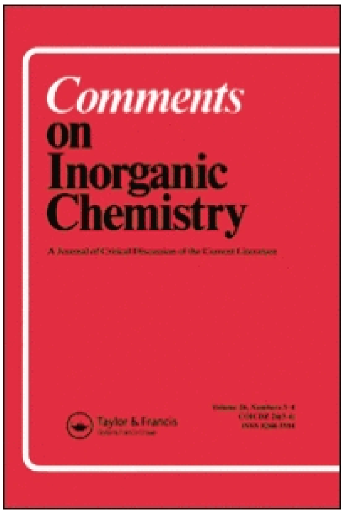

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Short and Supershort Cr-Cr Distances: A Vanishing Borderline Between Metal-Metal Bonds, Magnetic Couplings and Ligand Artifacts

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Short and Supershort Cr–Cr Distances: A Vanishing Borderline Between Metal–Metal Bonds, Magnetic Couplings and Ligand Artifacts

Dedicated to Prof. F. Basolo on the occasion of his 70th birthday.

The structural features of three classes of Cr(II) compounds (alkoxides, amides, aryls) are critically reviewed with the aim of investigating the role of ligand bridging interactions in the formation of short Cr–Cr quadruple bonds. A systematic failure of Cr–Cr bond formation is observed with either monodentate or bidentate ligands. Fairly short Cr–Cr contacts are easily elongated and dinuclear structures cleaved by simply coordinating a molecule of solvent either to chromium or to the alkali cation present in anionic chromates. Conversely, extremely short Cr–Cr contacts are almost invariably formed when particular bridging ligands with a three-center chelating geometry and the electronic configuration of an allylic system have been used. Comparison of the magnetic properties of two series of Cr(II) aryls and pyrrolyls, where the three center chelating geometries of the ligands have been progressively modified, indicated that three-center chelating ligands are able to determine the dimeric aggregation, the magnetic properties of chromium and ultimately the length of Cr–Cr contacts.

Key Words: *chromium, metal–metal bond, alkoxide, amide, aryl, dimers, clusters*

INTRODUCTION

The enormous complexity of the physical phenomena involved in the interaction between two transition metals of a dinuclear complex (metal–metal bond, antiferromagnetic exchange, ligand mediated superexchange, etc.)[1] is the target of continuous theoretical

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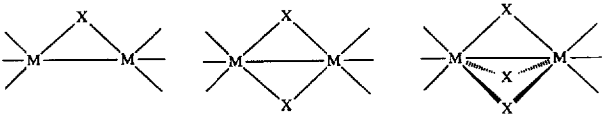
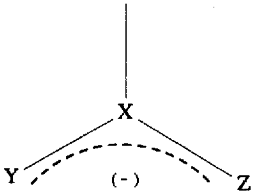
and experimental studies, due to the fact that understanding the nature of these phenomena is of fundamental importance in rationalizing the chemical behavior of clusters. In accordance with the present bonding theory, a short metal–metal contact observed in the crystal structure is symptomatic of a considerable *d*-orbital overlap and, provided the magnetic properties of the metal show an efficient magnetic coupling, the presence of direct metal–metal bond may be reasonably expected.[2] Today, single and multiple metal–metal bonds are well established, the strongest evidence of their existence being provided by the crystal structures of several complexes which showed short metal–metal distances as the shortest contacts existing between two monomeric fragments. The metal–metal bonding interaction is expected, in these cases, to provide the force and the energy necessary to hold together the dinuclear frame.



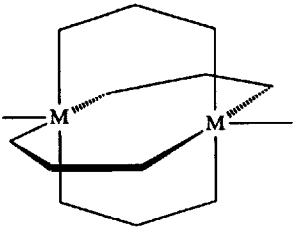
The nature of these bonds turns out to be more intriguing and elusive when one or more bridging ligands are placed in the region between the two transition metals. In these cases often encountered in both organometallic and coordination chemistry, it is impossible to decide whether the short intermetallic contact is a result of the tendency of the metal to form metal–metal bonds or of the ability of the bridging ligand to force the two transition metals to a close proximity. There is no doubt that bridging ligands have a unique ability to impose short, very short and supershort metal–metal distances. As an example of an extreme case, *supershort* Li–Li contacts (shorter than in both molecular Li_2 and metallic lithium) have been frequently observed in the crystal structure of several Li compounds,[3] where the occurrence of a Li–Li bond is obviously inconsistent in the context of the present bonding theory. On the other hand, this indicates that, at least in the case of Li derivatives, the molecular geometry is determined by the bridging ligands which are obviously able to prevail over the Li . . . Li electrostatic repulsions. Short metal–metal contacts are not peculiar only to lithium chemistry but are also often encountered in the chemistry of bridged Cu(I)[4] complexes where the d^{10} electronic configuration makes the existence of Cu–Cu bonds doubtful. Although *ab initio* calculations are in agreement with the existence of a certain degree of direct Cu–Cu bonding, there is general agreement that these interactions should be very weak and not likely able to preserve the dimeric structure in the absence of bridging ligands.[5] More examples are encountered in the chemistry of metals in the middle of the transition series, such as vanadium, where a considerably short vanadium–vanadium contact has been observed in a dimeric d^2 species $[CpV]_2[C_4H_8]_2$[6] in the absence of a direct V–V bond.[7] Several other puzzling examples of short nonbonding metal–metal contacts are present in the chemical literature, pointing out that the bridging ability of the ligands may play a predominant role in determining the molecular complexity (dimeric versus monomeric) and ultimately the value of the intermetallic separation.

