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Three-dimensional delocalization in tris(1,2-dithiolenes)

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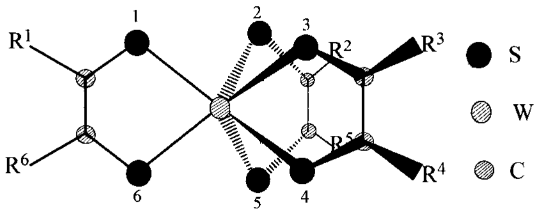
Tungsten tris(1,2-dithiolene) complexes $[W(S_2C_2R^1R^6)(S_2C_2R^2R^5)(S_2C_2R^3R^4)]$ ($R^{4,5,6}$ = H or Ph; $R^{1,2,3}$ = *para*-substituted Ph), have been found to exhibit properties (^1H NMR, UV/VIS, IR spectral) closely related to each other through Hammett constant σ_p^+, indicating extensive delocalization and conjugation. A comparative study of complexes containing differently substituted dithiolenic rings showed that the electron delocalization is not confined within each dithiolenic ring separately, but involves all of them, *i.e.* it is three dimensional. This is further supported by a NMR and/or UV/VIS study of the effect of water and acid on the dimethylamine derivative. The oxidation number was assigned by recording the NMR spectra of the metal nuclei; the metals have effectively been stripped of their valence electrons; which are placed on the ligands. The non-planar 'aromaticity' of the dithiolenes differs from the familiar flat organic aromaticity since it involves mixing of σ and π bonding.

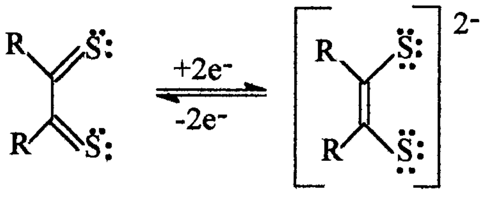
In organic aromaticity the overlap of the carbon p orbitals produces flat structures. In tris(dithiolenes) **A** the bonding system allows for three-dimensional delocalization. The question of aromaticity in dithiolenes (bis and tris) was first addressed and studied by Schrauzer and co-workers,[1] and later by Mueller-Westerhoff and co-workers.[2] The supporting evidence invoked includes the observation that the proton NMR peaks of $[V(S_2C_2H_2)_3]^-$, $[Re(S_2C_2H_2)_3]^-$ and $[Mo(S_2C_2H_2)_3]^{2-}$ appear [1a] in the region of the aromatic protons. A similar observation was made [3] for $[M(S_2C_2PhH)_3]$; the peak of the ring proton appears at δ 9.520 for Mo, 9.770 for W and 8.883 for V, as compared to 6.430 for $Me_2S_2C_2PhH$. A useful 'quick' diagnostic measure of the 'extent' of delocalization is the IR frequency assigned to the C=C stretching (ν_1). An increase in ν_1 indicates increase in the double-bond character and a corresponding decrease in delocalization. This is what happens for example upon reduction of the $[M(S_2C_2R_2)_3]$ complexes. In this respect there is a (qualitative) similarity to the decreased aromaticity of the hydrogenated organic aromatics. The number and intensities of the UV/VIS peaks, the electrochemical properties, and the ESR spectra of the paramagnetic species are also good indicators of aromaticity in dithiolenes.[1a]

The available evidence essentially refers to the aromaticity of the dithiolenic ring *per se*, and is similar in square bis and prismatic tris species; it does not refer to the communication between the rings. Yet, simple molecular orbital (MO) calculations [1a,4] indicate that there are strong σ- and π-bonding interactions, which led to the suggestion[1e] that there is ring communication. In this context it is important to note that the dithiolene ligands have two types of π orbitals:[4] the in-plane π_h orbitals which are responsible for the σ–π mixing, and the π_v, which are perpendicular to the ring, and are analogous to the usual organic π systems.

In dealing with delocalization in tris(dithiolenes) it must be emphasized at the outset that the ideal D_{3h} geometry is not the rule.[5] Only in $[Re(S_2C_2Ph_2)_3]$ the six sulfur atoms form a perfect trigonal prism.[6a,b] The other known structures [6c–i] are distorted: the dithiolenic rings are not planar or there is a twist towards the octahedral limit (triangle 123, formula **A**, not exactly ecliptic to 456), or the three ligands differ in corresponding bond lengths and angles. The solid-state geometry is influenced by minute perturbation of crystal-packing forces and electronic energies.[6i] The delicate structure is also apparent in the high stereochemical non-rigidity in solution.[7] The deformations observed in the solid state may be partly due to this stereochemical non-rigidity, and to the 'freezing' of some of the energetically nearly equivalent conformations, *e.g.* during the preparation of the crystals.



A



B **C**

Non-rigidity may also very well be the reason why different preparations of MoS_2 and analogous structures differ crystallographically.[8] The MoS_2 crystals consist of triple layers: one molybdenum layer sandwiched between two sulfur layers. Ideally the local environment around each Mo is trigonal prismatic. However, pretty much as with dithiolenes, several distortions have been observed,[8] depending on the method of synthesis.

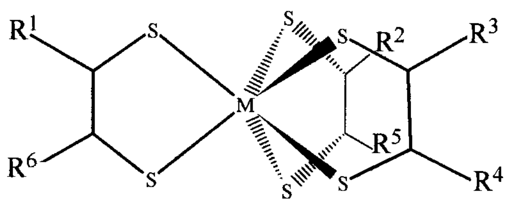
In tris(dithiolenes) with phenyl substituents the MS_2C_2 ring and the phenyls are not coplanar,[5] and effective purely π conjugation between them is impossible. The transmission therefore of any effects of substituents of the phenyl, like the ones studied here, must necessarily depend critically on the σ–π mixing in the electronic structure. The new documentation of the delocalization brings out again the non-innocent character of the dithiolenic ligands and the need to decide between the neutral dithioketone (**B**) and the dianionic dithiol (**C**) forms.

In this paper the answer is given experimentally (operationally) rather than theoretically;[1,4] it is based on the NMR signals of the metals. The oxidation states assigned to the metals are high, which explains the catalytic and photocatalytic activity of some tris(dithiolenes) in oxygen formation;[9] oxidation catalysts generally require high-oxidation-state metal species.

