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Dirhenium(III) complexes with *N,N*-dimethyladenine and 7-azaindole

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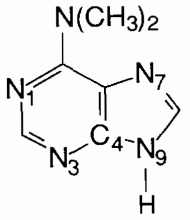
Abstract

$Re_2X_2(CH_3CO_2)_4$ (X = Cl, Br) reacts with anionic *N*6,*N*6-dimethyladenine ($dmad^-$) in ethanol to form dark purple $Re_2X_2(dmad)_4$, in which the acetate ligands are replaced by the N3/N9-bridging purine. Different relative orientations of the dissymmetric ligands about the Re–Re axis lead to four stereoisomers producing resolved signals in the ^1H NMR spectra. The compound can be reversibly protonated at N7 to yield the $[ReX_2(Hdmad)_4]^{4+}$ ion. Hdmad and $(Bu_4N)_2[Re_2Cl_8]$ in ethanol form a red-brown dinuclear material formulated as $[Re_2Cl_4(Hdmad)_2]Cl \cdot 4H_2O$ $0.5C_2H_5OH$, where the purine is N3/N9-bridging and N7-protonated. Heating $(Bu_4N)_2[Re_2Cl_8]$ and 7-azaindole (Haza) without solvent leads to a brown $Re_2Cl_2(aza)_4$ material, in which different orientations of the N1/N7-bridging ligand again produce various stereoisomers. Magnetic anisotropy of the quadruple metal–metal bond probably contributes to the very large downfield shifts observed for the ^{13}C signals of the carbon atoms just above the Re–Re vector.

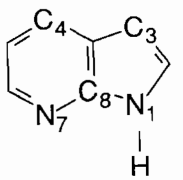
Key words. Rhenium complexes; Purine complexes, Dinuclear complexes

Introduction

As a continuation of our long-standing interest for metal coordination to purines, we have been looking recently at their ability to act as bridging ligands in dinuclear metal–metal bonded complexes. Purines are known to form $M_2(L\text{-}L')_n$ units with various dimetal centres [1–4], but the possibility of using them to induce or support metal–metal bonding has received so far little attention [5]. We wish to report here the synthesis and characterization of complexes of *N*6,*N*6-dimethyladenine (6-dimethylaminopurine) (I) with the Re_2^{6+} core, as well as a related compound with 7-azaindole (II), which serves as a simplified model for purines.



Hdmad (**I**)



Haza (**II**)

Experimental

Reactants and methods

$KReO_4$, $NaOCH_3$, $(Bu_4N)Br$ (Aldrich) and PhCOCl (American Chemicals) were used as received. Haza (Aldrich) was recrystallized from benzene. HBr and HCl gases were obtained from Matheson. Hdmad [6], $(Bu_4N)_2[Re_2Cl_8]$ [7], $Re_2Cl_4(CH_3CO_2)_2 \cdot 2H_2O$ [8] and $Re_2X_2(CH_3CO_2)_4$ (X = Cl, Br) [9] were prepared according to literature methods. $(Bu_4N)_2[Re_2Br_8]$ was made from the chloro compound [10] and used to prepare $Re_2Br_2(CH_3CO_2)_4$.

Solution ^1H and ^{13}C NMR spectra were obtained in $CDCl_3$ (Cambridge Isotopes) at 400 and 100.62 MHz, respectively, on the Bruker WH-400 spectrometer of the Centre Régional de RMN Haut Champ, situated at the Université de Montréal. Frequencies were referenced to the residual solvent signals (^1H, δ 7.265; ^{13}C, δ 76.94 ppm). Variable-temperature ^1H experiments were run on a WH-80 Bruker spectrometer. ^{13}C CP-MAS spectra were recorded at 75.43 MHz on a Varian VXR-300 apparatus. The aromatic signal of hexamethylbenzene (δ 132.1 ppm) was used as external reference. Other conditions: spinning rates, 3–4.8 KHz; recycle delay, 20–35 s; sideband suppression routine used.

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IR spectra were recorded as KBr or CsI pellets on a Perkin-Elmer 783 spectrophotometer between 4000 and 200 cm^{-1}. UV–Vis spectra were measured on a Varian DMS 100S instrument

Preparative work

Preparations were carried out under argon in dry degassed solvents, using standard Schlenk techniques. Compounds were isolated by filtration in air. Elemental analyses were done by Guelph Chemical Laboratories, Guelph, Canada.