The most intriguing example is offered by divalent chromium. The chemistry of this oxidation state is in fact characterized by the ability of chromium to form Cr–Cr quadruple bonds of unusual shortness (down to 1.82 Å), also known as *supershort*.[8,9] The unusual shortness of these intermetallic distances and the magnetic properties of the metal are the most convincing argument in support of the existence of Cr–Cr quadruple bonds. Therefore, the spectacular failure of theoretical calculations in describing Cr–Cr quadruple bonds[10] (case unique to chromium, since isoelectronic molybdenum and tungsten show reasonable agreement between experiment and theory)[11] has been attributed to the inability of theory to properly handle *ab initio* calculations on these molecules.[12] However, there is something unique in the nature of Cr–Cr quadruple bonds. The paradoxical weakness (Cr–Cr quadruple bond is expected to be as weak as a Cr–Cr single bond),[13] the easy dissociation into monomeric fragments[14] and the intriguing presence of residual paramagnetism[15] make the nature of the Cr–Cr interaction elusive and probably unclassical. It is quite remarkable in this respect that the existence of the Cr–Cr quadruple bond has been defined as a *semantic question*.[13] In other words, if we correctly interpret the idea of Hall, a quadruple bond is what we define as such, in disregard of the classical binomium bond strength/multiplicity, which is commonly respected in the chemistry of main group elements and of the transition metals without bridging ligands.

There are several arguments against the idea that the particular geometry of the ligands employed in these systems constrains the metal atoms to such short distance.[16] However, as a rule, with only two exceptions,[17,18] Cr–Cr quadruple bonds have been observed only with anionic chelating ligands containing a four electron system delocalized on three atoms (acetate-like). The nature of the donor atom has apparently no influence in this respect, while the three-center chelating frame can be incorporated into the most diverse molecular architectures.[8,9]



The first example of a Cr–Cr supershort bond was found using a 2,6-dimethoxyphenyl ligand.[8,9] However, the utilization of the same kind of ligand gave a similar geometry and short intermetallic contacts in the isostructural V(II) derivative[19] (where the existence of a strong V–V triple bond has been suggested[20]), in the Cu(I) complex[21] (where the existence of a Cu–Cu bond is doubtful) and even in a Li derivative[22] (where no Li–Li bond can possibly be claimed). Furthermore, three-center chelating ligands have a remarkable capability for enforcing dimeric aggregation and short metal–metal contacts with several transition and non-transition metals, by imposing a very unique molecular frame which is widely represented across the periodic table.[23] Therefore, we suggest as a provocative idea that in spite of the extremely short intermetallic contacts, Cr–Cr quadruple bonds may in fact be just artifacts of the bridging ability of the ligands, able to impose both a dinuclear structure and close proximity between the two metals.

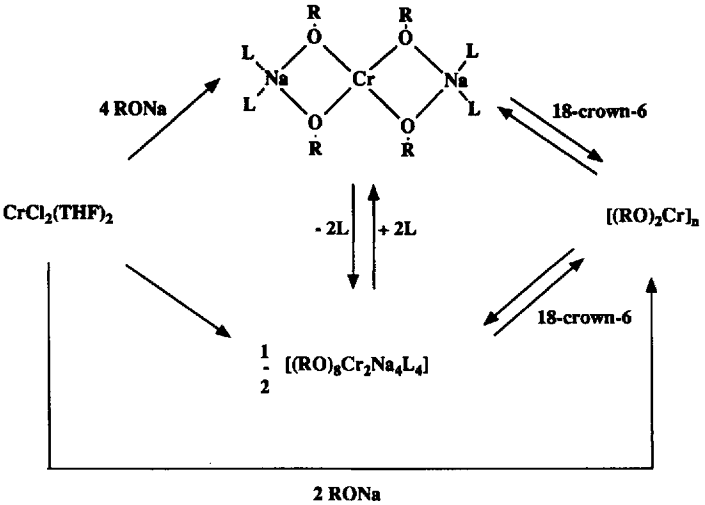


The most obvious strategy to adopt in order to gain insights into any ability of divalent chromium to form a Cr–Cr bond able to hold the molecular frame is to test for the occurrence of short Cr–Cr contacts in different classes of Cr(II) compounds, containing monodentate ligands or bidentate chelating ligands, where both the electronic configuration and the *bite* of the three-center chelating geometry are progressively modified.

