, 6b_{1u}, 11a_g, and 8b_{3u}. These correlate with a configuration for Cr₂⁴⁺ of $\sigma_g^2 \pi_u^2 \delta_g^2 \delta_u^2$. Thus the formal bond order between the metals in an ionic counting scheme is 2. The δ_u orbitals mix to a certain extent with a σ_u orbital, but this does not change the bond order. Excitation of one electron from the 8b_{3u} HOMO to the 9b_{3u} LUMO to form a triplet state does not change the bond order, as the LUMO is also comprised of a mix of δ_u and σ_u orbitals. The configuration differs from that normally associated with complexed Cr₂⁴⁺ where a $\sigma_g^2 \pi_u^4 \delta_g^2$ and quadruple bonding between the metals is traditionally assumed, though, as discussed above, multiconfigurational methods give a superior description of the bonding. In the case of these pentalene sandwich compounds the metal–metal interaction is considerably perturbed by the two ligands.

The metal–ligand interaction occurs principally with the π_3 , π_4 , and π_5 MOs of the ligands. Of particular note are the 4a_u orbital, formed from δ_u and π_5 orbitals, and 8b_{2u}, formed from π_u and π_4 orbitals; however there is metal content in most of the high-lying valence orbitals.

The fragment calculation enables quantification of the occupancy of the Cr dimer orbitals in the complex. With the assumption that the σ_g , π_u , and δ_g orbitals are bonding and the σ_u , π_g , and δ_u orbitals are antibonding, the fractional occupancy

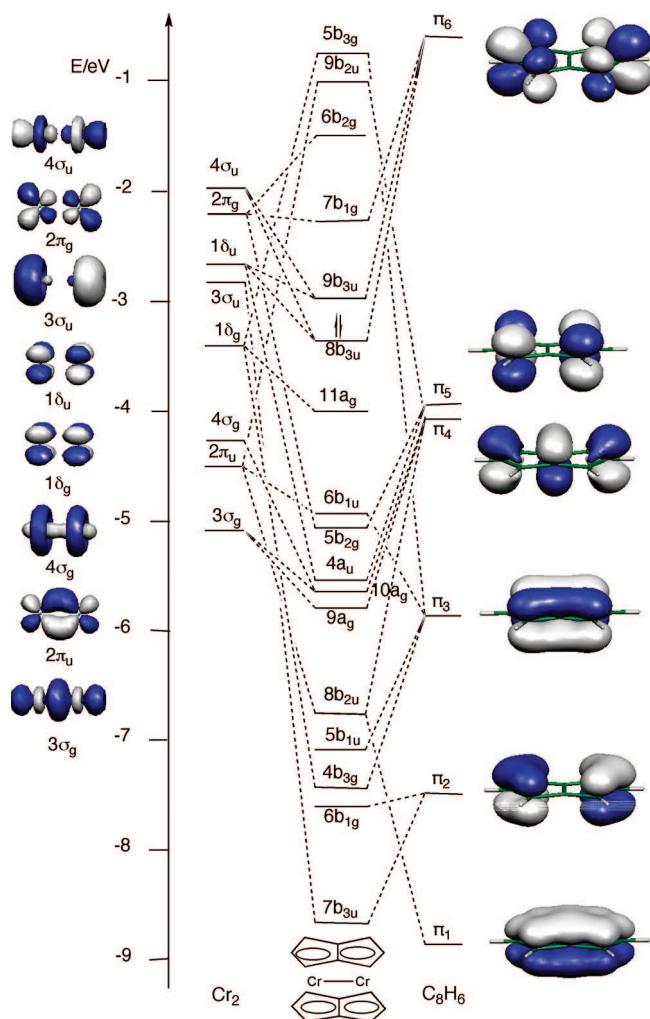


Figure 5. MO scheme for **I** (*S* = 0) showing the interactions of the Cr₂ fragment with the two pentalene ligands in *D*_{2h} symmetry. The labels for the Cr₂ fragment are given in the *D*_{∞h} symmetry.

leads to a bond order of 1.67. This can be compared with a similar calculation on the Mo analogue, which resulted in a bond order of 1.86.¹⁸ The higher ability of second-row transition metals to form metal–metal bonds is consistent with these relative values.