$Re_2Cl_2(dmad)_4$ (1)

Hdmad (0.84 g, 5.2 mmol) and $NaOCH_3$ (0.32 g, 5.9 mmol) were stirred in ethanol (50 ml). $Re_2Cl_2(CH_3CO_2)_4$ (0.71 g, 1.05 mmol) was then added and the solution became very dark immediately. The mixture was refluxed for 24 h and the solvent was reduced to half volume. The dark purple solid (0.95 g, 83%) was isolated by filtration and washed with ethanol (2 × 15 ml) and diethyl ether (2×15 ml). *Anal.* Found: C, 29.1; H, 2.8; N, 24.4; Cl, 6.5%. The best fit is obtained for the average formula $Re_2Cl_2(dmad)_{3.6}(CH_3CO_2)_{0.4}$. Calc. for $Re_2Cl_2C_{26}H_{30}N_{18}O_{0.80}$: C, 29.7; H, 2.9; N, 24.0; Cl, 6.7%, see discussion below. UV–Vis (nm (ε)) in $CHCl_3$: 737 (1430), 538 (5080), 357 (10 400), 320 (21 550), 278 (28 700); in 6 M aqueous HCl: 792 (4000), 558 (8230), 454 (sh), 324 (22 500), 288 (32 300). Substitution of axial Cl^- by CH_3O^- did not occur when a greater excess of $NaOCH_3$ was used.

$[Re_2Cl_4(Hdmad)_2]Cl_2 \cdot 4H_2O$ $0.5C_2H_5OH$ (4)

$(Bu_4N)_2[Re_2Cl_8]$ (0.17 g, 0.15 mmol) and Hdmad (0.05 g, 0.30 mmol) were refluxed in 20 ml of ethanol for 24 h. The volume of the resulting solution was reduced by half and 20 ml of diethylether were added. A red-brown product was isolated by filtration, washed with ether and dried under vacuum. *Anal.* Calc. for $Re_2Cl_6C_{15}H_{29}N_{10}O_{4.5}$: C, 17.9; H, 2.9; N, 13.9. Found: C, 17.9; H, 2.3; N, 13.6% Yield 0.122 g, 81%. Pink solutions were obtained in DMF, MeOH or acetone/water. UV–Vis (nm (ε)) in DMF: 730 (2090), 510 (5180), 326 (21 800), 289 (22 300), 277 (sh).

$Re_2Cl_2(aza)_4$ (5)

A mixture of $(Bu_4N)_2[Re_2Cl_8]$ (1.0 g, 0.88 mmol) and Haza (3.5 g, 30 mmol) was heated to the melting point (105 °C) and stirred at this temperature. After 10 min, the mixture had turned dark orange. Heating was maintained for 18 h. The brown solid was transferred to a glass frit, and washed with benzene and ethanol. It still contained free azaindolium ions as indicated by IR. By extraction with $CHCl_3$, the azaindolium salt was left behind and the solution was evaporated to obtain very small diamond-shaped orange crystals of the Re compound. *Anal.* Calc. for $Re_2Cl_2C_{28}H_{20}N_8$: C, 36.9; H, 2.2; N, 12.3, Cl, 7.8. Found: C, 36.6; H, 2.4; N, 12.6; Cl, 7.9%. Yield 0.52 g, 65% UV–Vis (nm (ε)) in $CHCl_3$: 721 (590), 661 (sh), 438 (9250), 355 (7760), 294 (11 500), 270 (17 800).

Results and discussion

Reaction of dimethyladenine with $Re_2Cl_2(CH_3CO_2)_4$

By refluxing $Re_2Cl_2(CH_3CO_2)_4$ and a small excess of $dmad^-$ ions (from Hdmad and $NaOCH_3$) in ethanol for 24 h, ~90% of the acetate ligands are displaced by N3/N9-bridging adenine units to produce $Re_2Cl_2(dmad)_4$ (**1**) molecules of the type depicted in Fig. 1 as the major product. The dark purple material is somewhat soluble in $CHCl_3$. The lowest-energy band in the visible spectrum (737 nm) should correspond to the δ–δ* transition in the Re_2^{6+} core [11–14]. The low-field portion of the 400 MHz ^1H NMR spectrum is shown in Fig. 2. A complex spectrum is obtained because unlike carboxylates, the bridging purine contains non-equivalent donors, leading to four combinations of relative ligand orientations in the $Re_2(L\text{-}L')_4$ core (Fig. 3). In each of the H2 (8.51–8.75 ppm) and H8 (8.02–8.17 ppm) regions, the six strongest signals, accounting for 90% of the intensity, originate from similarly bonded adenine units in these different stereoisomers Table 1 summarizes the predicted isomer distribution and NMR characteristics, assuming random orientations of the ligands about the Re–Re axis The presence of two strong and four weaker peaks in each region corresponds well with the intensities predicted for a statistical distribution of the four $Re_2Cl_2(dmad)_4$ isomers. The same spectral regions also contain weak signals for mixed $Re_2Cl_2(CH_3CO_2)(dmad)_3$ species due to incomplete acetate substitution (starred signals in Fig. 2). The number of resolved peaks does not correspond exactly with the predictions of Table 1, probably because some components are masked by those of $Re_2Cl_2(dmad)_4$. However, three close acetate signals (1.1:2 intensity ratio)