In this paper, we would like to critically review some recent synthetic and structure results in the chemistry of divalent chromium and to incorporate them into a short discussion on the tendency of divalent chromium to form metal–metal bonds.

Cr(II) ALKOXIDES

The structural features of Cr(II) alkoxides provide an example of systematic failure of Cr–Cr bond formation. The preparation of Cr(II) alkoxides has been achieved following the procedures summarized in Scheme I. The size of the alkoxide moiety dramatically affects the structure of the reaction products. While square-planar

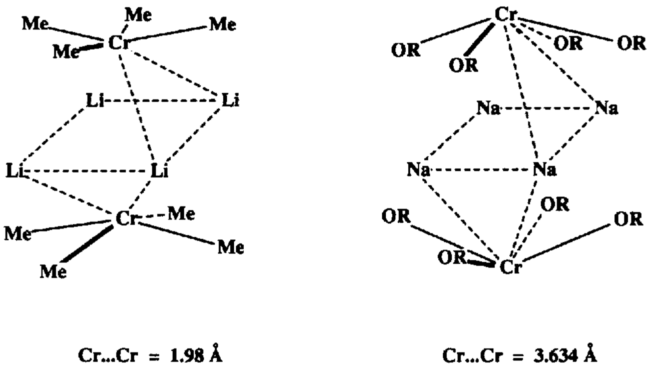


SCHEME I

monomeric complexes with high-spin electronic configuration have been isolated with bulky aryloxides,[24] in the case of smaller substituents [R = Me, i-Pr, t-Bu, Ph, 2,6-MeC$_6$H$_3$, β-C$_{10}$H$_7$], the reaction invariably gave highly insoluble pyrophoric materials, probably polymers.[25] The reaction with excess of NaOR proceeded forming anionic monomeric (RO)$_4$CrNa$_2$(THF)$_4$ as purple crystalline solids.[26] Spontaneous dissociation of solvent from the coordination sphere of the alkali cation led to a reversible dimerization reaction and formation of (RO)$_8$Cr$_2$Na$_4$(THF)$_4$.[26]

The absence of a Cr–Cr bond in these dimeric complexes is quite striking, especially when considering the close structural similarity with the quadruply bonded Me$_8$Cr$_2$Li$_4$(THF)$_4$[18b,c] (Scheme II). While this remarkable difference cannot be ascribed to the different dimensions of the two different alkali cations employed in the two complexes, the nature of the donor atom (oxygen instead of carbon) is most likely responsible.

In spite of the absence of a Cr–Cr bond, there is a considerable extent of electronic coupling between the two metal atoms. The behavior of the magnetic properties of these compounds suggests that a magnetic exchange between the two transition metals does not occur via direct Cr–Cr interaction, although the commonly observed highly negative value of θ might suggest so.[1] Ligand-mediated superexchange is more likely responsible for the low magnetic moment observed in this class of compounds, since within comparable Cr . . . Cr distances, the values of μ_{eff} seem to be



Cr...Cr = 1.98 Å

Cr...Cr = 3.634 Å

SCHEME II

strongly dependent on the nature of both the solvent coordinated to the alkali cation and the geometry of the alkoxide moiety (Table I).

The direct influence of the nature of the alkoxide and of the coordination environment of the alkali metal in determining the magnetic properties of the complex indicates that the bridging interaction $Cr-OR-Na_2-OR-Cr$ is strong and able to provide electronic communication between the two transition metals. We tentatively suggest that a similar interaction may occur in the isomorphous and almost diamagnetic $Me_8Cr_2Li_4(THF)_4$,[18a] where the presence of a supershort Cr–Cr quadruple bond is believed to hold together the molecular frame, the role of the alkali cation being regarded as purely electrostatic.

