DALTON
FULL PAPER

Transition metal complexes containing the 1,2-dicarba-*closo*-dodecaborane-1,2-dithiolate ligand: crystal structures of $[4\text{-MeC}_5H_4\text{NMe}]_2[\text{Pd}(S_2C_2B_{10}H_{10})I_2]$, $[\text{NEt}_3H][\text{Mo}(\eta^5\text{-C}_5H_5)(\text{NO})(S_2C_2B_{10}H_{10})I]$, $[\text{NBu}_4][\text{Re}(=\text{O})(S_2C_2B_{10}H_{10})_2]$ and $[4\text{-MeC}_5H_4\text{NMe}]_2[\{\text{Mo}(=\text{O})(\mu\text{-O})(S_2C_2B_{10}H_{10})\}_2]$

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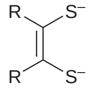
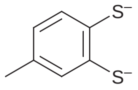
The dithiol ligand 1,2-dicarbaborane-1,2-dithiol, $1,2\text{-(HS)}_2\text{-}1,2\text{-C}_2B_{10}H_{10}$ (H_2cbdt), reacted with anhydrous PdI_2 to form $[\text{Pd(cbdt)}I_2]^{2-}$, isolated as its $[4\text{-MeC}_5H_4\text{NMe}]^+$ salt **1** and with $[\{\text{Mo}(\eta^5\text{-C}_5H_5)(\text{NO})I_2\}_2]$ in the presence of NEt_3 to afford the mononuclear complex $[\text{NEt}_3H][\text{Mo}(\eta^5\text{-C}_5H_5)(\text{NO})(\text{cbdt})I]$ **2**. Complete halide substitution occurred with $[\text{NBu}_4][\text{Re}(=\text{O})\text{Cl}_4]$ to give $[\text{NBu}_4][\text{Re}(=\text{O})(\text{cbdt})_2]$ **3** and the reaction with MoCl_5 in tetrahydrofuran afforded the oxo-bridged molybdenum(V) dimer $[4\text{-MeC}_5H_4\text{NMe}]_2[\text{Mo}(=\text{O})(\mu\text{-O})(\text{cbdt})\}_2]$ **4** which is diamagnetic. The salts **1**–**4** have been characterised by single crystal X-ray diffraction studies. In all cases only very limited conjugation appears to occur between the sulfur atoms and the carbon atoms of the carbaborane cage, C–S bond lengths averaging 1.785 Å, slightly shorter than the pure single bond value. The electrochemical properties of the new complexes were investigated but no simple reversible electron transfer processes were observed.

Complexes containing dithiolene ligands have played a well established role in modern co-ordination chemistry.[1] Initially such complexes were of interest because of their novel electronic and magnetic properties and the extended redox series which were found for some dithiolene complexes.[2] More recently this type of compound has become important in the study of new molecular materials.[3] In particular dithiolene complexes, and related materials such as salts of $[\text{Ni(dmit)}_2]^{2-}$, have been used to produce metal–organic materials which exhibit electrical conductivity[4] or third order non-linear optical properties.[5] Another type of dithiolate ligand which may be of interest in the synthesis of new molecular materials is represented by 1,2-dicarbadodecaborane-1,2-dithiol[6] (H_2cbdt).

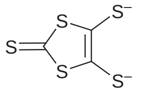
The chemistry of H_2cbdt has been little studied, although complexes with Co^{2+}, Ni^{2+} and Zn^{2+} have been described previously[7] and, more recently, a series of gold complexes has been reported.[8] In order further to develop the known chemistry of H_2cbdt, and assess its ability to form redox active transition metal complexes, we have examined its reactions with a selection of different transition metal compounds.



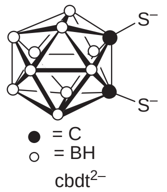
pfdt^{2-}, R = CF_3
mnt^{2-}, R = CN



tdt^{2-}



dmit^{2-}



cbdt^{2-}

Results and Discussion

Synthetic studies

The synthetic approach adopted involved the direct reaction of H_2cbdt with the appropriate transition metal reagent followed, where necessary, by treatment with a suitable cation. The reaction products were characterised by IR and ^{11}B NMR spectroscopy, positive and negative ion fast atom bombardment mass spectrometry (FABMS), elemental analyses and solution conductivity measurements.

The reaction of H_2cbdt with PdI_2 followed by the addition of $4\text{-MeC}_5H_4\text{NMe}^+$ ions afforded a product (**1**) which exhibits bands attributable to ν_{max}(BH) in its IR spectrum and for which the ^{11}B NMR spectrum indicates the presence of the ligand cbdt. The negative-ion FAB mass spectrum of **1** contains an ion at $m/z = 674$ attributable to $\{[4\text{-MeC}_5H_4\text{NMe}][\text{Pd(cbdt)}I_2]\}^-$ along with ions at $m/z = 566$ and 439 which correspond to $\{\text{H-}[\text{Pd(cbdt)}I_2]\}^-$ and $[\text{HPd(cbdt)}I]^-$ respectively. The positive ion FAB mass spectrum contains an ion at $m/z = 890$ attributable to $\{[4\text{-MeC}_5H_4\text{NMe}]_3[\text{Pd(cbdt)}I_2]\}^+$. These results indicate that substitution of the iodide ligands has not occurred and the elemental analyses are in accord with the formulation of **1** as $[4\text{-MeC}_5H_4\text{NMe}]_2[\text{Pd(cbdt)}I_2]$ which has been confirmed by a single crystal X-ray diffraction study described below.