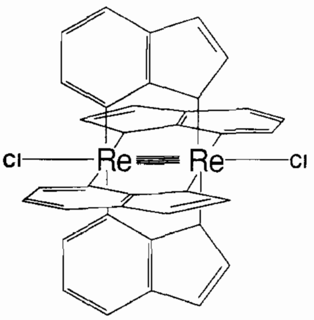

Fig 1 Diagram of one of the possible stereoisomers of an $Re_2Cl_2(L\text{-}L')_4$ molecule containing a bridging L-L′ ligand with non-equivalent rings similar to adenine and azaindole.

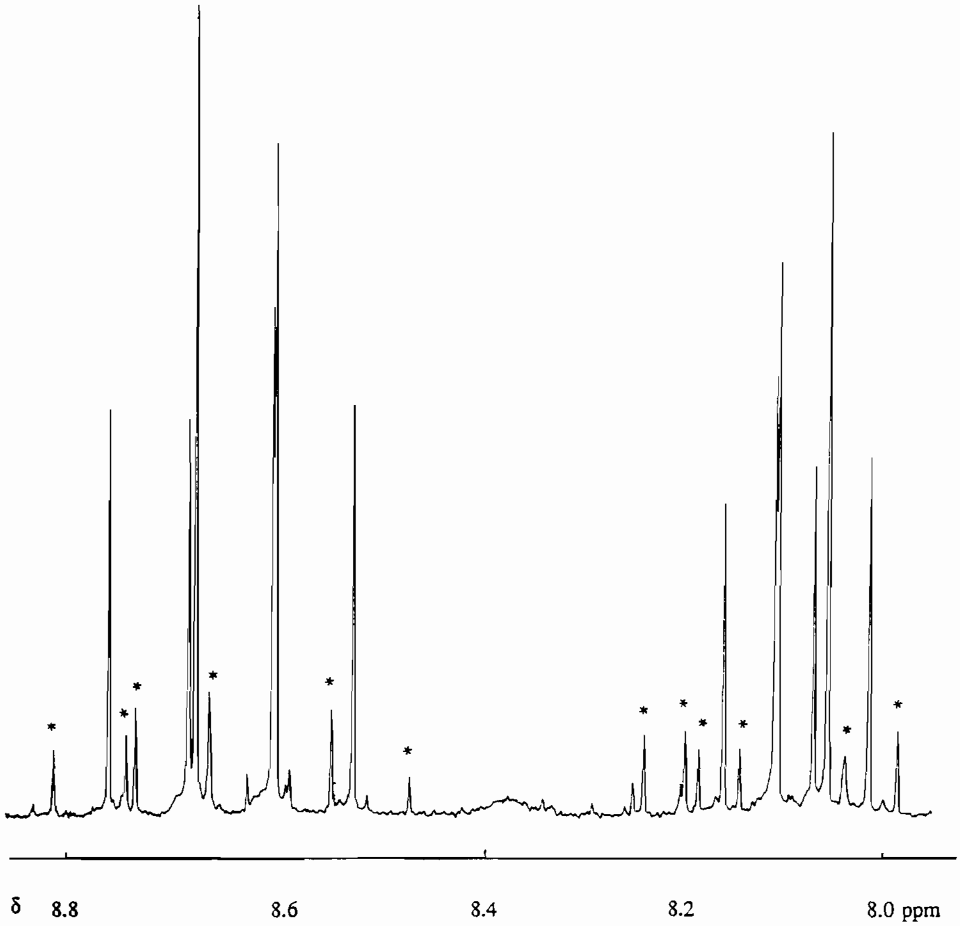

Fig. 2. H2 and H8 regions of the ^{1}H NMR spectrum of the product isolated from the reaction of $Re_2Cl_2(CH_3CO_2)_4$ with the *N*6,*N*6-dimethyladenine anion The main signals are due to the various $Re_2Cl_2(dmad)_4$ stereoisomers, starred signals correspond to partial substitution products $Re_2Cl_2(CH_3CO_2)(dmad)_3$ Room temperature, $CDCl_3$, 400 MHz

are found at ~3.21 ppm [12]. Samples completely free of $Re_2Cl_2(CH_3CO_2)(dmad)_3$ were not obtained, but substitution of acetate increased to ~98% when the mixture was refluxed for a week or more.