Experimental

The non-symmetrically substituted complexes used have the formulae shown. The IR spectra and the dithiolenic proton chemical shifts of those used in the Hammett analysis are given in Table 1. Most of the complexes are homoleptic; only **2** and **3** contain mixed ligands. Their synthesis has been described elsewhere.[9a,10] Only **2** and **3** were synthesized especially for the present purposes. A mixture of 4-(4-methoxyphenyl)-1,3-dithiol-2-one (0.560 g, 2.5 mmol), 4-(4-bromophenyl)-1,3-dithiol-2-one (0.680 g, 2.5 mmol) and $[WBr_4(MeCN)_2]$ (0.93 g, 1.6 mmol) was used as described in ref. 8. A mixture of the four possible species (**1**–**4**) were obtained in the form of a green powder, 150 mg of which was separated by column chromatography (silica gel 60). Elution with benzene–cyclohexane (1:9) gave 38 mg of complex **1**, benzene–cyclohexane (3:7) yielded 30 mg of **2**, benzene–cyclohexane (3:2) yielded 15 mg of **3**, and 100% benzene gave 10 mg of **4**. The molecular formulae were established using electrospray mass spectrometry.[10] As an example, Fig. 1 shows the spectrum of a freshly prepared acetonitrile solution of the mixed-ligand complex **2**. As can be seen the experimentally obtained pattern is in complete agreement with the theoretically expected isotopic distribution pattern. A similar result was obtained for complex **3**.

The mass spectral measurements were performed using a Fisons VG-Quattro mass spectrometer with a VG Biotech electrospray source, as described previously.[10] Infrared spectra were recorded with a Perkin-Elmer 883 spectrophotometer using KBr discs, variable-temperature ^1H NMR, ^{183}W–^1H heteronuclear multiple quantum coherence (HMQC) and two-dimensional exchange (EXSY) NMR spectra with a Varian Unity Plus 300 instrument as described previously.[7] The chemical shifts are referenced to Na_2WO_4 using the Ξ value of 4 166 355.3 Hz, determined in an independent experiment with basic aqueous 1 mol dm^{-3} $Na_2[WO_4]$. For ^{95}Mo an external standard of $Na_2[MoO_4]$ in D_2O was used. The UV/VIS spectra were recorded with Hitachi U-2000 and Cary 17D spectrophotometers using 1 cm quartz cells.



1 $R^1=R^2=R^3=p$-BrC_6H_4 $R^4=R^5=R^6=H$, M=W

2 $R^1=R^2=p$-BrC_6H_4 $R^3=p$-$MeOC_6H_4$ $R^4=R^5=R^6=H$, M=W

3 $R^1=R^2=p$-$MeOC_6H_4$ $R^3=p$-BrC_6H_4 $R^4=R^5=R^6=H$, M=W

4 $R^1=R^2=R^3=p$-$MeOC_6H_4$ $R^4=R^5=R^6=H$, M=W

5 $R^1=R^2=R^3=p$-ClC_6H_4 $R^4=R^5=R^6=H$, M=W

6 $R^1=R^2=R^3=Ph$ $R^4=R^5=R^6=H$, M=W

7 $R^1=R^2=R^3=p$-MeC_6H_4 $R^4=R^5=R^6=H$, M=W

8 $R^1=R^2=R^3=p$-$MeOC_6H_4$ $R^4=R^5=R^6=H$, M=Mo

9 $R^1=R^2=R^3=p$-$Me_2NC_6H_4$ $R^4=R^5=R^6=Ph$, M=W

10 $R^1=R^2=R^3=p$-$MeOC_6H_4$ $R^4=R^5=R^6=Ph$, M=W

11 $R^1=R^2=R^3=p$-MeC_6H_4 $R^4=R^5=R^6=Ph$, M=W

Table 1 Infrared spectral data[a] and the five-membered ring ^1H NMR chemical shifts[b] of non-symmetrically substituted tris(dithiolene) complexes[c]

M	$R^4 = R^5 = R^6$	$R^1 = R^2 = R^3$	ν_1	ν_2	ν_3	ν_4	δ
W	H	p-$MeOC_6H_4$	1452	1173	853	413	9.65
W	H	p-MeC_6H_4	1430	1181	852	408	9.73
W	H	Ph	1418	1144	848	401	9.78
W	H	p-ClC_6H_4	1391	1124	851	376	9.77
W	H	p-BrC_6H_4	1389	1097	850	367	9.77
Mo	H	p-$MeOC_6H_4$	1421	1207	858	401	9.45
W	Ph	p-$Me_2NC_6H_4$	1441	1193	868	417	—
W	Ph	p-$MeOC_6H_4$	1427	1177	839	413	—
W	Ph	p-MeC_6H_4	1425	1173	838	410	—
Mo	Ph	p-$MeOC_6H_4$	1420	1174	831	405	—

[a] ν_1(C=C), ν_2(C–S), ν_3[S(R)–C], ν_4(M=S), in cm^{-1}. The ν_5 frequency, which has been assigned to M–S stretching, appears clearly only for the molybdenum complexes, and it is not well resolved for the tungsten complexes. [b] For $R^4 = R^5 = R^6 = H$, reference $SiMe_4$, solvent $CDCl_3$. All shifts in the 'aromatic' region. [c] R^1, R^2 . . . R^6 refer to formula **A**.

The following Hammett σ_p^+ constants[11] were used: Me_2N, −1.7; MeO, −0.78; Me, −0.31; H, 0; Cl, 0.11 and Br, 0.15. Values for Hammett σ_p constants were Me_2N, −0.63; MeO, −0.28; Me, 0.14; H, 0; Cl, 0.24 and Br, 0.26.

Results and Discussion

Hammett relations

The existence of delocalization is demonstrated in a fairly general manner by the linear relation between widely different properties of several related tungsten dithiolenes and the Hammett constants σ_p and σ_p^+. The properties involved are the UV/VIS spectra,[9e] the IR spectra (Table 1 and ref. 5), the NMR spectra of the dithiolene hydrogen (Table 1), $E_{\frac{1}{2}}$ and $E^0(C^*–C^-)$ (C^* = excited state of C).[9e] The corresponding correlation coefficients are listed in Table 2.