The reactions between the binuclear complex $[\{\text{Mo}(\eta\text{-C}_5H_5)(\text{NO})I_2\}_2]$ and thiols or dithiols are of interest since any of a variety of products may form depending on the nature of the thiolate ligand.[9] The co-ordinatively unsaturated 16-electron complex $[\text{Mo}(\eta^5\text{-C}_5H_5)(\text{NO})(\text{SPh})_2]$ may be obtained with PhSH[9a] but with mnt^{2-} the seven-co-ordinate 18-electron complex $[\text{Mo}(\eta^5\text{-C}_5H_5)(\text{NO})(\text{mnt})I]^-$ is formed and with H_2tdt or pfdt^{2-} the binuclear complexes $[\{\text{Mo}(\eta^5\text{-C}_5H_5)(\text{NO})(\text{L–L})\}_2]$ ($\text{L–L}^{2-} = \text{tdt}^{2-}$ or pfdt^{2-}) are obtained.[9b] The reaction of H_2cbdt with $[\{\text{Mo}(\eta^5\text{-C}_5H_5)(\text{NO})I_2\}_2]$, in the presence of triethylamine, produced the salt $[\text{NEt}_3H][\text{Mo}(\eta^5\text{-C}_5H_5)(\text{NO})(\text{cbdt})I]$ **2**. The positive-ion FAB mass spectrum of **2** contains an ion at $m/z = 102$ which corresponds to the cation $[\text{NEt}_3H]^+$ and the highest mass ion appears at $m/z = 729$ which corresponds with the formula $\{[\text{NEt}_3H]_2[\text{Mo}(\eta^5\text{-C}_5H_5)(\text{NO})(\text{cbdt})I]\}^+$. The negative-ion FAB mass spectrum contains a highest mass ion cluster at $m/z = 527$ which corresponds to the formally seven-co-ordinate molybdenum complex $[\text{Mo}(\eta^5\text{-C}_5H_5)(\text{NO})(\text{cbdt})I]^-$. The solution conductivity and elemental analyses are consistent with the formulation of **2** as $[\text{NEt}_3H][\text{Mo}(\eta^5\text{-C}_5H_5)(\text{NO})(\text{cbdt})I]$ which was confirmed by a single crystal X-ray diffraction study

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described below. In this reaction it appears that H_2cbdt behaves more like mnt^{2-} than H_2tdt since a mononuclear iodo complex is obtained rather than a dimer in which both iodides have been replaced. In contrast to its cyclopentadienyl containing counterpart, the mononuclear co-ordinatively unsaturated complex [Mo(NO){HB(dmpz)$_3$}I$_2$] (dmpz = 3,5-dimethylpyrazolyl) reacts with PhSH or H_2tdt to produce the mononuclear six-co-ordinate, formally 16-electron complexes [Mo(NO){HB(dmpz)$_3$}(SPh)$_2$] and [Mo(NO){HB(dmpz)$_3$}(tdt)] respectively.[9c,10] However, under similar reaction conditions neither [Mo(NO){HB(dmpz)$_3$}(cbdt)] nor [Mo(NO){HB(dmpz)$_3$(cbdt)I]$^-$ could be obtained from H_2cbdt and [Mo(NO){HB(dmpz)$_3$}I$_2$]. This finding may result from the steric bulk of the HB(dmpz)$_3$ ligand, which favours six-co-ordination, precluding the formation of a stable seven-co-ordinate complex. It is further likely that a pyrazolyl 3-methyl substituent or the HB(dmpz)$_3$ ligand blocks binding of the bulky cbdt^{2-} in the first instance, although the less sterically demanding chelate ligand tdt^{2-} can be accommodated. The value of ν_{max}(NO) for [NEt$_3$H][Mo(η^5-C$_5$H$_5$)(NO)(cbdt)I] was found to be 1639 cm^{-1} which is comparable with respective values of 1640, 1630 and 1634 cm^{-1} for [{Mo(η^5-C$_5$H$_5$)(NO)(tdt)}$_2$], [Mo(η^5-C$_5$H$_5$)(NO)(mnt)I]$^-$ and [Mo(NO){HB(dmpz)$_3$}(tdt)].

The reactions of H_2cbdt with two higher oxidation state metal centres were also investigated. The complexes [NBu$_4$][ReOCl$_4$][11] and MoCl$_5$ were used as respective sources of Re^V and Mo^V. The positive-ion FAB mass spectrum of the product from the reaction of H_2cbdt with [NBu$_4$][ReOCl$_4$] contains an ion at m/z = 242 which corresponds to the cation [NBu$_4$]$^+$ and the negative-ion FAB mass spectrum contains a highest mass ion cluster at m/z = 615 which corresponds to [ReO(cbdt)$_2$]$^-$. The solution conductivity and elemental analyses of this salt are consistent with the formulation [NBu$_4$][ReO(cbdt)$_2$] **3** which was confirmed by a single crystal X-ray diffraction study described below. The formation of this product is in keeping with the general tendency of [ReOCl$_4$]$^-$ to form stable complexes with thiolate ligands.[12] The IR spectrum of the 4-MeC$_5$H$_5$NMe$^+$ salt of the product of the reaction between H_2cbdt and MoCl$_5$ in tetrahydrofuran contained strong bands attributable to ν_{max}(BH). The negative-ion FAB mass spectrum contains a highest mass ion at m/z = 777 which corresponds to {[4-MeC$_5$H$_4$NMe][{MoO$_2$(cbdt)}$_2$]}$^-$. An ion is also observed at m/z = 669 which corresponds to {H[{MoO$_2$(cbdt)}$_2$]}$^-$. The positive-ion FAB mass spectrum contains a highest mass ion at m/z = 994 which corresponds to {[4-MeC$_5$H$_4$NMe]$_3$[{MoO$_2$(cbdt)}$_2$]}$^+$. The solution conductivity of this salt is consistent with its formulation as a 2 : 1 electrolyte and the elemental analyses are consistent with the formulation [4-MeC$_5$H$_4$NMe]$_2$[{Mo(=O)(μ-O)(cbdt)}$_2$] **4** which was confirmed by the single crystal X-ray diffraction study described below. It is possible that the formation of this complex results from hydrolysis during the purification process which is carried out in air. However, oxygen abstraction from the thf solvent is also possible as has been observed previously in the formation of [MoO{HB(pz)$_3$}Cl$_2$] from MoCl$_5$ and K[HB(pz)$_3$] in thf.[13]