In these compounds, the $dmad^-$ ligands should be bridging via the N3/N9 pair, considering that the N3–C4–N9 region is structurally and electronically similar to a carboxylate and that the remaining nitrogen atoms are not available. Indeed, in adenines, the 6-NH_2 or 6-NR_2 lone pair participates in the purine π system and it has never been found to coordinate [4]. When the amino group is not substituted, adenines can coordinate via N7 and N1, but these sites are sterically hindered here by the methyl groups, held in the plane of the rings by the π system. The CH_3Hg^+ cation, whose steric demand is low, has been shown to coordinate only to the N3/N9 region of *N*6,*N*6-dimethyladenine [15] and the crystal structure of $[(CH_3Hg)_2(dmad)]ClO_4$ confirmed the bridging role of the purine via N3 and N9.

Direct indications for N3/N9 bonding in the complex are provided by the IR spectrum (see 'Supplementary material'). The vibrations of adenines have been discussed by various workers [16–18]. The changes in the spectrum of Hdmad upon CH_3Hg^+ coordination have been described in detail [19]. The spectrum provides clear evidence for ligand deprotonation in $Re_2Cl_2(dmad)_4$. The ν(N–H) vibration at ~2800 cm^{-1} is absent in the complex, leaving only weak peaks at 3119, 2921 and 2810 cm^{-1} for the ν(C–H) and $\nu(CH_3)$ modes. The ligand out-of-plane γ(N–H) band at 870 cm^{-1} is also removed. Other modifications observed here have been noted to occur for both the N9-bonded $[CH_3Hg(dmad)]$ and the N9/N3-bonded $[(CH_3Hg)_2(dmad)]^+$ species. They involve ring modes moving from 544, 646, 687 and 1301 cm^{-1} in Hdmad to 581, 656, 702 and 1278 cm^{-1}, respectively, in the complexes. The two $\nu(N–(CH_3)_2)$ bands at 963 and 1080 cm^{-1} are also displaced to 998 and 1097 cm^{-1}, respectively, by complexation. Distinction between N9- and N9/N3-coor-

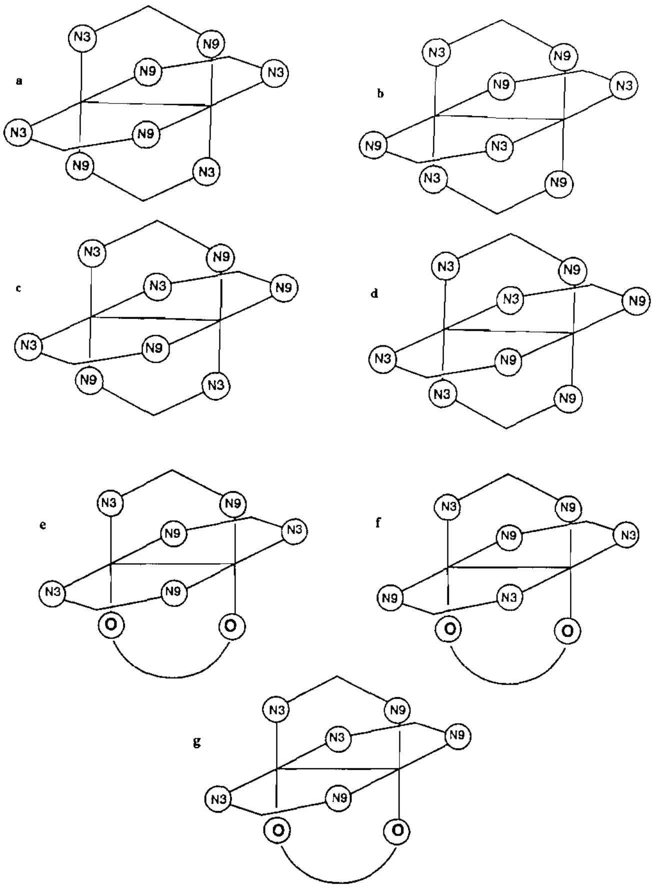

Fig 3. Schematic representation of the various stereoisomers of $Re_2Cl_2(dmad)_4$ (a–d) and $Re_2Cl_2(CH_3CO_2)(dmad)_3$ (e–g)

TABLE 1 Characteristics of the ligand NMR signals for a random distribution of orientation of the dmad⁻ units in the stereoisomers of $Re_2Cl_2(dmad)_4$ and $Re_2Cl_2(CH_3CO_2)(dmad)_3$

	Isomer			
	a	b	c	d
$Re_2Cl_2(dmad)_4$				
Population	2/8	1/8	4/8	1/8
No of signals	1	1	3	1
Relative intensity	4	4	1:1:2	4
Weighted intensity ratio	8	4	4:4·8	4
	e	f	g	
$Re_2Cl_2(CH_3CO_2)(dmad)_3$				
Population	2/4	1/4	1/4	
No of signals	3	2	2	
Relative intensity	1:1:1	2:1	2:1	
Weighted intensity ratio	2:2 2	2.1	2:1	

dination can be made from a number of specific spectral changes. Bands at 782, 899, 937, 1389, 1570 and 1607 cm^{-1} are found near the positions observed for $[(CH_3Hg)_2(dmad)]ClO_4$, whereas they occured at 798, 882, 950, 1370, 1540 and 1590 cm^{-1}, respectively, for $[CH_3Hg(dmad)]$. Another obvious modification is found for the ligand mode at 379 cm^{-1}, which appears here at 413 cm^{-1}. Similar patterns of shifts have been noted for various other complexes [5] and they provide strong support for N9/N3-bridging in the present case. A weak band is found at 217 cm^{-1} for the axial ν(Re–Cl) mode [11, 20].