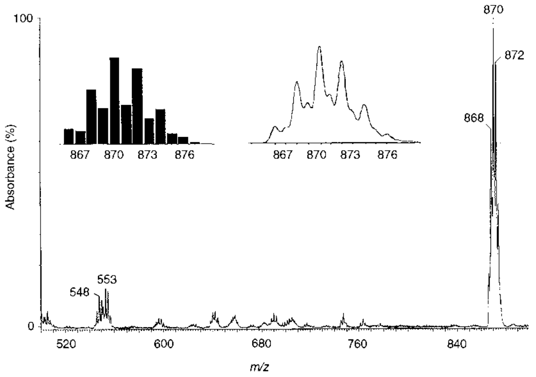


Fig. 1 The electrospray mass spectrum of complex **2**, the molecular ion peak (inset right) and the theoretical mass distribution pattern for it (inset left); acetonitrile solution, N_2 as nebulizing and bath gas,[10] focus and skimmer lens voltages 40 and 45 V, respectively

Table 2 Correlation coefficients between Hammett constants σ_p and σ_p^+ on the one hand and electrochemical properties, electronic, NMR and infrared spectra of tungsten complexes on the other

	$R^{4,5,6}$ = H[a]		$R^{4,5,6}$ = Ph[b]	
	σ_p	σ_p^+	σ_p	σ_p^+
$E_{\frac{1}{2}}(C–C^-)$[c]	0.933	0.986	0.989	0.987
$E_{\frac{1}{2}}(C^-–C^{2-})$[c]	0.960	0.919	0.994	0.992
$E^0(C^*\rightarrow C^-)$[d]	0.923	0.993	0.951	0.998
λ_1 (L–M)[e]	0.813	0.947	0.971	0.965
λ_2 (L–M)[e]	0.947	0.999	0.876	0.875
^1H NMR	0.819	0.971	*f*	*f*
^{183}W NMR	0.887	0.993	*f*	*f*
IR ν_1[g]	0.996	0.947	0.981	0.977
ν_2	0.927	0.808	0.997	0.991
ν_3	0.520	0.733	0.143	0.159
ν_4	0.968	0.825	0.931	0.924

[a] The five complexes of Table 1 with M = W and $R^{4,5,6}$ = H. [b] The three complexes of Table 1 with M = W and $R^{4,5,6}$ = Ph. [c] Ref. 10. [d] Ref. 9(*e*). [e] Assignments according to ref. 4. Used absorption maximum in cm^{-1}; λ_1 *ca.* 700–800 nm, λ_2 *ca.* 420 nm. [f] There is no dithiolene hydrogen and no corresponding NMR data for ^{183}W. [g] Table 1 and ref. 5.

The donating ability of the phenyl substituents used decreases in the order: Me_2N > MeO > Me > H > Cl > Br. The correlations with σ_p^+ are generally better compared with those with σ_p. As shown previously[9e] the yields of O_2 increase with the donating ability of the phenyl substituent. The $E_{\frac{1}{2}}$ values of both reduction steps and the wavenumbers of the charge-transfer electronic transitions increase from Me_2N to Br. The IR frequencies related well with σ_p^+ are ν_1, ν_2 and ν_4 which increase with increasing donation. The frequency ν_3 does not correlate very well, probably because the range it spans approaches the instrument's resolution. The value of $E^0(C^*-C^-)$ decreases with increasing donation, but remains highly oxidative. The chemical shift of the dithiolenic hydrogen is 'more aromatic' than that for the phenyl hydrogens (Table 1, ref. 3), and increases slightly with donor number. It is also interesting that the chemical shift of the precursor ketone (C=O instead of W) in chloroform is only *ca.* δ 6.9.

The existence of a multicorrelation, especially through σ_p^+ more than through σ_p, shows that the electrons are pushed towards the metal by effective donors at the *para* position of the phenyl substituent. The response to the perturbation caused by this substitution is collective. The data involved depend on different aspects of the electron distribution, *i.e.* of the occupied MOs. However, even properties which depend partially on empty MOs, like the UV/VIS spectra and the $E^0(C^*-C^-)$ values, are related to σ_p^+ as well.

It is important to note that the substituents varied occupy positions quite remote from the MS_2C_2 ring. Furthermore, as mentioned above, the two ring systems (Ph and MS_2C_2) are not coplanar. The transmission of the effects must therefore necessarily involve the σ skeletons, and should depend strongly on σ–π mixing.

Communication between dithiolenic rings

A referee noted the fact that the sensitivity of $\delta(^1H)$ of the dithiolenes to *para* substitution, as measured by the slope ρ in Hammett equations,[12] is the same as that $\delta(^1H)$ of the *cis* protons in styrenes (0.135 ± 0.019 and 0.136 ± 0.011, respectively). The sensitivity across the carbons in dithiolenes bridged by a S–M–S loop, is the same as that across the double bond of styrene. Yet in dithiolenes the rings are not isolated from each other, they are connected through the metal, unlike the styrene double bonds. Thus the relations with the Hammett constant σ_p^+ are not inconsistent with the idea that the three ligand rings 'communicate' *via* a three-dimensional delocalization network, but they do not constitute certain proof of it. Direct evidence for interligand effects was obtained by comparing the ^1H NMR spectra (Fig. 2) of complexes **1–4** which contain electron-withdrawing (Br) and -donating (MeO) substituents.

For the mixed-ligand complexes **2** and **3** the ^1H NMR peaks at 25 °C of the Br- and the MeO-substituted species together with the ^{183}W satellites are well resolved, and appear in the region between the peaks of the homoleptic species **1** and **4**. It is remarkable, however, that although the peak of the tribromo species **1** is downfield in relation to the trimethoxy species **4**, for the mixed-ligand complexes this order is reversed: the peaks of the bromophenyl-substituted dithiolenic rings appear upfield relative to those of the methoxyphenyl-substituted ones. A plausible explanation is that the electron-withdrawing or donating capacity of the phenyl substituent influences the hydrogens (**D**) on the other rings (b) more than its own (a). Regarding the ^1H NMR shifts, the through-metal interaction between the ligands is stronger than the intraligand one. The dithiolenic rings are in effect heterocycles containing three different elements, MS_2C_2. Two of these rings in tris(dithiolenes) can be regarded as substituents on the third. The results depicted in Fig. 2 then indicate that these two substituents have a stronger influence compared to other substituents, such as Br or MeO. The intraligand interaction is related to a π-type organic-like delocalization, which is ineffective because of the non-planarity of the phenyl and dithiolenic rings. The interligand interaction is metal mediated, involving σ–π mixing. An alternative approach is to regard the six-sulfur-atom core as a cluster rather than a system of flat (or nearly flat) rings. In the known structures intra- and inter-ligand average distances are nearly equal,[5b] indicating that the corresponding interactions or their perturbations should also be comparable.