Structural studies

All four complexes whose crystal structures have been determined contain as a common feature a metallo-1,2-dicarbadodecaborane-1,2-dithiolate moiety. The B–B, B–C, C–C and C–S bond lengths agree closely, irrespective of the nature of the metal (Table 1). The overall mean values, 1.767, 1.720, 1.644 and 1.785 Å, respectively, are similar to the mean lengths of the corresponding bonds 1.778, 1.727, 1.632 and 1.781 Å measured[14] in $C_2B_{10}S_2C$=S and 1.775 and 1.716 Å given by Allen *et al.*[15] for B–B and B–C bonds in comparable cage structures. The C–S bonds are only slightly shorter than the standard single bond value, indicating an only relatively small degree of π-electron delocalisation between the sulfur and the carborane cage (see Table 1). For comparison, C–S bond lengths in M(SC=CS) (M = Pd, Mo or Re) moieties, which might be expected to show some electron delocalisation, average[16] 1.709 [M = Pd (21 structures)], 1.733 [M = Mo (20 structures)] and 1.721 Å [M = Re (five structures)], some 0.05–0.08 Å smaller than our mean values, whereas in the saturated systems M(SC–CS) the C–S bond lengths average[16] 1.828 Å for M = Pd (one structure), 1.816 for M = Mo (13 structures) and 1.826 Å for M = Re (five structures), approximately 0.04 Å greater than our mean values. This effect can also be gauged by comparing the lengths of the C–S bonds in the bis(1,2-dithiooxalato)oxorhenium(V)[17] and the bis(ethane-1,2-dithiolato)oxorhenium(V)[18] anions. In the former, which allows conjugation in the S–C=O system, C–S bonds are in the range 1.730–1.766 Å, mean 1.742(8) Å, whereas in the latter, saturated system, C–S bonds are 1.795–1.849, mean 1.809 Å. Thus, for all three metals our C–S lengths are intermediate, but rather closer to the pure single bond value. Metal–sulfur lengths, however, do not show any systematic trend.

Table 1 Bond lengths (Å) for the carbaborane cage

	1	**2**	**3**	**4**
B–B	1.765(3)[a]	1.769(3)[b]	1.770(2)[c]	1.765(3)[b]
B–C	1.713(9)[d]	1.726(6)[e]	1.717(5)[a]	1.723(4)[e]
C–C	1.638(10)	1.659(9)	1.636(7)[f]	1.652(7)
S–C	1.788(16)[f]	1.783(3)[f]	1.790(2)[d]	1.773(2)[f]

[a] Mean of 16 values. [b] Mean of 21 values. [c] Mean of 42 values. [d] Mean of 4 values. [e] Mean of eight values. [f] Mean of two values.

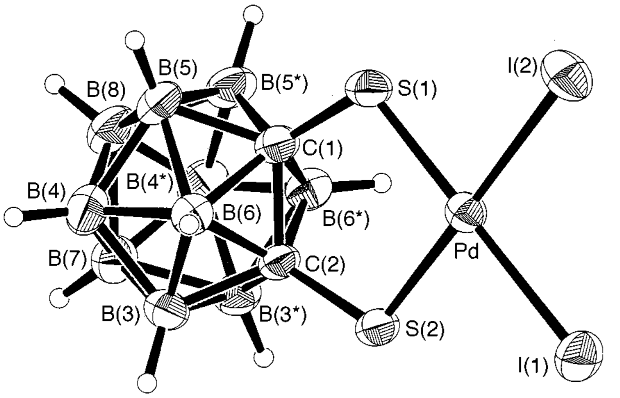

Fig. 1 View of the dianion in compound **1**

In the palladium complex [4-MeC$_5$H$_4$NMe]$_2$[Pd^{II}(cbdt)I$_2$] **1**, shown in Fig. 1, crystallographic mirror symmetry imposes a planar geometry on the metal co-ordination but deviations from a square planar geometry of up to 5.3° occur (see Table 2). The large I(2)–Pd–I(1) angle of 95.28(3)° is presumably due to repulsion between the large iodide ligands. Similarly, in the crystal structure of [1,2-bis(phenylsulfanyl)benzene] diiodo palladium–diiodine,[19] the I–Pd–I angle is 92.3° and the Pd–I and Pd–S bond lengths are 2.606 and 2.292 Å, respectively (*cf.* our values in Table 2).

The structure of the anion [Mo(η^5-C$_5$H$_5$)(NO)(cbdt)I]$^-$ **2** is shown in Fig. 2. If the cyclopentadienyl ligand is represented by its centroid (denoted Cn), the co-ordination geometry can be considered as very roughly approximating to trigonal bipyramidal. The axial angle I(1)–Mo–S(1) is 143.3(1)° and the basal angles, involving Cn, N(1) and S(2), are in the range 117.4–124.9°. In the somewhat analogous structures of (η^5-cyclopentadienyl)[2-(1-dimethylamino)ethylphenyl-*C,N*]iodonitrosylmolybdenum[20] and the closely related [Mo(η^5-C$_5$H$_5$){C$_6$H$_2$(OCH$_2$O)-2,3-CH$_2$NMe$_2$-6}(NO)I][20] the geometry at molybdenum approximates to square pyramidal with the centroid of the cyclopentadienyl ring axial. The Mo–I bond

Table 2 Selected bond lengths (Å) and angles (°) involving the metal centres of the anions **1**–**4**