The ^1H NMR data are given in Table 2. The complexity of the H2 and H8 regions (Fig. 1) has been commented on above. Complex patterns are also observed for the methyl groups, because of multiple stereoisomers and non-equivalence of the two methyl groups. For free Hdmad, the 80 MHz spectrum shows a single methyl signal at 3.62 ppm, because of fast rotation about the $C6–N(CH_3)_2$ bond, as do the CH_3Hg^+ complexes mentioned earlier [15] However, rotation is slowed down in the present Re compound. The 80 MHz spectrum at room temperature shows two very broad, partly overlapping, signals typical of near-coalescence. At 213 K, the spectrum contains two narrow signals at 3.82 and 3.42 ppm, respectively, showing some fine structure due to the various stereoisomers. Above 338 K, the two regions merge into a single multicomponent system at 3.62 ppm. In the 400 MHz spectrum, fast rotation is not observed even at room temperature: each type of ligand in each isomer gives two resolved methyl signals near 3.82 and 3.42 ppm, respectively. From the coalescence temperature of 330 K observed at 80 MHz, the rate constant is calculated to be 71 s^{-1} [21], leading to an activation energy $\Delta G^{\neq}$ of 16.6 kcal/mol (69.4 kJ/mol) [22]. A comparable value of ~15 kcal/mol has been reported for the N1-protonated ligand H_2dmad^+ and other adenines [23]. Coordination of the Re_2^{6+}

TABLE 2. ^1H NMR data[a]

	H2	H3	H4	H5	H6	H8	CH_3	
Hdmad	8.393					7.964	3 58	
1[b]	8.665					8.066	3.894	3 462
	8.591					8 112	3 855	3.434
	8.747					8.164	3 819	3 404
	8 671					8 116	3 718	3 372
	8 593					8 079		
	8.518					8 028		
Haza	7 36	6 45	7 92	7 03	8.32			
5[b,c]	8.150	6 610	7 975	7.101	9.065			
	8.094	6.590	7.884	7.063	8.937			
	8.056	6.580	7.819	7.049	8.921			
	8.047	6 520	7 774	6 958	8 810			
		6 392	7.754		8.765			

[a] 400 MHz, room temperature, $CDCl_3$. [b] Assignments to individual isomers cannot be made and signals of some stereoisomers are masked for certain protons [c] $J_{23}=3.4$, $J_{45}=7.4$, $J_{46}=1\ 1$, $J_{56}=6\ 0$ Hz.

TABLE 3 ^{13}C NMR data

	C2	C3	C4	C5	C6	C8	C9	CH_3	Solvent
Hdmad[a]	151.76		151.23	118.95	154.29	137.74		37.87	$(CD_3)_2SO$
Hdmad	151.7		151.7	119.4	154.8	140.3		36.5, 39.1	solid
$[(CH_3Hg)_2(dmad)]NO_3$[a]	149.9		151.2	120.7	153.9	146.4		38.5	$(CD_3)_2SO$
1	151.9[b]		167.3	120.0	154.5	146.2[b]		39.5, 37.4[b]	$CDCl_3$
	152.3[e]					147.2[e]			
1	155.0[f]		168.7	121.0	155.0[f]	148.5		37.3	solid
4	156.5		167.4	108.8	152.6	146.5		42.9	solid
Haza[c]	128.0	99.3	129.6	113.9	141.5	148.4	121.1		solid
	126.1	99.9	128.2	115.5	142.6	148.6	119.7		$(CD_3)_2SO$
5	140.1[d]	104.9	131.5	114.9	141.0[d]	162.6	127.2		solid
$[(CH_3Hg)_2(aza)]ClO_4$[c]	136.8	104.1	136.8	116.3	141.4	150.1	128.9		solid
	138.2	101.3	132.6	114.3	140.4	149.9	126.5		$(CD_3)_2SO$

[a] Ref 15. [b] ^{1}J(C2–H2) = 214, ^{1}J(C8–H8) = 215, ^{1}J(C–H) (methyl) = 139 Hz. [c] Ref. 24 [d] These assignments could be interchanged. [e] Weaker signals half intensity [f] Not resolved.

unit (this case) or N1-protonation (to form H_2dmad^+) [23] induce a π-electron transfer from the amino group into the ring, thereby increasing the double-bond character of the C6-NR_2 bond.