In a topological analysis of the electron density in **I**, Bader’s “atoms in molecules” approach³⁶ leads to a bond critical point (BCP) (3,−1) between the two chromium atoms with the electron density at the BCP $\rho(r) = 0.106$ e/a₀³ and the Laplacian $\nabla^2\rho(r) = 0.299$ e/a₀⁵. The high ellipticity (0.44) at the BCP shows a high deformation from the cylindrical symmetry—preferential accumulation of the electron density in one direction—and therefore a high π -character. This reflects the fact that the 6b_{1u} orbital is predominantly metal in character and forms a π -bond in the plane parallel to the pentalene ligands, whereas the 8b_{2u} orbital is predominantly ligand in character and ensures a lower occupancy of the Cr–Cr π -bond perpendicular to the ligand plane. To gain more information about the bonding in **I**, the Wiberg bond indices were calculated in a NBO analysis,³⁷ which leads to a bond order of 0.76.

Conventional electron counting for a metal dimer decrees an electron count of (36−2*n*) where *n* is the M–M bond order.

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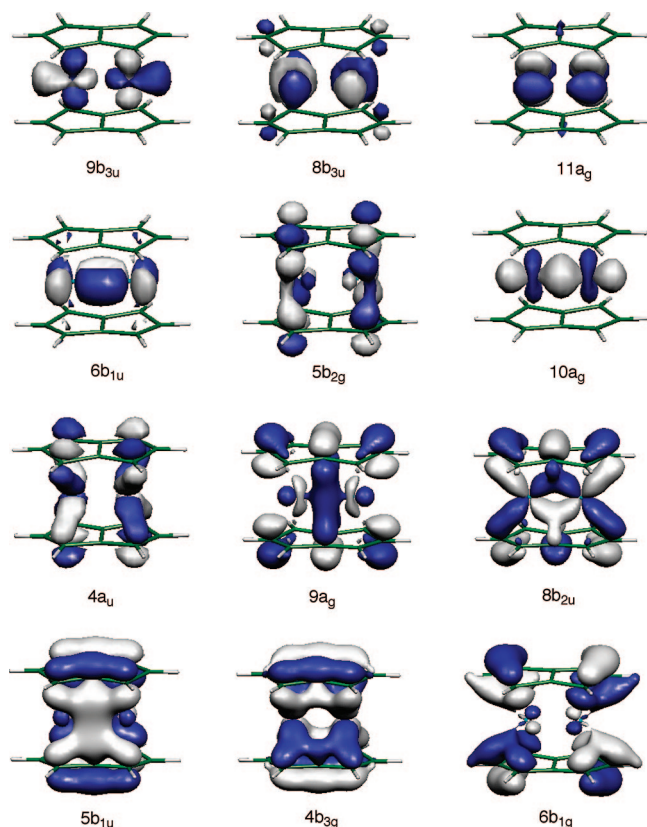


Figure 6. Isosurfaces for selected orbitals of **I**.

Table 3. MO Energies for **I** (D_{2h} , BP86, $S = 0$) Together with the Ligand Orbital (LO) Contributions from a Fragment Calculation

orbital	energy/eV	Cr ₂ (%) (LO)	C ₈ H ₆ (%) (LO)
9b _{3u}	-3.00	30 (1δ _u) 52 (4σ _u)	8 (π ₆)
8b _{3u}	-3.35	54 (1δ _u) 14 (4σ _u)	25 (π ₆)
11a _g	-3.87	75 (1δ _g)	
6b _{1u}	-4.70	78 (2π _u)	11 (π ₃)
5b _{2g}	-4.99	14 (2π _g)	83 (π ₅)
4a _u	-5.56	35 (1δ _u)	57 (π ₅)
10a _g	-5.60	35 (4σ _g) 34 (3σ _g)	25 (π ₄)
9a _g	-5.63	12 (3σ _g)	67 (π ₄)
8b _{2u}	-6.89	31 (2π _u)	45 (π ₄) 12 (π ₁)
5b _{1u}	-7.07		85 (π ₃)
4b _{3g}	-7.43	23 (1δ _g)	64 (π ₃)
6b _{1g}	-7.68		76 (π ₂)
7b _{3u}	-8.53	10 (3σ _u)	74 (π ₂)

Use of this rule would predict a bond order of 4 for the dimer, which is not the case. It is well established in the case of bridging hydrides, for example, that this simple rule breaks down. A bridging hydride is most consistently treated as donating two electrons to both metals. In an analogous manner, one can regard the $\eta^5:\eta^5$ -pentalene dianion as donating six electrons to each metal, or in a neutral counting scheme five electrons to each. The two metals are both within bonding distance of the two bridgehead carbons, and both share in the two electrons offered by these atoms. Under this counting regime, with the proposal of a double bond between the metals, both metals satisfy the 18-electron count. This rationalization accounts for the fact that these group 6 pentalene dimers show no tendency to coordinate extra ligands.