$[Pd(C_2B_{10}H_{10}S_2)I_2]^{2-}$ **1**			
Pd–S(1)	2.268(2)	Pd–I(1)	2.625(1)
Pd–S(2)	2.265(2)	Pd–I(2)	2.643(1)
I(1)–Pd–I(2)	95.28(3)	I(2)–Pd–S(2)	178.77(5)
I(1)–Pd–S(1)	179.90(4)	S(1)–Pd–S(2)	93.95(7)
I(1)–Pd–S(2)	85.95(5)	Pd–S(1)–C(1)	104.7(3)
I(2)–Pd–S(1)	84.82(6)	Pd–S(2)–C(2)	105.4(2)
$[Mo(\eta^5\text{-}C_5H_5)(NO)(C_2B_{10}H_{10}S_2)I]^-$ **2**[a]			
Mo–S(1)	2.477(2)	Mo–C(3)	2.443(8)
Mo–S(2)	2.514(2)	Mo–C(4)	2.394(8)
Mo–N	1.768(6)	Mo–C(5)	2.305(8)
Mo–I	2.844(1)	Mo–C(6)	2.313(7)
Mo–Cn	2.050	Mo–C(7)	2.398(7)
N(1)–O	1.200(7)		
I–Mo–S(1)	143.3(1)	S(2)–Mo–N	117.6(2)
I–Mo–S(2)	73.9(1)	S(2)–Mo–Cn	124.9
I–Mo–N	85.0(2)	N–Mo–Cn	117.4
I–Mo–Cn	107.8	Mo–S(1)–C(1)	109.6(2)
S(1)–Mo–S(2)	81.4(1)	Mo–S(2)–C(2)	108.4(2)
S(1)–Mo–N	82.8(2)	Mo–N–O	169.4(6)
S(1)–Mo–Cn	108.6		
$[Re(=O)(C_2B_{10}H_{10}S_2)_2]^-$ **3**			
Re–S(1)	2.310(2)	Re–S(2′)	2.323(2)
Re–S(2)	2.314(2)	Re–O	1.678(5)
Re–S(1′)	2.306(2)		
S(1)–Re–S(2)	87.9(1)	S(1′)–Re–S(2′)	88.5(1)
S(1)–Re–S(1′)	141.3(1)	S(1′)–Re–O	108.8(2)
S(1)–Re–S(2′)	79.9(1)	S(2′)–Re–O	107.1(2)
S(1)–Re–O	109.8(2)	Re–S(1)–C(1)	107.3(2)
S(2)–Re–S(1′)	81.1(1)	Re–S(2)–C(2)	107.8(2)
S(2)–Re–S(2′)	145.5(1)	Re–S(1′)–C(1′)	108.0(2)
S(2)–Re–O	107.4(2)	Re–S(2′)–C(2′)	107.7(2)
$[\{Mo(=O)(\mu\text{-}O)(C_2B_{10}H_{10}S_1)\}_2]^{2-}$ **4**[b]			
Mo–S(1)	2.423(2)	Mo–O(2)	1.933(4)
Mo–S(2)	2.424(1)	Mo–O(2*)	1.943(3)
Mo–O(1)	1.673(4)	Mo–Mo*	2.565(1)
S(1)–Mo–S(2)	85.3(1)	O(1)–Mo–O(2)	113.0(2)
S(1)–Mo–O(1)	107.2(2)	O(1)–Mo–O(2*)	110.9(2)
S(1)–Mo–O(2)	139.4(1)	O(2)–Mo–O(2*)	91.4(1)
S(1)–Mo–O(2*)	79.3(1)	Mo–S(1)–C(1)	105.2(2)
S(2)–Mo–O(1)	104.5(1)	Mo–S(2)–C(2)	105.7(2)
S(2)–Mo–O(2)	79.5(1)	Mo–O(2)–Mo*	82.9(1)
S(2)–Mo–O(2*)	144.1(1)		

[a] Cn denotes the centroid of the cyclopentadienyl ring. [b] Starred atoms are related to the corresponding unstarred ones by a crystallographic two-fold axis.

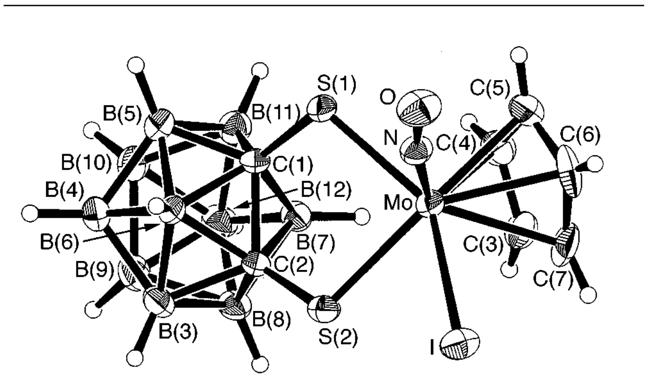

Fig. 2 View of the anion in compound **2**

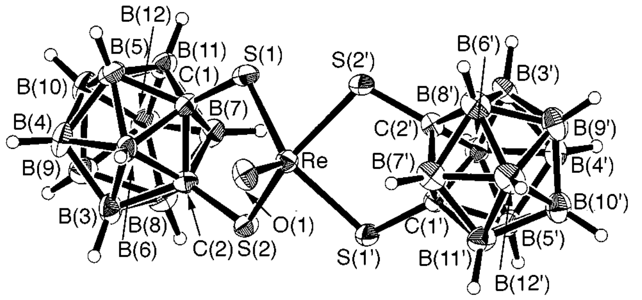

Fig. 3 View of the anion in compound **3**

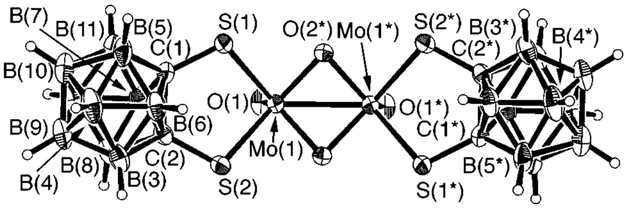

Fig. 4 View of the dianion in compound **4** along the crystallographic two-fold symmetry axis. Starred atoms are related to the corresponding unstarred ones by the symmetry axis

lengths in these structures at 2.857 and 2.870 Å are slightly longer than the corresponding length in **2** [2.844(1) Å], but the Mo–N(O) bonds, 1.770 and 1.775 Å, agree well with our value of 1.768(6) Å. The Mo–S bonds in **2**, mean 2.495(19) Å, are significantly longer than the mean length of 2.418 Å found for this bond in 13 structures containing the $Mo(SCH_2CH_2S)$ fragment extracted from the CSD.[16] The very long Mo–S(2) bond of 2.514(2) Å in **2** may be affected by the *trans*-lengthening influence of the cyclopentadienyl ring, angles C(5)–Mo–S(2) and C(6)–Mo–S(2), 146.6(2) and 145.9(3)° respectively, involving the two shortest Mo–C distances (see Table 2). The flexibility of Mo–S bonds is however demonstrated by the range of lengths found,[16] 2.339–2.497 Å.