The ^{13}C NMR data are collected in Table 3. The C2 and C8 resonances were identified from the proton-coupled spectrum. Most of the peaks are slightly broadened by the presence of isomers. Only C2 and C8, which are adjacent to the coordination sites, are split into two components ~1 ppm apart with a roughly 1:2 ratio. Correlations between these two components and particular stereoisomers cannot be made. No significant signals are seen in the solution spectrum for the acetate group of the small amount of $Re_2Cl_2(CH_3CO_2)(dmad)_3$ present. The ^{13}C CP-MAS spectrum of the solid was also recorded. The signals are very close to those obtained in solution, except for C2 and C8, which appear ~2 ppm downfield in the solid and show no splitting at the present resolution. An additional weak signal at ~24 ppm is due to the acetate methyl group, but nothing is seen for the carboxyl group.

The ^{13}C chemical shifts observed for **1** are close to those found for the same bridging ligand in $[(CH_3Hg)_2(dmad)]ClO_4$, except for C4, which appears 16 ppm downfield. This large deshielding could be related to its location just above the Re–Re quadruple bond, where the influence of diamagnetic anisotropy is expected to be important. To our knowledge, diamagnetic anisotropy for Re–Re quadruple bonds has not been evaluated, but very large values have been calculated for the Mo–Mo quadruple bond from ^1H NMR spectra [25–27]. Diamagnetic anisotropy χ can be determined from the equation $\sigma = \chi[(1-3\cos^2\theta)/12\pi r^3]$, where σ is the chemical shift produced by anisotropy on the nucleus considered, r is the distance between this nucleus and the electric centre of gravity of the metal–metal bond, and θ the angle between the r vector and the bond axis [25]. Assuming that the 16 ppm shift is wholly due to anisotropy and that the geometry ($r = 2.82 \times 10^{-10}$ m, $\theta = 90°$) found for the related complex $Mo_2(CH_3CO_2)_2(aza)_2$ [1] is applicable here, χ is estimated to be -13500×10^{-36} m^3 per molecule for the Re–Re quadruple bond, that is, roughly twice the value for the Mo–Mo bond. Shifts on ^{13}C resonances can depend on a number of other factors at least as large as diamagnetic anisotropy. For instance, bridging probably requires significant ligand deformation to adjust the N3/N9 'bite'; to the Re–Re separation. Nevertheless, considering that large downfield shifts are also found in our other compounds (see below) and that the ^{13}C CP-MAS carboxyl signals for $Re_2Cl_2(CH_3CO_2)_4$ and $Re_2Cl_4(CH_3CO_2)_2 \cdot 2H_2O$ (198.7 and 196.3 ppm, respectively) also appear at much lower field than for free acetate*, anisotropy of the Re_2^{6+} unit probably makes a substantial contribution to the observed shift.

$Re_2Br_2(CH_3CO_2)_4$ reacts with $dmad^-$ like the chloro analogue, forming $Re_2Br_2(dmad)_4$ (**2**) as the major product. The two first bands in the UV–Vis spectrum in $CHCl_3$ (744 and 550 nm) occur at slightly lower energies than for the chloride (737 and 538 nm), whereas the remaining bands are virtually unaffected. The IR spectra of the bromo and chloro materials are superposable, except for the ν(Re–Cl) band at 217 cm^{-1}. The various stereoisomers produce resolved ^1H NMR signals for each type of proton. The methyl resonances are not greatly displaced, but those of H2 (8.79–8.90 ppm) and H8 (8.15–8.30 ppm) appear at slightly lower field than for the chloro analogues.

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*Chemical shifts for the free acetate ion in $CDCl_3$ are 20.8 (methyl) and 177.6 (carboxyl) ppm [28]. The acetate methyl signals in our CP-MAS ^{13}C spectra are 25.8/24.5 ppm for $Re_2Cl_2(CH_3CO_2)_4$ and 27.1 ppm for $Re_2Cl_4(CH_3CO_2)_2 \cdot 2H_2O$

Protonation of [$Re_2Cl_2(dmad)_4$] (1)

In the above compounds, the formally anionic N3/N9-bridging ligand possesses lone pairs on N7 and N1, where protons can be accepted. Formation of tetraligand–dimetal units containing formally neutral N7-protonated adenine has been reported for other metals in mild acidic solutions [2, 4]. N1/N7-diprotonation can even be achieved at higher acidity [3, 4]. With *N*6,*N*6-dimethyladenine, the crystal structure of the N7-protonated N3/N9-bridged [$(CH_3Hg)_2$(Hdmad)]$(NO_3)_2$ compound [15] indicates that steric hindrance from the methyl groups does not inhibit protonation.