The suggestion which emerges from these results is that the Cr–Cr distance of dimeric Cr(II) alkoxides is mainly determined by two factors intrinsic to the nature of the ligand: (a) the nature of the donor atom (oxygen), which probably modifies the relative population of the bonding and antibonding configurations in the ground state and (b) the presence in the molecular frame of alkali cation able to play a fundamental (and unexpected) role in determining the assemblage of the dimeric units and the magnetic properties of the molecule. A further confirmation of the dominant role of these two factors in determining the structure of these systems has been carried out in three different directions:

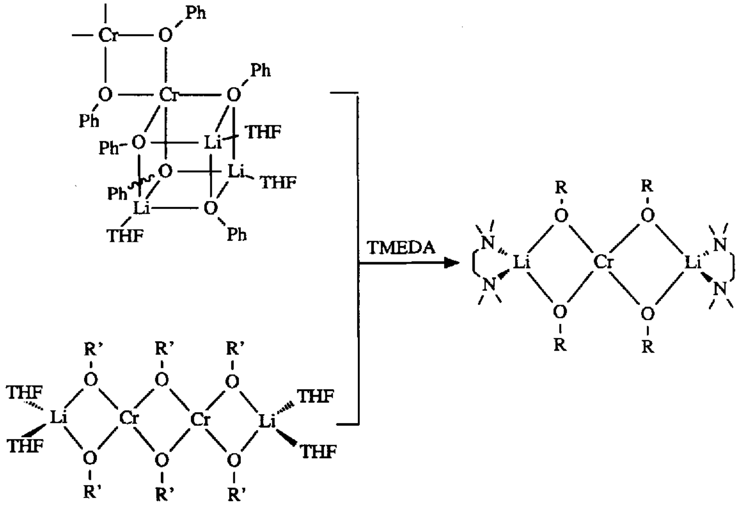
1. replacement of the alkali cation (Li, K);
2. modification of the coordination sphere of the alkali cation via introduction of a Lewis base;
3. modification of the geometry of the organic alkoxo moiety by introducing an additional donor atom.

TABLE I

Magnetic moments of $(RO)_8Cr_2Na_4(L)_4$

R	L	μ_{eff} (B.M.)	Cr . . . Cr (Å)	Ref.
Ph	pyridine	3.46	3.634	24
Ph	THF	2.84	3.622	26
β-$C_{10}H_7$	THF	2.83	–	26
i-Pr	THF	3.25	3.739	27

1. *Replacement of the alkali cation.* While attempts to introduce a larger alkali cation (K) in the molecular structure led only to the formation of homoleptic polymeric materials, the employment of smaller lithium derivatives gave dimeric species with remarkably different molecular frames (Scheme III).[28] Questions arise about the absence in these complexes of Cr–Cr bonds. In fact, assuming that the supershort Li . . . Li [2.626 Å] contacts observed in $(PhO)_{10}Cr_2Li_6(THF)_6$ are just the result of the ability of the η^3-OR groups to enforce close contacts between the two alkali cations against the electrostatic repulsion, it remains quite difficult to understand the length of the Cr . . . Cr distances, which exists in spite of the presence of two bridging μ-OR groups and the expected great ability of Cr to form Cr–Cr quadruple bonds.[8] Furthermore, a Cr . . . Cr distance, comparable to those of the two complexes reported in Scheme III, has been found in the very crowded $\{[(t\text{-}Bu)_3CO]Cr[\mu\text{-}OCH(t\text{-}Bu)_2]\}_2$ complex[29] (having a similar Cr_2OR_2 core), which indicates that the organic moiety of the alkoxo group has only a small influence on the value of the intermetallic separation. Therefore, we suggest that the fairly short non-



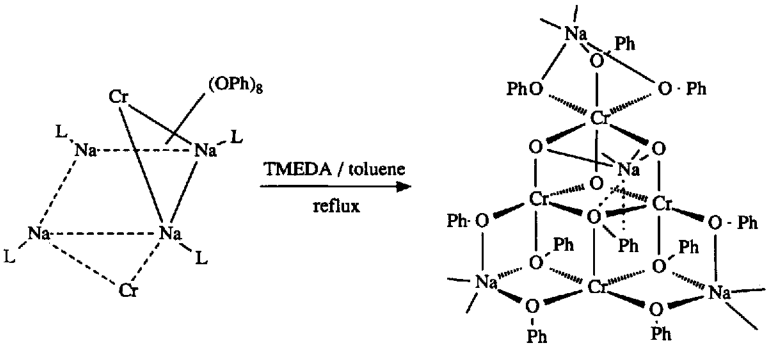
R = Ph, R'[R' = 2,6-$(Me)_2C_6H_3$]

SCHEME III

bonding distances observed in both $(PhO)_{10}Cr_2Li_6(THF)_6$ and $(2,6\text{-}Me_2C_6H_3O)_6Cr_2Li_2(THF)_4$ [3.149 Å and 3.091 Å, respectively] are just the optimal result of the bond distances and angles imposed on the $(RO)_2Cr_2$ core by the oxygen atoms of the two μ-OR groups.