The metal centres of both the anions **3** and **4** show approximate square pyramidal co-ordination. In $[Re(=O)(cbdt)_2]^-$ **3** (see Fig. 3) the rhenium atom lies 0.726(1) Å from the best plane of the four sulfur atoms, with the apical oxygen atom 2.404(6) Å from this plane on the same side as the rhenium. The Re–S bond lengths average 2.313(4) Å (see Table 2), in good agreement with those measured in two comparable square pyramidal $Re(=O)(SCHRCHRS)_2$ anions, mean 2.310 Å for both R = H[18] and CO_2H.[21] The Re–O bonds are 1.742,[18a] 1.673[18b] (two independent determinations) and 1.699 Å,[21] compared to 1.678(5) Å in **3**.

The dimeric anion $[\{Mo(=O)(\mu\text{-}O)(cbdt)\}_2]^{2-}$ **4** (Fig. 4) has crystallographic two-fold (C_2) symmetry. Excluding the 2.565(1) Å Mo–Mo interaction, the square pyramidal co-ordination at molybdenum has the two sulfur atoms and the bridging oxygen atoms forming the basal plane (coplanar to within 0.045 Å), the Mo atom being displaced by 0.699(3) Å from this plane and the apical oxygen atom by 2.372(5) Å. The two edge-sharing, symmetry related pyramids are tilted by 25.4(1)° with respect to one another. The Mo–S, Mo–O (bridging) and Mo–O (terminal) lengths are 2.424(1) (mean of two values), 1.938(5) (mean of two values) and 1.673(4) Å, respectively. In the di-μ-oxo-bis[di(benzenethiolato)oxomolybdate(V)] dianion,[22] which is based on the same central atomic configuration, mean bond lengths are Mo–S 2.447 Å, Mo–O (bridging) 1.937 Å and Mo–O (terminal) 1.677 Å, with a 27° angle between the basal planes of the molybdenum co-ordinating square pyramids, very similar to the situation in our structure (**4**).

Five-co-ordinated rhenium in $Re(=O)S_4$ moieties and five-co-ordinated molybdenum in $Mo(=O)S_2O_2$ moieties, whose structures are presently known,[16] adopt, without exception, an essentially square pyramidal co-ordination geometry, with the doubly bonded oxygen ligand axial. The metal atom is displaced from the basal plane in the same direction as the apical oxygen atom by 0.66–0.76 Å in the rhenium complexes[17,18,21,23] and by 0.66–0.73 Å in the molybdenum complexes,[22,24] comfortably spanning our measured metal atom displacements from their respective basal planes.

No abnormally close intermolecular contact distances are observed in any of the four structures. However, a significant intermolecular interaction occurs in compound **2** where there is a hydrogen bond between the triethylammonium ion and an iodine atom of the anionic complex, N $\cdots$ I 3.795, H $\cdots$ I 2.92 Å, and angle N–H $\cdots$ I 163°.

Electrochemical studies

Metal–1,2-dithiolene complexes often undergo sequential electron transfer reactions which are usually reversible.[2] Electrochemical studies were carried out on the new carboranedithiolate complexes to establish whether they too would exhibit well defined electron transfer processes. The complexes [4-Me$_5$H$_4$NMe]$_2$[Pd(cbdt)I$_2$] and [NBu$_4$][ReO(cbdt)$_2$] did not undergo any well defined reduction or oxidation processes in the potential range −1.4 to +1.4 V *vs.* SCE. However, [NEt$_3$H][Mo(η^5-C$_5$H$_5$)(NO)(cbdt)I] oxidised at +0.61 V, although the process is electrochemically and chemically irreversible. These findings suggest that the carboranedithiolate ligand does not support the range of electron transfer processes found for complexes of dithiolene ligands.

Conclusion

The dithiol proligand H$_2$cbdt has been found to react with several transition metal complexes. The heteroleptic complex $[\mathrm{Pd(cbdt)I_2}]^{2-}$ can be obtained from PdI$_2$ but single crystal X-ray crystallography studies reveal no close intermolecular contacts or stacking of the {PdS$_2$I$_2$} moieties. The reaction of H$_2$cbdt with [{Mo(η^5-C$_5$H$_5$)(NO)I$_2$}$_2$] affords the mononuclear complex $[\mathrm{Mo(\eta^5\text{-}C_5H_5)(NO)(cbdt)I}]^-$ and, in this respect, cbdt^{2-} behaves more like mnt^{2-} than tdt^{2-} which forms the dimer [{Mo(η^5-C$_5$H$_5$)(NO)(tdt)}$_2$]. The reaction with $[\mathrm{ReOCl_4}]^-$ proceeds according to expectation affording the five-co-ordinate rhenium(V) complex $[\mathrm{ReO(cbdt)_2}]^-$. In the case of MoCl$_5$ the reaction in thf involves oxygen abstraction, either from thf during the reaction or water during the purification procedure, and formation of the diamagnetic binuclear molybdenum(V) complex [{MoO(cbdt)(μ-O)}$_2$]. The structural results suggest that cbdt^{2-} behaves primarily as a dithiolate ligand with little delocalisation of charge between the cababorane cage, the sulfur donor atoms and the metal. The electrochemical behaviour of the new complexes suggests that the cbdt^{2-} ligand is unable to support the rich electron transfer chemistry associated with dithiolene complexes.