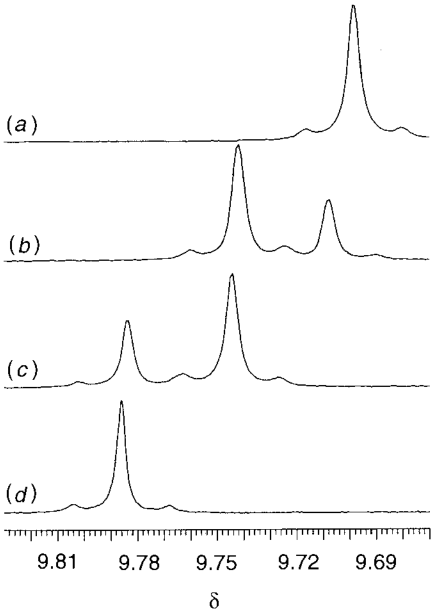
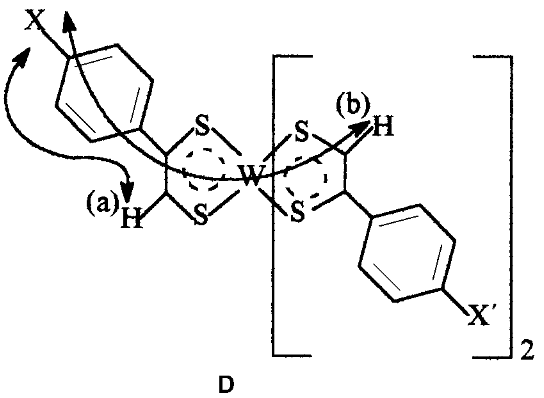


Fig. 2 Proton NMR spectra of complexes **4** (*a*), **3** (*b*), **2** (*c*) and **1** (*d*) in $CDCl_3$ at 25 °C, in the dithiolenic proton region



D

A characteristic feature of the peaks which were recorded in 25 °C in Fig. 2 is their broadness, which is mainly attributed to the *cis–trans* isomerization.[7] In trigonal-prismatic geometry *cis* and *trans* configurations are possible,[7] which can be resolved by lowering the temperature. The possible structures of the mixed-ligand complexes **2** and **3** are shown in **E** and **F**. The dots denote the single ligand, *i.e.* $MeOC_6H_4$ in **2** or BrC_6H_4 in **3**. There is only one *cis* isomer for each mixed-ligand complex (**E**), but three *trans* (**F**).

Typical low-temperature spectra are shown in Fig. 3. The two broad peaks observed at room temperature, one for the MeO-substituted and one for the Br-substituted rings, are now resolved into five peaks for complex **2** and six for **3** [Figs. 3(*a*) and 4(*a*), respectively]. Two peaks are expected in each case for the *cis* isomers of the mixed-ligand complexes, one for H_α and two for H_β. Similarly two for the *meso* (H_γ, H_δ) and three for the enantiomers (H_ε, H_ζ, H_η), a total of the seven peaks. Experimentally, only partial resolution was achieved; there is obviously some overlap.

The assignments were made with the aid of the two-dimensional $^1H-^{183}W$ HMQC patterns and the two-dimensional-

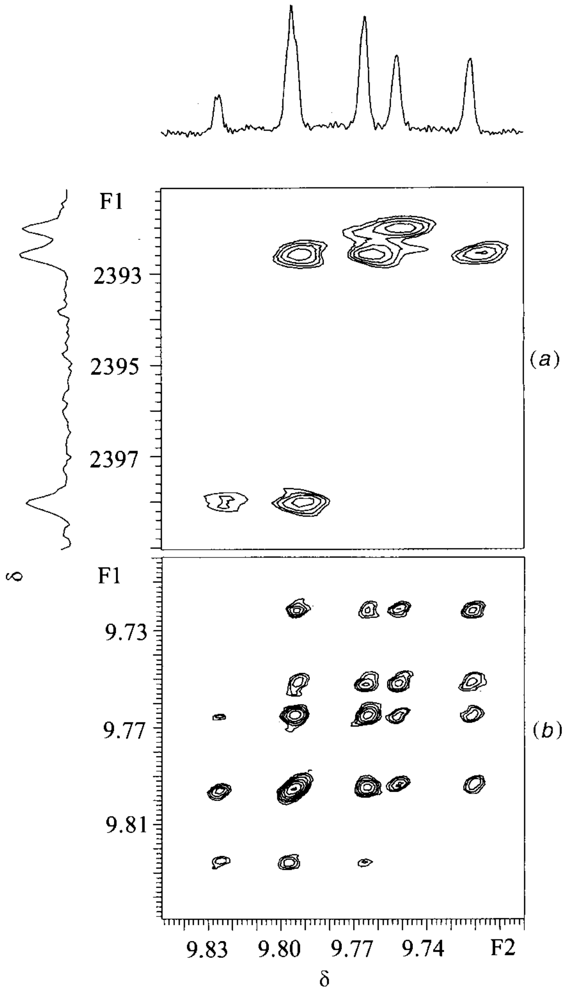
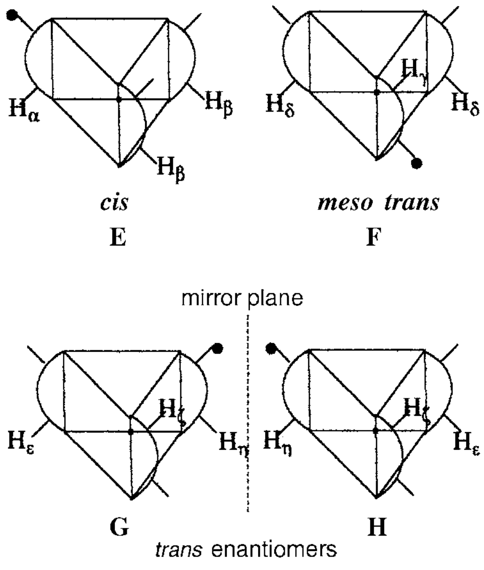


Fig. 3 Proton NMR and ^1H–^{183}W HMQC (*a*) and two-dimensional-EXSY (*b*) spectra of complex **2** in $CDCl_3$ at −40 °C, in the dithiolenic proton region