2. *Coordination sphere of the alkali cation.* In accordance with the fundamental role of lithium in determining both the bonding and the structure of these complexes, simple modification of the coordination sphere of the alkali cation by replacing THF with a fairly strong Lewis base such as TMEDA [TMEDA = N,N,N′,N′-tetramethylethylenediamine] gave a major molecular rearrangement and cleavage of the $Cr_2(OR)_2$ unit (Scheme III). Similar treatment of the sodium-containing dimers $(RO)_8Cr_2Na_4(THF)_4$ showed a completely different behavior. While the isopropyl derivative gave the polymeric $[(i\text{-}PrO)_2Cr]_n$, the reaction of the phenyl derivative required several hours of refluxing in TMEDA/toluene mixtures (2:1) to form a Cr(III) complex $(PhO)_{10}Cr_4(\eta^3\text{-}O)_3Na_4(TMEDA)_4$ via a surprising oxidation reaction (Scheme IV).[27]

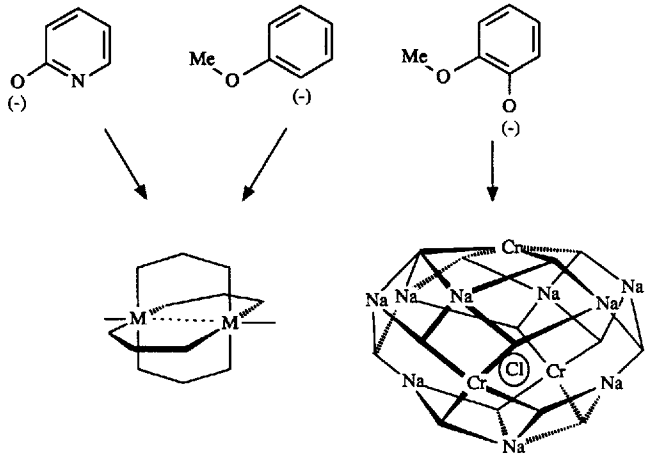
Although the origin of the three $(\eta^3\text{-}O)$ groups present in the complex is unclear, their presence can probably be ascribed to a deoxygenation reaction of either NaOPh or THF, analogous to the cases of yttrium[30] and zirconium alkoxides.[31] While a very large excess of TMEDA is necessary for a complete reaction, deliberate addition of stoichiometric amounts of H_2O to either the reaction



SCHEME IV

mixture or toluene solutions containing smaller amounts of TMEDA (5 eq.) led to a completely different result and formation of a brown intractable material. While there is no doubt that these transformations are driven by the alkali cation, it is unclear why the same treatment, which gave the cleavage of the Cr_2OR_2 core of lithium derivatives, increased the nuclearity of the corresponding sodium species. There are no Cr–Cr bonds in $(PhO)_{10}Cr_4(\eta^3\text{-}O)_3Na_4(TMEDA)_4$, whose intermetallic distances [av. Cr . . . Cr = 3.313 Å], although slightly longer, are comparable with those of other $Cr_2(OR)_2$ cores.

3. *Nature of the alkoxide.* A quadruply-bonded dichromium alkoxide has been reported only in the case of a 2-hydroxopyridine Cr(II) derivative,[32] where the characteristic three-center chelating geometry of the bridging ligand (common feature among quadruply-bonded chromium systems) has been obtained by placing one hydroxyl group at the ortho position of a pyridine ring. However, when the *bite* of the three-center chelating ligand has been slightly enlarged, as in the case of guaiacol, the trinuclear species $(GuO)_{14}Cr_3Na_9Cl$ [GuO = $2\text{-}MeOC_6H_4O$] has been obtained[28] (Scheme V). The bonding is realized in the molecule via a network of bridging interactions of the oxygen of the guaiacolate moiety



SCHEME V

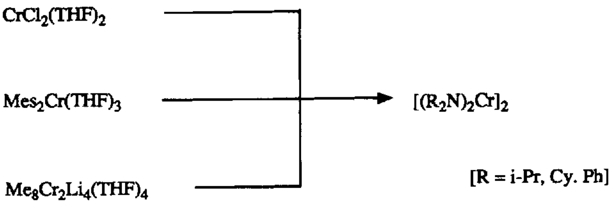
with the nine sodium and three chromium atoms. A curious encapsulation of a chlorine atom has been observed in this Cr(II) complex along with the absence of Cr–Cr bonds. Attempts to modify the coordination environment of sodium via coordination of TMEDA or reaction with crown ethers led to the invariable formation of the polymeric $[(\mathrm{GuO})_2\mathrm{Cr}]_n$.