By bubbling HCl gas in a $CHCl_3$ solution of **1**, an insoluble blue–violet powder containing the N7-protonated [Re_2Cl_2(Hdmad)$_4$]$^{4+}$ cation (**3**) deposited. The distinctive IR features mentioned above for N3/N9-bridging are retained here (415, 585, 655, 710, 780, 940, 984, 1100 and 1395 cm^{-1}). N7-protonation leads to a number of spectral changes, similar to those noted for [$(CH_3Hg)_3$(Hdmad)]$(NO_3)_2$ [19]. The spectrum contains a strong ν(N–H) massif centred at 2860 cm^{-1} and a broad weaker γ(N–H) band near 915 cm^{-1}. The high-frequency ring modes, displaced to 1607 and 1570 cm^{-1} by N3/N9-complexation in [Re_2Cl_2(dmad)$_4$], are now found at 1640 and 1620 cm^{-1}, respectively A weak ligand band at 629 cm^{-1}, not detected for **1**, gains intensity and shifts to 620 cm^{-1} for **3**. The 1301/1259/1209/1136 cm^{-1} pattern of the free ligand becomes 1278/1243/1212/1151 cm^{-1} in **1** and 1290/1265/1220/1170 cm^{-1} in **3**. This set of spectral modifications, also observed for Re_2Cl_6(Hdmad)$_2$ below, is consistent with N7-protonation N3/N9-coordination in [Re_2Cl_2(Hdmad)$_4$]$^{4+}$.

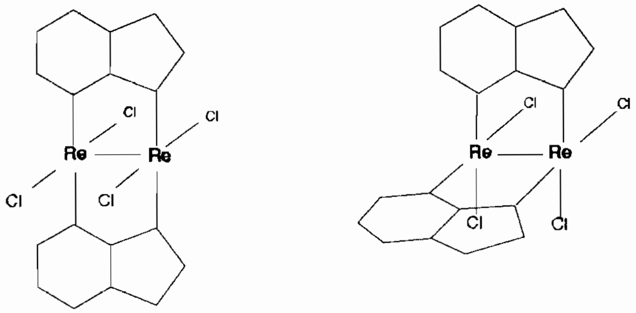
Re_2Cl_2(dmad)$_4$ can be dissolved in HCl: the UV–Vis spectrum recorded in 6 M HCl has its two first bands at 792 and 558 nm, indicating that the Re_2^{6+} core is still present, although at this acidity, the solution most probably contains some N1/N7-diprotonated molecules. Protonation is reversible and **1** can be regenerated by addition of Et_3N or dilute KOH or NH_4OH (provided no excess is used). Attempts to dissolve the solid in solvents like DMF, methanol or acetone gave **1** back with loss of HCl. Protonation can also be achieved with CF_3CO_2H, but addition of various counter-anions failed to precipitate appreciable quantities of the protonated salts. Decomposition occurred with other strong acids.

Reaction of dimethyladenine with [Re_2Cl_8]$^{2-}$

Since complete acetate substitution was difficult to achieve when $Re_2Cl_2(CH_3CO_2)_4$ was used as the source of Re_2^{6+} units, dimethyladenine was reacted with $(Bu_4N)_2[Re_2Cl_8]$. A reaction did take place, but the product was a brown material of composition Re_2Cl_6(Hdmad)$_2\cdot 4H_2O\cdot 0.5C_2H_5OH$. The compound is insoluble in most solvents and only a small amount can be dissolved in DMF, acetone or methanol. The UV–Vis spectrum of such a fresh DMF solution shows low-energy bands at 730 and 510 nm for the Re_2^{6+} core. Decomposition with liberation of HCl starts shortly after dissolution.

The IR spectrum of the solid above 350 cm^{-1} is superposable with that of the N7-protonated [Re_2Cl_2(Hdmad)$_4$]$^{4+}$ species discussed above. An extra band is observed at 339 cm^{-1} for the non-axial ν(Re–Cl) vibration [14, 20, 29]. Spectra of good quality could not be obtained below 250 cm^{-1}, so that no conclusions can be drawn concerning a possible axial ν(Re–Cl) band. The ^{13}C CP-MAS NMR data (Table 3) indicate that the ligand is N3/N9-bridging, since C4 is again observed at very low field. The C5 signal is displaced 12 ppm upfield with respect to **1**. This, and smaller upfield shifts on C8, C6 and C4, are good evidence for N7-protonation, since the same pattern has been observed when guanine [30] and 3-butyladenine [31] are protonated at this site. The very small downfield shift on C2 indicates that N1 is not protonated here, since a large upfield shift is expected for N1-protonation [32].