EXSY (Figs. 3 and 4) as follows. For complex **2** the peaks at δ 9.72, 9.75, 9.76 and 9.79 are assigned to bromo-bearing rings, those at δ 9.83, 9.79 and 9.76 to methoxy-bearing rings. Obviously, there is an overlap in the peaks at δ 9.79 and 9.76. The ^{183}W peak at δ 2398 is assigned[7] to the *cis* isomer, so the peak at δ 9.83 corresponds to the hydrogen of the methoxy ring, that at 9.79 to the bromo ring. The peaks at δ 2392.6 and 2392.0 correspond to the *trans* enantiomers and the *trans meso* form, respectively. The peak at δ 9.75 is assigned to the ring having the bromo substituent, while the peak at 9.76 is assigned to the ring having the methoxy substituent of the *trans meso* form. The three hydrogens of the *trans* enantiomers appear at δ 9.79 (methoxy), 9.76 (bromo) and 9.72 (bromo). The relative populations of the species, as derived from the integrals of the ^1H NMR lines, are within experimental error, as expected, *cis*-:*meso trans*:*trans* enantiomers 1.15:1.03:1.97 (theoretical 1:1:2).

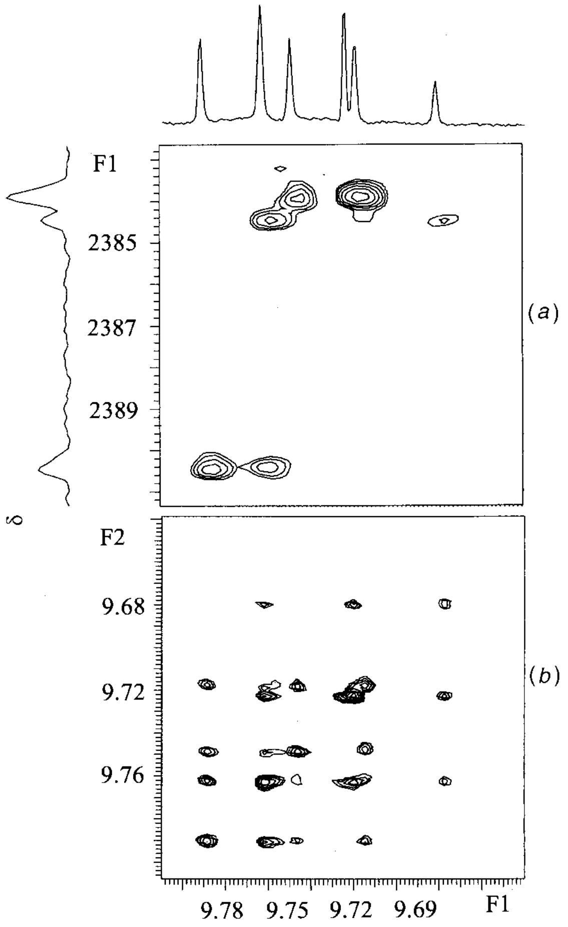
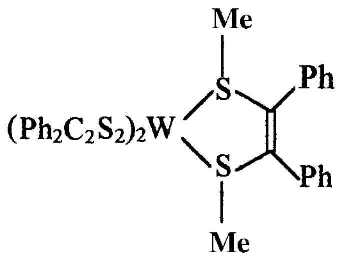


Fig. 4 Proton NMR and ^1H–^{183}W HMQC (*a*) and two-dimensional-EXSY (*b*) spectra of complex **3** in $CDCl_3$ at −40 °C, in the dithiolenic proton region

The case for complex **3** is analogous: peaks at δ 9.68, 9.73 and 9.76 are assigned to bromo-substituted ligands, those at δ 9.72, 9.75, 9.76 and 9.79 to the methoxy-substituted ones. The peak of the methoxy-substituted ligand for the *cis* isomer appears at δ 9.79 and the bromo one at δ 9.76, while the ^{183}W peak is at δ 2390.4. The *meso trans* hydrogens are at δ 9.68 (bromo) and 9.76 (methoxy). The *trans* enantiomer peaks are at δ 9.75 (methoxy), 9.73 (bromo) and 9.72 (methoxy). Interestingly, in the case of the *trans* enantiomers, the bromo-bearing dithiolenic hydrogen appears between the two methoxy hydrogens. The ^{183}W peaks are at δ 2384.4 (*meso trans*) and 2383.8 (*trans* enantiomers). The relative populations of the species are within experimental error, *cis*:*meso trans*:*trans* enantiomers 1.04:0.85:2.12 (theoretical 1:1:2). As can be seen, in both cases there is no favouring of any species; in each case the statistically expected amount is observed.

It is clear that the resolution, the position and the sequence on the ppm scale of the various protons in the four complexes investigated differ considerably. Each Br- and MeO-substituted ring is certainly not isolated. On the other hand the consistent fit of the statistical distribution of the populations, and of the other data as well, to the trigonal-prismatic geometry seems to rule out any serious deviations from this geometry (in solution).



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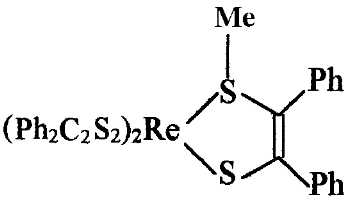

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Octahedral symmetry or distortion towards it or other distortions are expected to give a completely different, more complex experimental pattern.

The chemical consequence of the three-dimensional delocalization is that the three-ring system is 'more aromatic' than the individual rings. If $[W(S_2C_2Ph_2)_3]$ in tetrahydrofuran, is treated with hydrazine and MeI the methylated product **12** is obtained. Further alkylation of **12** is impossible.[13] The two-ring delocalization in **12** is less nucleophilic. Similar observations were made for the corresponding complexes of Cr, Mo and V. Under the same conditions $[Re(S_2C_2Ph_2)_3]$ gives **13**.

Transmittance of medium effects

Two medium effects were investigated: the effect of adding water to the solvent (acetone) and the effect of acid.