In this diversified collection of Cr(II) alkoxides we observe a systematic absence of Cr–Cr bonds, the only exception being offered by species which contain a three-center chelating alkoxide. In contrast to the inability of chromium to form dimers through formation of metal–metal bonds, the alkali cation has a preeminent role in assembling dimers or even oligomers. The unpredictable structure of $[(\mathrm{GuO})_{14}\mathrm{Cr}_3\mathrm{Na}_9\mathrm{Cl}]$, the facile cleavage of $[(\mathrm{PhO})_{10}\mathrm{Cr}_4(\eta^3\text{-O})_3\mathrm{Na}_4(\mathrm{TMEDA})_4]$ and $[(2,6\text{-}\mathrm{Me}_2\mathrm{C}_6\mathrm{H}_3\mathrm{O})_6\mathrm{Cr}_2\mathrm{Li}_2(\mathrm{THF})_4]$ (Scheme III) and the considerable structural differences between Li and Na alkoxo chromates suggest in fact that the alkali metal provides a delicate balance of factors (Lewis acidity, dimension, preferential coordination number) which determine the final degree of molecular aggregation. While there is no doubt that the modification of the coordination sphere of Li and Na is the driving force of the transformations reported above, it remains unclear why this simple replacement of ligands coordinated to the alkali cation is able to modify the molecular structure in such a spectacular manner. Although a rationalization of this remarkable behavior is so far not possible, the fundamental role of the alkali cation and of the nature of the ligand in determining the bonding, the nuclearity and the magnetic properties of Cr(II) alkoxo chromates remains ascertained.

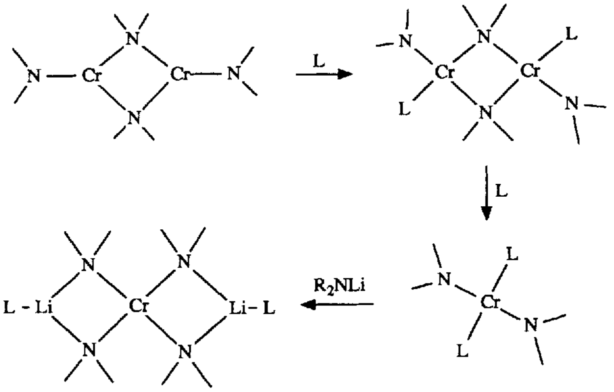
Cr(II) AMIDES

In contrast to the case of the alkoxide oxygen atom which can engage up to six electrons in bonding a transition metal, the nitrogen atom of an amide has available a maximum of only four electrons. Therefore, if we accept the idea that the systematic failure of Cr–Cr bond formation observed in chromium alkoxide chemistry is the result of the population of Cr–Cr antibonding orbitals with non-bonding electrons from the oxygen donor atom, nitrogen as a donor atom may be expected to give better chances for the formation of Cr–Cr multiple bonds. The synthetic strategies adopted in the preparation of Cr(II) amides are summarized in Scheme VI.[33] In spite of the fact that both monomeric and dimeric quadruply bonded complexes have been deliberately used with the purpose of investigating the tendency of chromium to form or to preserve Cr–Cr bonds, the nature of the reaction product was not affected by the choice of the starting material. The chemical behavior and the structural features are summarized in Scheme VII.

In the case of the cyclohexyl, isopropyl and phenyl substituents, the reaction proceeds in a similar manner, forming the dimeric homoleptic complexes $[(R_2N)_2Cr]_2$. Although the Cr–Cr distances determined in the crystal structures of the cyclohexyl and isopropyl