Various functionals and basis sets were used to model the structures and energies for the singlet and triplet states of **I** (Table

4). The geometry of **I** was optimized in D_{2h} symmetry; however the two pentalene units in **I** are deviated by about 10–14° from an eclipsed conformation in the crystal structure. A geometry optimization of **I** starting from a geometry similar to that found in the crystal structure of **I** and without any symmetry constraints leads to an optimized structure with D_{2h} symmetry. The energy minimum of that structure was proved by the absence of the imaginary frequencies in a frequency calculation.

Geometry optimization in ADF using the BP86 functional resulted in an overestimation of the Cr–Cr bonding and too short a distance in both the singlet (2.145 Å) and triplet (2.151 Å) spin states. In the quintet spin state the Cr–Cr distance is much longer (2.284 Å), but that spin state is also much higher in energy. The triplet spin state is the lowest in energy, although the singlet state lies only 11 kJ mol⁻¹ higher in energy. The quintet spin state is 41 kJ mol⁻¹ higher in energy than the triplet state. The change of the spin state from singlet to triplet leads to insignificant change in the Cr–Cr bond length as expected from the MO analysis. In order to test whether the spin state order was distance dependent, calculations were performed at a variety of fixed Cr–Cr distances, other structural parameters being optimized. The results are shown in Figure 7. The triplet state always lies below the singlet over the range of Cr–Cr values studied; above 2.4 Å the quintet state becomes the most stable.

Geometry optimizations of **I** in the singlet and triplet spin states with the hybrid B3LYP functional using a 6-31+G* basis set gave similar results. However, in this case the Cr–Cr distance in the triplet state is 2.212 Å, somewhat closer to the experimental value. However the triplet is again lower in energy by 8 kJ mol⁻¹. The singlet–triplet energy differences found by DFT and hybrid methods are small and in the same ballpark as that estimated experimentally; however, the ordering differs from that indicated by the magnetic measurements. It should also be remembered that the calculated values correlate most closely with the gas phase.

To examine whether neglect of the SiⁱPr₃ substituents had a significant effect on the structure, calculations were carried out on Cr₂{C₈H₄(1,4-SiH₃)₂ (**II**) using BP86/TZP. The optimized structure had eclipsed rings in both the singlet and triplet states and the Cr–Cr distances were found to be 2.148 and 2.153 Å, respectively. Thus introduction of the substituents has very little effect on the geometry of the core. We assume the rotation of the rings from the eclipsed geometry found by diffraction techniques is due to crystal packing forces.

The difference between experimental and calculated values of the bond length, coupled with the discrepancy of the predicted ground state from that found from magnetic measurements, suggests that **I** may not be accurately treated as a single configuration and is best described using multiconfigurational methods.

The relative CASPT2 energies of the singlet, triplet, and quintet spin states were computed at the singlet DFT/BP86-optimized geometry. At this geometry the triplet was found to be 0.003 kJ mol⁻¹ lower in energy than the singlet. The quintet lies 127 kJ mol⁻¹ higher in energy than the triplet. Both the singlet and triplet wave functions are single-determinantal. Selected bond distances (Cr–Cr bond distance, Cr–pentalene bond distance) for the singlet and triplet states were reoptimized at the CASPT2 level of theory. At their respective optimized geometries, the triplet was found to be lower in energy by 4.85 kJ mol⁻¹. The internuclear distance between the two chromium atoms is 2.19 Å for the singlet state and 2.16 Å for the triplet state.