The NMR peak of the dithiolenic hydrogen in complex **4** at room temperature is narrow enough to permit observation of the two satellite ^{183}W peaks. The spectrum in Fig. 5(*a*) was obtained in anhydrous acetone. Similar results were obtained in other common solvents, and also with the other complexes investigated ($R^4 = R^5 = R^6 = H$). By adding a little (*ca.* 5%) water to the acetone, however, the peak broadens and the satellites overlap with the central peak [Fig. 5(*b*)]. Additional broadening, due to *cis–trans* exchange,[7] appears at lower temperatures [10 °C, Fig. 5(*c*)]. At higher water or D_2O content the broadening increases further [Fig. 5(*d*), 25–30% D_2O]. The fact that D_2O is equally effective as water and does not eliminate the peak rules out the possibility that there is a proton exchange of the dithiolenic hydrogen with the solvent. Instead, the dynamic path causing the broadening should involve interaction of solvent molecules through the metal (additional co-ordination) or the sulfur atoms (dipole interaction), which is transmitted by the delocalized electronic system.

More evidence was obtained by examining the broadening in complex **9** in the presence of water and acid. The broadening in this case, caused by the presence of water, is illustrated in Fig. 6(*a*). There is more broadening for the protons closer to the dithiolenic ring (δ 6.6–7.3) than for the methyl group (δ 3), indicating that the interaction involves the dithiolenic ring rather than the amine group.

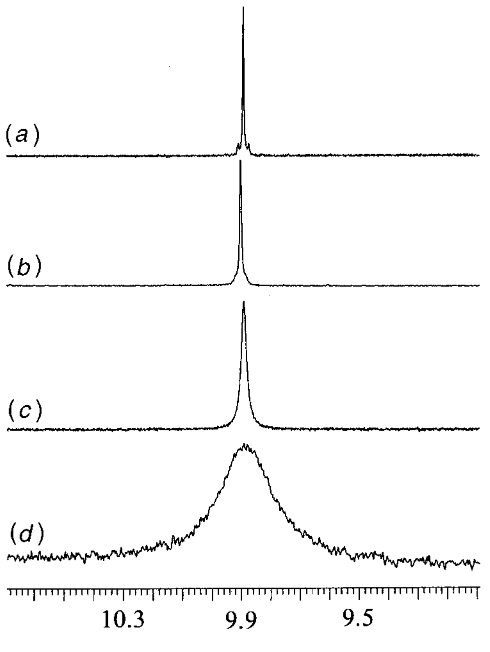

Fig. 5 Proton NMR spectra of complex **4** in the dithiolenic proton region: (*a*) in anhydrous acetone at 25 °C, (*b*) in acetone–water (19 : 1) at 25 °C, (*c*) in acetone–water (19 : 1) at 10 °C and (*d*) in acetone–D_2O (7 : 3) at 25 °C

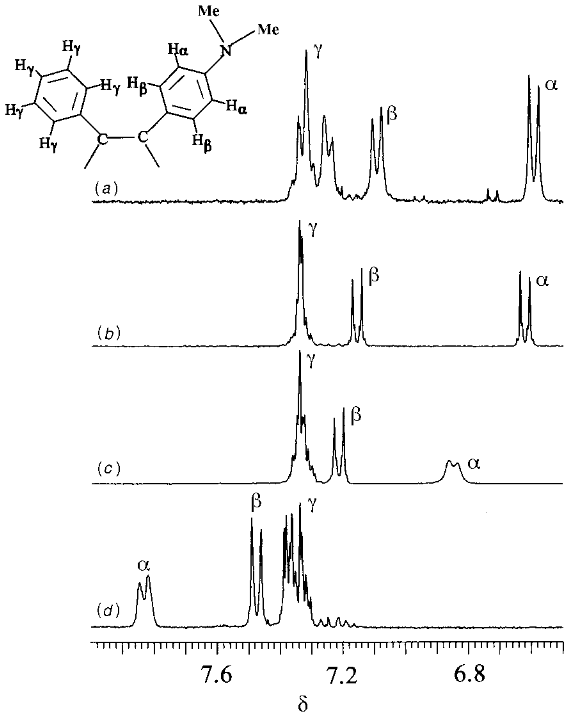

Fig. 6 Proton NMR spectra of complex **9** in the phenyl protons region: (*a*) in acetone–water (4 : 1) at 25 °C, (*b*) in anhydrous acetone at 25 °C, (*c*) in anhydrous acetone with a small amount of gaseous HCl at 25 °C and (*d*) in anhydrous acetone with a high concentration of gaseous HCl at 25 °C

In the mechanism postulated for the photooxidation of water in the visible region,[9] it is necessary to have an interaction of the photocatalyst with water. The broadening reported here can be considered as direct evidence of such an interaction. The photochemistry of complexes without proton-acceptor groups, such as **10**, is dramatically affected by adding acid; in acidic solutions the yields for the photooxidation of water decrease, while the photostability increases.[14] Yet, the UV/VIS spectrum remains practically unchanged, and there is no indication in general for appreciable protonation of the sulfur. With complex **9** on the other hand the situation is quite different (Fig. 7). If enough acid is added the original non-protonated complex ($\lambda_{max} = 805$ nm in acetone) is replaced by one protonated species ($\lambda_{max} = 640$ nm in acetone). The replacement is gradual with no 'titration breaks'. Isosbestic points do not appear, which implies that more than one protonated species is formed,

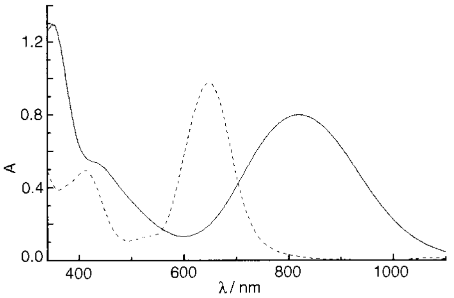

Fig. 7 The UV/VIS spectra of complex **9** (3.4×10^{-5} mol dm^{-3}) in acetone–water (4 : 1) without HCl (——) and with 2.4 mol dm^{-3} HCl (– – –)

presumably by successively adding protons to two or three dimethylamino groups. The protonation is favoured in mixed solvents with low water content. In pure acetone an increase in temperature shifts the protonation equilibrium towards the neutral complex; the process is exothermic. As the percentage of water in the mixed solvent increases the effect of temperature decreases. With 20% water there is hardly any temperature effect. Boyde, Garner and co-workers[15] found that three protons can add to ligand nitrogen atoms of prismatic $[Mo^{IV}(qdt)_3]^{2-}$ (qdt = quinoxaline-2,3-dithiolate) which is analogous to what is being reported here. The shift in the UV/VIS spectra in this case is to longer wavelengths rather than to shorter as in Fig. 7, but this is probably because different energy levels are involved in the transition; our lowest unoccupied molecular orbital (LUMO) corresponds to their highest occupied molecular orbital (HOMO).