Experimental

Reaction solvents were purified by distillation under nitrogen from standard drying agents before use. The reagents H$_2$cbdt,[6] [NBu$_4$][Re$^{\mathrm{V}}$OCl$_4$][25] and [{Mo(η^5-C$_5$H$_5$)(NO)I$_2$}$_2$][26] were prepared by previously reported methods. All commercial reagents were pre-dried before use but were otherwise used as received. Reactions were carried out under an atmosphere of dry nitrogen but purification procedures were carried out in air. Column chromatography was carried out using silica gel (Merck; Kiesel gel 60, 70–230 mesh) or alumina (Merck, 70–230 mesh) with the eluents stated. The IR spectra were recorded from KBr discs using a Perkin-Elmer 1600 series FT-IR spectrophotometer, ^{11}B NMR spectra at 86 MHz from dichloromethane or acetonitrile solutions using a JEOL GX270 spectrometer, ^{1}H NMR 300 MHz spectra using a Bruker AC300 spectrometer and mass spectra using a Kratos MS80 instrument with positive or negative ion fast atom bombardment of a 3-nitrobenzyl alcohol matrix. Conductivity measurements were recorded from 10^{-4} mol dm^{-3} solutions of the new compounds in acetonitrile using a PTI 58 digital conductivity meter. Elemental analyses were performed by the Microanalytical Service, School of Chemistry, University of Birmingham or the Microanalytical Service, School of Chemistry, University of Sheffield.

Preparations

[4-MeC$_5$H$_4$NMe]$_2$[Pd(cbdt)I$_2$] 1. Palladium(II) iodide (0.36 g, 1.00 mmol) was dissolved in acetonitrile (10 cm^3), the solution added dropwise to a solution of H$_2$cbdt (0.21 g, 1.00 mmol) in acetonitrile (15 cm^3) and the mixture stirred for 30 min at room temperature then heated under reflux for 16 h. The salt [4-MeC$_5$H$_4$NMe]I (0.47 g, 2.00 mmol) in acetonitrile (10 cm^3) was added dropwise and the solution heated under reflux for 2 h. The solvent was removed *in vacuo* and the residue dissolved in dichloromethane (10 cm^3), filtered, the solution warmed to 35 °C and hexane added until the product just started to precipitate. On standing a red crystalline solid was formed (0.65 g, 83%) (Found: C, 25.1; H, 3.95; N, 3.58. C$_{16}$H$_{30}$B$_{10}$I$_2$N$_2$PdS$_2$ requires C, 24.6; H, 3.86; N, 3.58%), ν_{max}(BH) 2566s cm^{-1}. ^{11}B-{^{1}H} NMR (CH$_2$Cl$_2$): δ −19.82, −25.05, −27.64 and −30.17. ^{1}H NMR (CD$_3$CN): δ 8.54 and 7.84 (2 H, d, J = 8; 2 H, d, J = 8 Hz, C$_5$H$_4$N), 4.24 (3 H, s, C$_5$H$_4$NCH_3) and 2.63 (3 H, d, CH_3C$_5$H$_4$N). Mass spectrum [m/z, I(%)]: positive-ion FAB, 890 (42) $\{[\mathrm{4\text{-}MeC_5H_4NMe}]_3[\mathrm{Pd(cbdt)I_2}]\}^+$; 783 (100), $\{\mathrm{H}[\mathrm{4\text{-}MeC_5H_4NMe}]_2[\mathrm{Pd(cbdt)I_2}]\}^+$, negative-ion FAB, 674 (6), $\{[\mathrm{4\text{-}MeC_5H_4NMe}][\mathrm{Pd(cbdt)I_2}]\}^-$; 566 (10), $\{\mathrm{H}[\mathrm{Pd(cbdt)I_2}]\}^-$; 439 (55), $\{\mathrm{H}[\mathrm{Pd(cbdt)I}]\}^-$. Λ_{m} 277 Ω cm^2 mol^{-1}.

[NEt$_3$H][Mo(η^5-C$_5$H$_5$)(NO)(cbdt)I] 2. Triethylamine (0.061 g, 0.60 mmol) was added dropwise to a solution of H$_2$cbdt (0.063 g, 0.30 mmol) in toluene (15 cm^3) with stirring. A solution of [{Mo(η^5-C$_5$H$_5$)(NO)I$_2$}$_2$] (0.164 g, 0.30 mmol) in toluene (10 cm^3) was then added dropwise and the mixture heated under reflux for 16 h, the solvent evaporated *in vacuo* and the residue redissolved in dichloromethane (10 cm^3). The solution was filtered, warmed to 35 °C and hexane added until the product just started to precipitate. On standing dark red crystals of the product were deposited (0.113 g, 60%) (Found: C, 25.3; H, 5.00; N, 4.35. C$_{13}$H$_{31}$B$_{10}$IMoN$_2$OS$_2$ requires C, 24.9; H, 4.99; N, 4.47%). ^{1}H NMR (CDCl$_3$): δ 5.94 (5 H, s, η-C$_5$H$_5$), 3.22 (6 H, q, J = 6, HNCH_2CH$_3$) and 2.45 (9 H, t, J = 6 Hz, HNCH$_2$CH_3). ν_{max}(BH) 2568s, ν_{max}(NO) 1639s cm^{-1}. Mass spectrum [m/z, I(%)]: positive-ion FAB, 729 (10), $\{\mathrm{H}[\mathrm{Et_3NH}][\mathrm{Mo(\eta^5\text{-}C_5H_5)(NO)(cbdt)I}]\}^+$; negative-ion FAB, 524 (100), $[\mathrm{Mo(\eta^5\text{-}C_5H_5)(NO)(cbdt)I}]^-$; 494 (65), $[\mathrm{Mo(\eta^5\text{-}C_5H_5)(cbdt)I}]^-$. Λ_{m} 143 Ω cm^2 mol^{-1}.