CASPT2 calculations were performed starting also from the B3LYP geometries. At these geometries the Cr–Cr and Cr–

Table 4. Selected Experimental Distances (Å) for **1** and Those Calculated for **I** and **II** (energies (kJ mol⁻¹) are given relative to the $S = 0$ state)

parameter	BP86 I		BP86 II		B3LYP I		experimental 1
	$S = 0$	$S = 1$	$S = 0$	$S = 1$	$S = 0$	$S = 1$	
Cr–Cr	2.145	2.151	2.148	2.153	2.095	2.212	2.2514(15)
Cr–C _{bridge}	2.232	2.262	2.242	2.254	2.227	2.254	2.203–2.292
Cr–C _{α}	2.132	2.165	2.143	2.170	2.169	2.145	2.138–2.186
Cr–C _{β}	2.149	2.154	2.146	2.185	2.196	2.162	2.136–2.151
C _{bridge} –C _{bridge}	1.463	1.458	1.461	1.455	1.463	1.463	1.418–1.420
C _{bridge} –C _{α}	1.456	1.473	1.454	1.466	1.451	1.456	1.445–1.476
C _{α} –C _{β}	1.441	1.483	1.436	1.447	1.427	1.435	1.400–1.448
energy (kJ mol ⁻¹)	0	-11	0	-27	0	-10	

pentalene bond distances were optimized at the CASPT2 level of theory. These distances remain unchanged with respect to those obtained starting from the BP86 geometries. The singlet–triplet energy difference at this geometry is 2.57 kJ/mol.

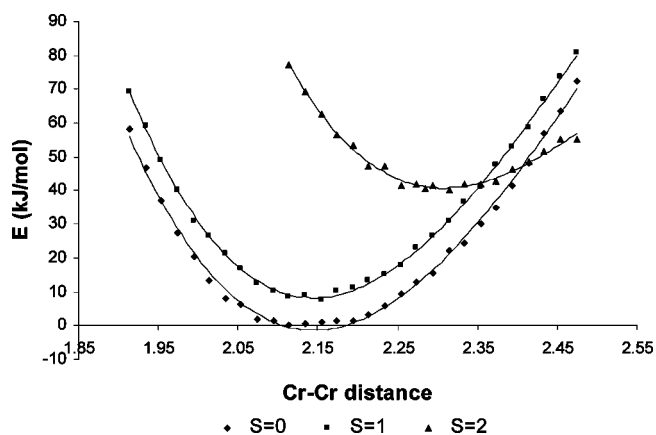
The various theoretical methods are in reasonable agreement and indicate that in the case of these Cr₂ dimers a single configuration gives a credible description of the metal–metal bonding.

Conclusions

In conclusion, Cr₂(η^5 : η^5 -C₈H₄^{SiPr₃})₂ is paramagnetic with a room-temperature magnetic moment of 2.12 μ_B , a value whose temperature dependence is consistent with two $S = 1/2$ centers interacting antiferromagnetically and a resulting thermal equilibrium between a singlet ground state and a triplet excited state. As a consequence, the Cr–Cr interaction in Cr₂(η^5 : η^5 -C₈H₄^{SiPr₃})₂, formally a Cr=Cr double bond, has a calculated bond order of 1.67. This is in marked contrast to the Mo analogue, which is rigorously diamagnetic, with a calculated bond order of 1.86 for the formally double bonded Mo–Mo interaction, a reflection of the established tendency for second- and third-row transition metal–metal bonded dimers to spin pair and to form stronger M–M bonds.

Experimental Methods

The reactions described below were conducted under purified argon using standard Schlenk double-manifold, high-vacuum or glovebox techniques. Solvents were predried over activated 5 Å molecular sieves or sodium wire and then distilled over potassium (tetrahydrofuran), sodium–potassium alloy (pentane), or sodium (toluene) under a slow passage of nitrogen. Deuterated solvents were dried over molten potassium and distilled. Elemental analyses were carried out at the University of North London. Mass spectra

**Figure 7.** Potential energy surface of **I** for singlet, triplet, and quintet spin states.

were recorded by Dr. Ali Abdul-Sada at University of Sussex, on a VG autospec Fisons instrument (electron impact ionization at 70 eV). NMR spectra were recorded using a Bruker Spectrospin AG 300DPX spectrometer operating at 300.13 MHz for ¹H measurements. The starting materials Cr₂(OAc)₄ and C₈H₄^{SiPr₃}[K]₂ were prepared according to literature procedures.^{38,39}