These data are consistent with the presence of an $Re_2Cl_4(L\text{-}L')_2$ unit (**III**) of the type known for bridging ligands like carboxylates, amidines, hydroxypyridines and bidentate phosphine [33]. However, no definite conclusions can be drawn concerning the *cis* or *trans* arrangements about the Re–Re axis. Easy loss of HCl immediately after dissolution in DMF suggests that Cl$^-$ ions are not coordinated to axial sites, which are probably occupied by H_2O.



III

Reaction of [Re_2Cl_8]$^{2-}$ with 7-azaindole

Azaindole can be regarded as a simplified purine, containing only two potential donor atoms, N7 and N1, in the same arrangement as N3 and N9 of purines. A few experiments were run with this ligand under the conditions used above for Hdmad. No reaction occurred with $Re_2Cl_2(CH_3CO_2)_4$ in ethanol, probably because appreciable amounts of aza$^-$ anions could not be generated by addition of $NaOCH_3$, the acidity of N1–H being very weak (pK ~15) [24] and similar to those of the alcohols (pK_a ~16) [34]. When $[Re_2Cl_8]^{2-}$ was used, a reaction took place, but it yielded mixtures that could not be separated and characterized. For the corresponding reaction with Hdmad, no net liberation of protons was needed to obtain the $Re_2Cl_6(Hdmad)_2$ compound containing N7-protonated adenine. In the present case, azaindole bridging can only be achieved by displacing the N1–H proton and part of the azaindole present must act as proton quencher (pK_a of H_2aza^+ ~4.6) [35], leading to complex mixtures. However, a clean reaction was observed when $(Bu_4N)_2[Re_2Cl_8]$ was reacted with melted azaindole. The azaindolium salt and excess reactants could be separated and a brown $Re_2Cl_2(aza)_4$ solid (**5**) was isolated.

The low-energy UV–Vis bands (721 and 661 nm) indicate the presence of the Re_2^{6+} unit. The IR spectrum unambiguously shows that azaindole is deprotonated and N1/N7-bridging. The strong ν(N–H) massif at 2900 cm^{-1} and the γ(N–H) band at 850 cm^{-1} are absent. Between 400 and 2000 cm^{-1}, all azaindole bands occur virtually unshifted with respect to those reported for the $Mo_2(CH_3CO_2)_2(aza)_2$ dimer [1]. From previous work on CH_3Hg^+ complexes [24], it can be anticipated that the spectrum would show appreciable differences if azaindole were monodentate. In the low-frequency region, there is a band at 217 cm^{-1} for the terminal ν(Re–Cl) mode and weaker features at 283 and 298 cm^{-1} probably corresponding to Re–N motions. Therefore, $Re_2Cl_2(aza)_4$ (**5**) very likely adopts the same structure as $Re_2Cl_2(dmad)_4$ (**1**) (Fig. 1).

The ^{1}H data are collected in Table 2. Signals can be assigned from their chemical shifts and coupling constants as described earlier [24]. Substitution of the N1–H proton is supported by the absence of a low-field signal usually observed for Haza and its non-deprotonated complexes in halogenated solvents [36] and by the lack of extra H1–H2 and H1–H3 couplings. As noted for **1**, each proton shows multiple signals due to the presence of stereoisomers, although the number of components is less than predicted from Table 1, probably because weak multiplets are masked by the strongest ones.

This compound is not soluble enough to give good solution ^{13}C spectra. The CP-MAS data for the solid are given in Table 3. The signals are somewhat broadened, but they show no splitting for the various stereoisomers. By comparing with $[(CH_3Hg)_2(aza)]ClO_4$, N1/N7-complexation of aza^- is obvious: the chemical shifts of the two systems are very close, except for the bridgehead C8 carbon, which appears 13 ppm downfield in the Re compound. As proposed above for the C4 signal of **1**, this probably originates, at least partly, from the anisotropic effect of the Re–Re quadruple bond on the carbon situated directly above.

Conclusions

This work shows that *N*6,*N*6-dimethyladenine and 7-azaindole can play roles similar to carboxylates, amidines and related ligands in stabilizing quadruply-bonded dirhenium compounds. Dimethyladenine has the interesting peculiarity of possessing extra donor atoms available to accept protons and impart acid–base properties to these molecules. Thus, they could lead to valuable materials in which optical and other properties would be pH-sensitive. Efficient studies and applications of such systems are still hampered by the formation of multiple stereoisomers difficult to separate. New approaches based on the condensation of suitable monomers are currently being explored to circumvent these difficulties.

^{1}C NMR spectroscopy proved to be a valuable tool to ascertain the bridging character of the ligand, since the carbon situated directly above the metal–metal bond undergoes a very large downfield shift, in which diamagnetic anisotropy of the metal–metal bond likely plays an important part.

Supplementary material

Full tables of IR frequencies for the complexes are available upon request from the authors.

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