[NBu$_4$][ReO(cbdt)$_2$] 3. The salt [NBu$_4$][ReOCl$_4$] (0.07 g, 0.12 mmol) was dissolved in thf (10 cm^3) and the solution added dropwise to a solution of H$_2$cbdt (0.10 g, 0.48 mmol) in thf (15 cm^3). The mixture was stirred vigorously for 30 min at room temperature during which time it changed from yellow to green. The mixture was then heated under reflux for 2 h. During this time it changed from green to bright yellow. The solvent was evaporated *in vacuo* and the residue recrystallised twice from dichloromethane–hexane to yield bright yellow crystals (0.087 g, 85%) (Found: C, 28.1; H, 6.75; N, 1.56. C$_{20}$H$_{56}$B$_{20}$NOReS$_4$ requires C, 28.0; H, 6.58; N, 1.56%); ν_{max}(BH) 2583s, 2614, ν_{max}(Re=O) 980s cm^{-1}. ^{11}B-{^{1}H) NMR (CH$_2$Cl$_2$): δ −19.86 (1B), −25.78 (4B), −26.99 (3B) and −29.07 (1B). Mass spectrum [m/z, I(%)]: positive-ion FAB 242 (100), $[\mathrm{Bu_4N}]^+$; negative-ion FAB, 615 (100), $[\mathrm{ReO(cbdt)_2}]^-$. Λ_{m} 160 Ω cm^2 mol^{-1}.

[4-MeC$_5$H$_4$NMe]$_2$[{Mo(O)(μ-O)(cbdt)}$_2$] 4. A solution of H$_2$cbdt (0.21 g, 1.00 mmol) in thf (20 cm^3) was added dropwise to a suspension of MoCl$_5$ (0.082 g, 0.30 mmol) in thf (15 cm^3). The mixture was stirred vigorously for 30 min at room temperature then heated under reflux for 4 h to give a yellow solution.

Table 3 Crystallographic and experimental data for compounds **1**–**4**

	1	**2**	**3**	**4**
Formula	$C_2H_{10}B_{10}I_2PdS_2\cdot2C_7H_{10}N$	$C_7H_{15}B_{10}IMoNOS_2\cdot C_6H_{16}N$	$C_4H_{20}B_{20}OReS_4\cdot C_{16}H_{36}N$	$C_4H_{20}B_{20}Mo_2O_4S_4\cdot2C_7H_{10}N$
M	782.9	626.5	857.3	884.8
Crystal system	Orthorhomic	Orthorhombic	Monoclinic	Orthorhombic
Space group	*Pbam*	$P2_12_12_1$	$P2_1/n$	$P2_12_12$
a/Å	18.706(5)	14.222(3)	10.989(2)	12.226(4)
b/Å	20.764(5)	16.514(3)	24.156(5)	22.511(5)
c/Å	7.505(2)	10.959(3)	16.069(4)	7.215(4)
β/°	—	—	105.99(2)	—
$U/\text{Å}^3$	2915(1)	2574(1)	4100(2)	1986(1)
Z	4	4	4	2
$D_c/\text{g cm}^{-3}$	1.784	1.617	1.389	1.480
μ(Mo-Kα)/mm^{-1}	2.908	1.881	3.188	0.872
Crystal size/mm	0.4 × 0.35 × 0.25	0.2 × 0.15 × 0.15	0.2 × 0.2 × 0.15	0.35 × 0.3 × 0.3
θ Range/°	1.5–25.2	1.9–25.2	1.6–25.2	3.3–25.3
Reflections measured (unique)	13 515 (2531)	15 230 (4464)	15 875 (6259)	4748 (2887)
R_{int}	0.1040	0.0448	0.0430	0.0280
Variables	175	271	424	226
$\Delta\rho/\text{e Å}^{-3}$	0.49, −0.79	0.54, −0.50	0.47, −0.90	0.40, −0.64
$\Delta/\sigma_{\max}$	0.001	0.002	0.001	0.001
R, $wR2^a$	0.0580, 0.1148	0.0533, 0.0869	0.0623, 0.1058	0.0355, 0.0869
$w(a,b)^b$	0.050, 0.82	0.015, 7.40	0.024, 13.78	0.033, 3.18
Observed reflections [$I > 2\sigma(I)$]	2222	4300	5649	2843
$R[I > 2\sigma(I)]$	0.0415	0.0494	0.0518	0.0345

^{a} $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$. ^{b} $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$.

This was allowed to cool to room temperature before adding [4-MeC_5H_4NMe]I (0.24 g, 1.00 mmol) over a 10 min period and stirring the mixture for a further hour. The solvent was removed *in vacuo* and the residue dissolved in dichloromethane (10 cm^3), filtered, the solution was warmed to 35 °C and hexane added until the product just started to precipitate. On standing a yellow crystalline solid deposited (0.144 g, 54%) (Found: C, 24.4; H, 4.42; N, 3.06. $C_9H_{20}B_{10}MoNO_2S_2$ requires C, 24.4; H, 4.56; N, 3.17%); $\nu_{\max}$(BH) 2575s, $\nu_{\max}$(Mo=O) 964s cm^{-1}. ^{11}B-{^{1}H} NMR (CH_2Cl_2): δ −16.36, −23.38, −25.16 and −29.04. ^{1}H NMR [$(CD_3)_2CO$]: δ 8.85 and 8.01 (2 H, d, *J* = 3.9; 2 H, d, *J* = 3.9 Hz, C_5H_4N), 4.49 (3 H, s, $C_5H_4NCH_3$) and 2.86 (3 H, d, $CH_3C_5H_4N$). Mass spectrum [*m*/*z*, *I*(%)]: positive-ion FAB, 994 (17), {[4-MeC_5H_4NMe]$_3$[{MoO(μ-O)(cbdt)}$_2$]}$^+$; 850 (7), {[4-MeC_5H_4NMe]$_3$[MoO(cbdt)$_2$]}$^+$; negative-ion FAB, 777 (32), {[4-MeC_5H_4NMe][{MoO(μ-O)(cbdt)}$_2$]}$^-$, 669 (100), {H[{MoO(μ-O)(cbdt)}$_2$]}$^-$; 525 (37), {H[MoO(cbdt)$_2$]}$^-$. Λ_m 260 Ω cm^2 mol^{-1}.