Cr₂(C₈H₄^{SiPr₃})₂ (1**).** To a suspension of Cr₂(OAc)₄ (86 mg, 0.25 mmol) in THF (30 mL) was added dropwise a solution of C₈H₄^{SiPr₃}[K]₂ (250 mg, 0.5 mmol) with stirring. Over the course of the addition the light orange suspension darkened to a cherry red; after 24 h stirring a mixture of white solids suspended in a very dark red solution was obtained. Removal of THF *in vacuo* and subsequent extraction (Celite) with pentane gave a dark brown solution. The solution was concentrated (30 mL) and recrystallized at -50 °C to give **1** as a black crystalline solid. Yield: 49 mg (0.0525 mmol), 21% yield based on Cr₂(OAc)₄. Anal. Calc (found) for C₅₂H₉₂Si₄Cr₂: C 66.90 (66.69), H 9.93 (10.14). MS (EI): *m/z* = 932 (M⁺, 100%), 785 (M⁺ - SiPr₃, 50%). ¹H NMR (C₆D₆, 293 K): NMR silent.

Crystal Structure Determination of 1. Data were collected at 173 K on a Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Crystal data: C₅₂H₉₂Cr₂Si₄, $M = 933.62$, monoclinic space group $C2/c$ (No.15), $a = 21.713(2)$ Å, $b = 13.2479(13)$ Å, $c = 21.2951(18)$ Å, $\alpha = 90^\circ$, $\beta = 118.579(4)^\circ$, $\gamma = 90^\circ$. $V = 5379.3(9)$ Å³, $Z = 4$, $D_{\text{calcd}} = 1.15$ Mg/m³, abs coeff = 0.53 mm⁻¹, $R(F; F^2 > 2\sigma) = 0.082$, $R_w(F^2; \text{all data}) = 0.132$, theta range for data collection 3.56 to 26.00°, largest diff peak and hole 1.31 and -0.54 e Å⁻³ (near Cr), reflections collected 15 523, independent reflections 5152 [$R(\text{int}) = 0.090$], reflections with $I > 2\sigma(I)$ 3539. Data collection KappaCCD, Program package WinGX, abs correction MULTISCAN, refinement using SHELXL-97, drawing using ORTEP-3 for Windows.

Computational Methods

The quantum chemical calculations were performed using density functional methods of the Amsterdam Density Functional (Version ADF2004)^{40–43} and Gaussian03⁴⁴ package. In the calculations performed with ADF the generalized gradient approximation was employed, using the local density approximation of Vosko, Wilk, and Nusair,⁴⁵ together with nonlocal exchange correction by Becke⁴⁶ and the nonlocal correlation corrections by Perdew.⁴⁷ TZ2P basis sets were used with triple- ζ accuracy sets of Slater-type orbitals, with two additional polarization functions added to all

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atoms. Relativistic corrections were made using the ZORA (zero-order relativistic approximation) formalism. The core electrons were frozen up to 1s for carbon and 2p for chromium. In the geometry optimization performed with the Gaussian package the hybrid-B3LYP^{48–53} functional was used with a 6-31+G* basis set. The Bader analysis was performed with the XAIM⁵⁴ program, for which the input file was generated with the Gaussian package using the BP86 functional.

Multiconfigurational quantum chemical calculations were performed using the complete active space method (CASSCF),⁵⁵ followed by second-order perturbation theory (CASPT2). The

orbitals formed by linear combinations of the Cr 3d orbitals and the C 2p orbital were included in the active space.⁵⁶ This added up to an active space formed of 10 electrons in 12 orbitals. Basis sets of the atomic natural orbital type were used for all atoms. For Cr, a primitive set 21s15p10d6f4g was contracted to 6s5p3d2f1g,⁵⁷ for C, a primitive set 10s6p3d was contracted to 3s2p1d,⁵⁸ and for H, a primitive set 7s3p was contracted to 2s1p.⁵⁹ The method has proven to be successful to study the spectroscopy of several systems containing transition metals⁶⁰ and actinides.⁶¹ The MOLCAS-7.0 package was employed.⁶²

Acknowledgment. We thank Dr. Charles Monroe for help with the magnetic studies, Dr. Ali Abdul Sada for mass spectrometry, and EPSRC for financial support. Part of this work was carried out using the facilities of the Oxford Supercomputer Centre. L.G. gratefully acknowledges support for this research from the Swiss National Science Foundation (grant no. 200021-111645/1). G.B. thanks the von Humboldt Foundation for a fellowship.

Supporting Information Available: A cif file giving information about the crystal structure. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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