The NMR spectra of complex **9** in acetone and the corresponding assignments are shown in Fig. 6(*b*). Upon addition of a small amount of gaseous HCl the peaks at δ 6.58–6.65 (H_α are shifted downfield and broadened [Fig. 6(*c*)]. A similar effect is observed for the peaks at δ 7.17–7.18 (H_β), but less pronounced. The peaks of the unsubstituted phenyl (δ 7.28–7.38) are not shifted or broadened appreciably, but the number and positions of the peaks, resulting from coupling, are influenced. The influence is more dramatic at high acidity where the peaks of the substituted phenyls move downfield to the left of those of the unsubstituted [Fig. 6(*c*)]. At intermediate acid concentrations all peaks mix.

The fast protonation equilibrium obviously involves the dimethylamine group, and affects more the closest-lying nuclei. It is remarkable, however, that only average peaks for the whole molecule appear. An averaging is expected because of the protonation–deprotonation equilibria, but this is not confined locally, it spreads over the whole molecule. At room temperature the rate of the intramolecular transmission of the effect of protonation is comparable to the rate of the proton-exchange reaction. The ratio of each of the integrals of the three kinds of substituted phenyl hydrogens, to that of the unsubstituted phenyls, remains constant; it does not depend on the extent of protonation. The protonated system effectively acts as a unified monoprotic acid.

The metal oxidation state

Given that the electrons are highly delocalized, it is a difficult task indeed to assign them to the metal or to the ligands,[16] and to decide on theoretical grounds about the oxidation state of the metal.[1,4] However, metal NMR chemical shifts can give a satisfactory picture of the actual electron distribution, more realistic perhaps than that given by the conventional oxidation number or by largely arbitrary theoretical assignments.

In this paper we concentrate on molybdenum and tungsten complexes. Molybdenum-95 is a spin $\frac{5}{2}$ nucleus with a nuclear quadruple moment of 0.120, and its observation in non-symmetric (non-tetrahedral or non-octahedral) environments is difficult, but a direct observation was possible, in the form of wide hump at δ 1470 with a band width of 1200 Hz (100 mg of complex **8** in a 10 mm tube over a *ca.* 18 h period). In this region, the chemical shift of ^{95}Mo is observed for compounds such as $[Mo(S_4)]^{2-}$ and $[Mo(O_xS_{4-x})]^{2-}$, while for compounds like $[Mo(CO)_6]$ the chemical shift appears at *ca.* δ −1800, with $[MoO_4]^{2-}$ at δ 0.

The results for the seven tungsten complexes investigated here (**1**–**7**) showed that all the chemical shifts observed are in the δ 2400 region and comparable to that of WCl_6 (δ 2000), while $[WO_{42}]^{2-}$ appears at δ 0 and $[W(CO)_6]$ at *ca.* δ −3000. The ratio of the chemical shifts of ^{183}W to ^{95}Mo in dithiolenes is *ca.* 1.6 : 1, close to the 1.5 : 1 recorded for other classes of compounds of these metals.[17] The metals are effectively 'naked', having been stripped of their valence electrons. The electrons are spread over the ligand, and the charge-transfer transitions observed must be from orbitals of predominantly ligand character to those of predominantly metal character. This picture is intriguing, especially since the metal is the conspicuous active centre in the interaction with external donors and in catalysis and photocatalysis as well.[9] In the case of the large chemical shifts of ^{95}Mo and ^{183}W the effect of the ring currents is negligible (a few ppm). The observed deshielding must originate almost entirely from the displacement of the electron towards the ligand.

Conclusion

Unlike the usual organic aromaticity the metal-mediated delocalization investigated here is three dimensional and involves rings which can be non-planar. Also, unlike conventional organometallics, the compounds have no localized M–C bonds, yet the metals certainly interact with next neighbour carbon atoms, even to substituents to these atoms several bonds away. This delocalization involves mixing of σ–π functions and is responsible for the existence of a multicorrelation of a variety of experimental data with the sensitive to conjugation Hammett constant σ_p^+. The highly delocalized electron distribution obviously affects these experimental data differently, but the correlation is good for all of them.

The electron distribution can in principle be changed for each of the three dithiolenic rings separately, by changing the substitution. However, the change in one ring strongly affects the others as well, as indicated by their NMR spectra. At room temperature there is a through-the-electronic-distribution transmission of the substituent effects from one ring to another, but there is also intramolecular exchange between rings, since in the prismatic geometry the *cis* and *trans* configurations are rapidly exchanged. At lower temperatures the two effects are resolved.

In addition to substitution, the three-dimensional delocalized system is affected by the medium. It is significant that water interacts strongly with the dithiolenic molecule. This interaction is obviously intermolecular, presumably involving an increase in the co-ordination number of the metal and/or dipole–dipole interactions, and it is 'felt' by the molecule as a whole. The effect of the acid was also studied. The dithiolenic rings have nucleophilic sites which can in principle act as proton receptors, namely the sulfur atoms. This however does not happen, at least to a measurable extent. There is an effect, however, if the dithiolene has a basic substituent, even a weakly basic one like NMe_2. Local attachment of protons on such groups affects remote sites of the molecule.

The high delocalization demonstrated again raises the question of the oxidation state of the metal. The answer given here depends on measurements of the chemical shifts of the metal nuclei themselves. It is shown that W and Mo in the neutral tris(dithiolenes) studied are highly electron deficient, more deficient than in compounds like WCl_6 and $[MoO_4]^{2-}$ where the conventional oxidation numbers are VI.

References

1 (*a*) G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc*., 1966, **88**, 3235; (*b*) D. C. Olson, V. P. Mayweg and G. N. Schrauzer, *J. Am. Chem. Soc*., 1966, **88**, 4876; (*c*) G. N. Schrauzer, V. P. Mayweg and W. Heinrich, *J. Am. Chem. Soc*., 1966, **88**, 5174; (*d*) G. N. Schrauzer, *Acc. Chem. Res*., 1969, **2**, 72; (*e*) A. E. Smith, G. N. Schrauzer, V. P. Mayweg and W. Heinrich, *J. Am. Chem. Soc*., 1965, **87**, 5798.

2 U. T. Mueller-Westerhoff and B. Vance, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, Pergamon, Oxford, 1987, vol. 2, ch. 16, pp. 595–631; U. T. Mueller-Westerhoff and A. Alscher, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 638.