SCHEME VI

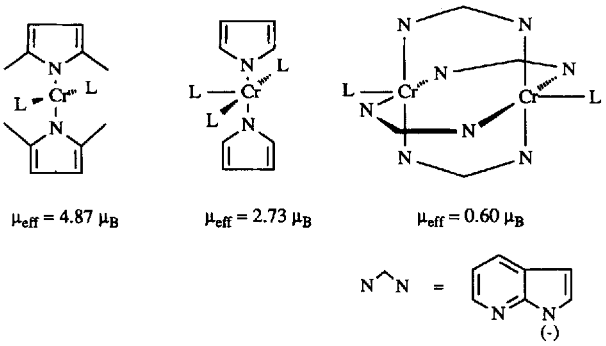


SCHEME VII

derivatives [2.866 and 2.834, respectively] may suggest the presence of a Cr–Cr single bond, the temperature dependence of the magnetic properties [μ_{eff} = 2.30 and 2.62 μ_B, respectively] encourage the idea that no real bond exists, in spite of the fairly short intermetallic distance.[33] Furthermore, treatment with coordinating solvents (THF, pyridine) gave a surprising increase of the intermetallic distance [up to 3.152 Å], while preserving the $Cr_2(NR_2)_2$ core. The magnetic moment of $[(R_2N)_2CrL]_2$ [μ_{eff} = 3.58 μ_B], although still in agreement with the existence of a Cr–Cr single bond, showed a temperature dependence which is characteristic of the antiferromagnetic exchange. Although in this case one may only speculate about the existence of a Cr–Cr bond, the fact is that the Cr–Cr interaction is very weak in terms of contribution to the bond stabilization energy, since the Cr–Cr distance and the magnetic moment respond so strongly to simple solvent coordination. Furthermore, treatment with an excess of coordinating solvent (THF, pyridine) systematically cleaved the $Cr_2(NR_2)_2$ core, forming monomeric, square-planar $(R_2N)_2Cr(L)_2$ species with the expected high spin electronic configuration [μ_{eff} = 4.68 μ_B]. Reaction with an excess of $LiNR_2$ leads to the formation of monomeric anionic chromates $[(R_2N)_4CrLi_2(THF)_2]$, isostructural with the monomeric alkoxides, building blocks of the dimeric species described above. However, formation of the hypothetical dimeric $(R_2N)_8Cr_2Li_4$, through desolvation of the alkali cation, was not possible in this case, probably due to the scarce ability of the amide nitrogen donor atom to give the η^3-bonding mode necessary for assembling the dimeric species.

These results have confirmed the surprising magnetic flexibility of Cr(II) already observed in the alkoxides. In other words, the magnetic properties of the metal depend on the value of the intermetallic separation imposed on the Cr_2X_2 core by the bridging ligand, without which the electronic pairing would necessarily be accompanied by a significant energetic gain (chemical bond). Once again, when the three-center 2-pyridylamido ligand [2-HN,6-$CH_3C_5H_4N$] has been used, a supershort Cr–Cr contact (1.870 Å) was observed in the resulting dimeric Cr(II) amide derivative.[34]

Although these observations gave some insight into a unique feature of the Cr–Cr interaction (not necessarily bonding) and the ability of three-center chelating ligands to impose dinuclear structures, the evidence is still not very striking. Results recently obtained in the chemistry of Cr(II) pyrrolyls offer a consistent series of complexes where the three-center chelating geometry is progressively restored.[35] While the reaction of $CrCl_2(THF)_2$ with the Na salt of the sterically encumbered pyrrole 2,5-$Me_2C_4H_2NH$ gave the usual square-planar complex $[(2,5\text{-}Me_2C_4H_2N)_2Cr(L)_2]$ [L = THF, pyridine], utilization of the less crowded C_4H_4NNa formed a square pyramidal complex $[(C_4H_4N)_2Cr(L)_3]$. This structural modification is accompanied by a surprising variation of the magnetic properties (Scheme VIII). The coordination geometry of $[(C_4H_4N)_2Cr(L)_3]$ is reminiscent of the pyramidal geometry of the mononuclear fragments which are the building blocks of the quadruply bonded systems of dichromium, containing three-center chelating ligands, where an additional donor atom (from either a coordinating solvent or the ligand itself) on the axial coordination site plays an important role in determining the value of the intermetallic separation.[8] Questions then arise about which factors inhibited the formation of Cr–Cr quadruple bond in $[(C_4H_4N)_2Cr(L)_3]$. We believe that the lack of dimeric aggregation is merely a result of the 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 is restored like in the case of 7-azaindole, the classical structure of a dichromium complex is observed. However, the long Cr–Cr distance [Cr . . . Cr = 2.604 Å] (the longest ever found in this class of dichromium



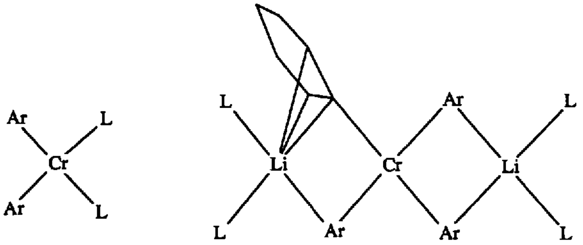
SCHEME VIII

complexes) is not likely in agreement with the presence of a Cr–Cr quadruple bond, although the magnetic moment is very comparable with that of the quadruply bonded systems. Therefore, we conclude that three-center chelating ligands may not only be capable of enforcing dimeric aggregation through the establishment of a very peculiar dimeric frame, but also of determining a very efficient electronic coupling between the two metals, probably via ligand-mediated superexchange.

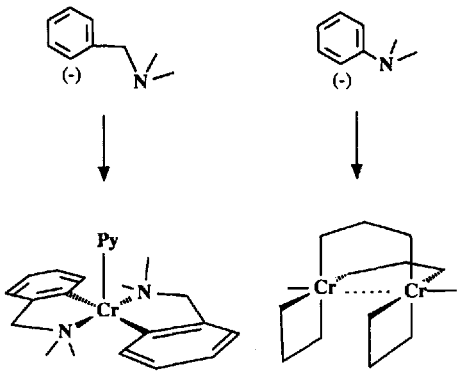
Cr(II) ARYLS

From the sizeable collection of complexes, available in the literature, containing very short Cr–Cr contacts, it seems that the use of carbon as a donor atom is the winning strategy for the achievement of dinuclear structures and the enforcement of short metal–metal distances. Furthermore, the chemistry of Cr(II) alkyls provides the only two cases of quadruply bonded dichromium systems using bridging ligands different from the three-center chelating type.[8,9] Therefore, considering that carbon as a donor atom might have a particular ability to establish short Cr–Cr contacts, it is important to try to generalize the structural features of Cr(II) alkyls and aryls using monodentate ligands without special bridging or chelating abilities.