3 S. Boyde, C. D. Garner, J. A. Joule and D. J. Rowe, *J. Chem. Soc., Chem. Commun*., 1987, 800.

4 E. I. Stiefel, R. Eisenberg, R. C. Rosenberg and H. B. Gray, *J. Am. Chem. Soc*., 1966, **88**, 2956.

5 (*a*) J. A. McCleverty, *Prog. Inorg. Chem*., 1968, **10**, 49; (*b*) R. Eisenberg, *Prog. Inorg. Chem*., 1970, **12**, 295; (*c*) A. D. Wentworth, *Coord. Chem. Rev.*, 1972, **9**, 171.

6 (*a*) R. Eisenberg and J. A. Ibers, *Inorg. Chem*., 1966, **3**, 411; (*b*) A. Davison, B. V. Howe and E. T. Showl, *Inorg. Chem*., 1967, **6**, 458; (*c*) R. Eisenberg, E. I. Stiefel, R. C. Rosenberg and H. B. Gray, *J. Am. Chem. Soc*., 1966, **88**, 2874; (*d*) E. I. Stiefel, Z. Dori and H. B. Gray, *J. Am. Chem. Soc*., 1967, **89**, 3353; (*e*) G. F. Brown and E. I. Stiefel, *Inorg. Chem*., 1973, **12**, 2140; (*f*) M. J. Bennet, M. Cowie, J. L. Martin and J. Takats, *J. Am. Chem. Soc*., 1973, **75**, 7504; (*g*) M. Cowie and M. J. Bennett, *Inorg. Chem*., 1970, **15**, 1584, 1589, 1595; (*h*) K. Tatsumi, Y. Sekiguchi, A. Nakamura, R. E. Crammer and J. S. Rupp, *Angew. Chem., Int. Ed. Engl*., 1986, **25**, 86; (*i*) K. Tatsumi, I. Matsubara, Y. Sekiguchi, A. Nakamura and C. Mealli, *Inorg. Chem*., 1989, **28**, 773.

7 D. Argyropoulos, C. A. Mitsopoulou and D. Katakis, *Inorg. Chem*., 1996, **35**, 5549.

8 B. G. Dickinson and L. Pauling, *J. Am. Chem. Soc*., 1923, **45**, 1465; A. E. Van Arkel, *Recl. Trav. Chim. Pays-Bas*, 1926, **45**, 442; E. Bell and R. E. Herfert, *J. Am. Chem. Soc*., 1957, **79**, 3351; A. N. Zelikman, Ju. D. Cistjakou, G. V. Indenbaum and O. E. Krein, *Sov. Phys. Crystallogr.* (*Engl. Transl.*), 1961, **6**, 308; A. Semiletov, *Sov. Phys. Crystallogr.* (*Engl. Transl.*), 1961, **6**, 428; Y. Takeuchi and W. Nowacki, *Schweiz. Mineral Petrogr. Mitt*, 1964, **44**, 105; F. Hulliger, *Struct. Bonding* (*Berlin*), 1968, **4**, 83; R. Huisman, R. De Jonge, C. Haas and F. Jellinek, *Solid State Chem*., 1971, **3**, 56; B. L. Evans, *Physics and Chemistry of Compounds with Layered Structures*, Reidel, Dordrecht, 1976, vol. 4, p. 1; F. Hulliger, *Structural Chemistry of Layer Type Phase, in Physics and Chemistry of Materials with Layered Structures*, ed. F. Levy, Reidel, Dordrecht, 1976; D. O'Hare, *Inorganic Intercalation Compounds, in Inorganic Methods*, eds. D. W. Bruce and D. O'Hare, Chichester, 1991, p. 165.

9 (*a*) C. Mitsopoulou, J. Konstantatos, D. Katakis and E. Vrachnou, *J. Mol. Catal.*, 1991, **67**, 137; (*b*) E. Vrachnou, C. A. Mitsopoulou, J. Konstantatos and D. Katakis, in *Photochemical and Photobiological Research and Development*, eds. G. Grassi and D. O. Hall, Elsevier Applied Science, London, 1989, vol. 5, pp. 1098–1115; (*c*) D. Katakis, C. Mitsopoulou, J. Konstantatos, E. Vrachnou and P. J. Falaras, *J. Photochem. Photobiol. A: Chem*., 1992, **68**, 375; (*d*) D. Katakis, C. Mitsopoulou and E. Vrachnou, *J. Photochem. Photobiol. A: Chem*., 1994, **81**, 103; (*e*) E. Lyris, D. Argyropoulos, C. Mitsopoulou and D. Katakis, *J. Photochem. Photobiol. A: Chem*., in the press.

10 P. Falaras, C. A. Mitsopoulou, D. Argyropoulos, E. Lyris, N. Psaroudakis, E. Vrachnou and D. Katakis, *Inorg. Chem*., 1995, **34**, 4536.

11 J. March, *Advanced Organic Chemistry*, 3rd edn., Wiley-Eastern, New Delhi, 1987, pp. 242–250; P. Sykes, *A Guidebook to Mechanism in Organic Chemistry*, 5th edn., Longman, London and New York, 1981, pp. 345–359; H. Shiozaki, H. Nakazumi and T. Kitao, *J. Soc. Dyers Colour.*, 1988, **104**, 173.

12 G. P. Ford, A. R. Katritzky and R. D. Topsom, *Correlation Analysis in Chemistry*, eds. N. B. Chapman and J. Shorter, Plenum, New York, 1978, p. 306.

13 G. N. Schrauzer and H. N. Rabinowitz, *J. Am. Chem. Soc*., 1969, **91**, 6322.

14 G. A. Mitsopoulou and D. Katakis, unpublished work.

15 S. Boyde, C. D. Garner, J. H. Enemark and R. B. Ortega, *Polyhedron*, 1986, **5**, 377; S. Boyde and C. D. Garner, *J. Chem. Soc., Dalton Trans.*, 1987, 297, 2267; 1991, 713.

16 R. Hoffmann, J. M. Howell and A. R. Rossi, *J. Am. Chem. Soc*., 1976, **98**, 2484; S. Alvarez, R. Vicente and R. Hoffmann, *J. Am. Chem. Soc*., 1985, **107**, 6253; S. Alvarez and R. Hoffmann, *Anal. Quim*, 1986, **82**, 52.

17 D. Rehder, *Coord. Chem. Rev*., 1991, **110**, 161.

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