Recently published structural work in the chemistry of Cr(II) aryls has shown that both neutral and anionic phenyl and mesityl Cr(II) derivatives[36] possess a monomeric nature (Scheme IX).



SCHEME IX



SCHEME X

When the chelating ability of the aryl ligand was restored by placing a dimethylaminomethyl group in the *ortho* position of the phenyl ring, a monomeric pentacoordinated $(2\text{-}Me_2NCH_2C_6H_4)_2$-Cr(L) complex was obtained[37] (Scheme X). The square pyramidal geometry, observed along with the low-spin electronic configuration of chromium [$\mu_{eff} = 2.56\ \mu_B$], poses, in close analogy with the case of the pyrrolyl derivative [$pyrr_2CrL_3$], the same type of question. It is not apparent, if chromium has a real tendency to form a significant quadruple bond, why this complex does not dimerize via formation of metal–metal bonds, able to hold together the dinuclear frame. Even more intriguing is the fact that no special steric hindrance is present in the molecule and the correct geometry is available for the formation of a quadruply bonded system. Once again, when the characteristic *bite* of the three-center chelating ligand has been restored by removing the CH_2 methylene group, a supershort Cr–Cr contact (1.88 Å) has been observed in the structure of $[(2\text{-}Me_2NC_6H_4)_2Cr]_2$ (Scheme X).[37]

CONCLUSION

The structural analogy between the two pentacoordinated compounds $(2\text{-}Me_2NCH_2C_6H_4)_2Cr(L)$ and [$pyrr_2CrL_3$] is striking, and due to the diversity of the ligands employed in the two cases, gives the impression that a general trend may hold. The behavior of Cr(II) as emerging from these results, can be summarized with respect to the formation of short Cr–Cr distances, in the following points:

1. No metal–metal bonds are observed in the absence of special bridging interactions, the only exception to this rule being provided by one macrocyclic Cr(II) derivative, able to enhance the scarce ability of Cr(II) to form metal–metal bonds by imposing a unique crystal field.[38]
2. Dinuclear frames are invariably formed with three-center chelating ligands.
3. Efficient electronic pairing is performed by these ligands.

These observations together with the remarkable response of the Cr–Cr distances and of the magnetic properties of the transition metal to factors (nature of the donor atom, coordination of solvent molecule, Lewis acidity of the alkali cations) which usually have only marginal influence on the molecular structure of complexes suggest that Cr–Cr multiple bonds might not exist, at least by the usual definition of a chemical bond. Given that the orbitals of the two chromium atoms are largely overlapped (as at a distance as short as 1.84 Å), the question then is why not enough energy is released to hold the dinuclear frame together, and to prevail over the small steric repulsions, in spite of the considerable electronic coupling. The ability of three-center chelating ligands to so strongly determine the dinuclear structure and the magnetic couplings also gives rise to the question of what makes these ligands so special. It is clear that these ligands are able to enforce dinuclear structures with an impressive series of metals,[8a,23] provided no unfavorable steric interactions oppose the formation of the dimeric unit. What remains unclear is the importance of their particular electronic configuration. It is possible that the π-electron system of the ligand is crucial in establishing an efficient electronic communication between the two transition metals, via a considerable electronic delocalization of the five membered ring formed with the Cr_2 unit. In accordance with this hypothesis, the three-center chelating phosphine $Me_2PCH_2PMe_2$ (formally a four electron donor, without the electronic delocalization of an allylic system) is forming dimeric complexes with quite long metal–metal non-bonding distances.[39]

In summary, divalent chromium shows a surprisingly passive behavior compared to the dominance of the ligand. In other words, the geometry of the dinuclear frame seems to be determined exclusively by ligand features (donor atom, geometry, alkali cation, etc.), able to impose dimeric aggregation and to determine the value of the intermetallic separation. The Cr_2 unit responds to the dominant role of the ligand by overlapping orbitals and coupling electrons (depending on the Cr–Cr distance imposed by the ligand), but providing at the same time far less energy than obtained by the formation of metal–ligand bonds. While the existence of Cr–Cr single bonds may be reconcilable with this behavior, it turns out to be almost chemical nonsense when supershort metal–metal distances suggest the existence of a higher degree of metal–metal bond multiplicity.

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