Crystallography

Data for all four structures **1**–**4** were collected on a Rigaku R-axis II imaging plate area-detector diffractometer at 293(2) K using graphite-monochromated Mo-Kα radiation. The structures were determined by direct methods[27] and refined[28] on F^2 by full-matrix least squares with anisotropic displacement parameters for the non-hydrogen atoms. Hydrogen atoms were placed in calculated positions with isotropic displacement parameters. Specific absorption corrections were not applied since the crystals used were nearly equidimensional (see Table 3) and averaging of the symmetry-equivalent reflections largely compensates for any absorption effects. Figures depicting the structures were prepared using ORTEP,[29] the thermal ellipsoids being drawn at the 30% probability level.

In compound **1** of the two dimethylpyridinium counter ions, one is disordered, so that the NMe and CMe moieties could not be distinguished; in the refinement the relevant ring atoms were treated as ($\frac{1}{2}$N + $\frac{1}{2}$C). In **4** the dimethylpyridinium cation is similarly disordered, and was treated in the same way. The atoms of the triethylammonium counter ion in **2** exhibit high anisotropic displacement parameters and may also be affected by disorder.

CCDC reference number 186/1010.

See http://www.rsc.org/suppdata/dt/1998/2163/ for crystallographic files in .cif format.

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References

1 U. T. Mueller-Westerhoff and B. Vance, in *Comprehensive Coordination Chemistry*, eds. R. D. Gillard, J. A. McCleverty and G. Wilkinson, Pergamon, Oxford, 1987, vol. 2, ch. 16.5, pp. 595–631.

2 J. A. McCleverty, *Prog. Inorg. Chem.*, 1968, **10**, 49; G. N. Schrauzer, *Acc. Chem. Res.*, 1969, **2**, 72.

3 T. Jørgensen, T. K. Hansen and J. Becher, *Chem. Soc. Rev.*, 1994, **23**, 41; T. K. Hansen and J. Becher, *Adv. Mater.*, 1993, **5**, 288; S. R. Marder, in *Inorganic Materials*, eds. D. W. Bruce and D. O'Hare, Wiley, New York, 1992, ch. 3; A. Kreif, *Tetrahedron*, 1986, **42**, 1209; A. F. Garito and A. J. Heeger, *Acc. Chem. Res.*, 1974, **7**, 232.

4 (*a*) P. Cassoux and L. Valade, in *Inorganic Materials*, eds. D. W. Bruce and D. O'Hare, Wiley, New York, 1992, ch. 1; (*b*) P. Cassoux, L. Valade, M. Kobayashi, A. Kobayashi, R. A. Clark and A. E. Underhill, *Coord. Chem. Rev.*, 1991, **110**, 115; (*c*) J. R. Ferraro and J. M. Williams, *Introduction to Synthetic Electrical Conductors*, Academic Press, New York, 1987, pp. 1–327; (*d*) J. M. Williams, *Adv. Inorg. Chem. Radiochem.*, 1983, **26**, 235; (*e*) M. Williams, A. J. Schultz, A. E. Underhill and D. M. Watkins, *Extended Linear Chain Compounds*, Plenum, New York, 1982, p. 73; (*f*) J. S. Miller and A. J. Epstein, *Prog. Inorg. Chem.*, 1976, **20**, 152.

5 W. Wenseleers, E. Goovaerts, A. S. Dhindsa and A. E. Underhill, *Chem. Phys. Lett.*, 1996, **254**, 410; C. A. S. Hill, A. Charlton, A. E. Underhill, K. M. A. Malik and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1995, 587; C. A. S. Hill, A. Charlton, A. E. Underhill, S. N. Oliver, S. Kershaw, R. J. Manning and B. J. Ainslie, *J. Mater. Chem.*, 1994, **4**, 1233.

6 H. D. Smith, jun., C. O. Obenland and S. Papetti, *Inorg. Chem.*, 1966, **5**, 1013.

7 H. D. Smith, jun., M. A. Robinson and S. Papetti, *Inorg. Chem.*, 1967, **6**, 1014.

8 O. Crespo, M. C. Gimeno, P. G. Jones, B. Ahrens and A. Laguna, *Inorg. Chem.*, 1997, **36**, 495; O. Crespo, M. C. Gimeno, P. G. Jones and A. Laguna, *J. Organomet. Chem.*, 1997, **547**, 89.

9 (*a*) M. T. Ashby and J. H. Enemark, *J. Am. Chem. Soc.*, 1986, **108**, 730; (*b*) T. A. James and J. A. McCleverty, *J. Chem. Soc. A*, 1971, 1068; (*c*) T. A. James and J. A. McCleverty, *J. Chem. Soc. A*, 1970, 3308; (*d*) J. A. McCleverty and D. Seddon, *J. Chem. Soc.*, *Dalton Trans.*, 1972, 2588.

10 J. A. McCleverty, A. S. Drane, N. A. Bailey and J. M. A. Smith, *J. Chem. Soc.*, *Dalton Trans.*, 1983, 91; N. AlObaidi, C. J. Jones and J. A. McCleverty, *Polyhedron*, 1989, **8**, 1033.

11 J. R. Dilworth, W. Hussain, A. J. Hutson, C. J. Jones and F. S. McQuillan, *Inorg. Synth.*, 1996, **3**, 257.

12 J. R. Dilworth, B. D. Neaves, J. Hutchinson and J. Zubieta, *Inorg. Chim. Acta*, 1982, **65**, L223; P. J. Blower, J. R. Dilworth, J. P. Hutchinson, T. Nicholson and J. Zubieta, *Inorg. Chim. Acta*, 1984, **90**, L27.

13 W. E. Cleland, K. M. Barnhart, K. Yamanouchi, D. Collison, F. E. Mabbs, R. B. Ortega and J. H. Enemark, *Inorg. Chem.*, 1987, **26**, 1017.

14 J. D. McKinney, T. A. Hamor, C. J. Jones and K. Paxton, *Polyhedron*, 1997, **16**, 1819.

15 F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen and R. Taylor, *J. Chem. Soc.*, *Perkin Trans. 2*, 1987, S1.

16 Cambridge Structural Database, Cambridge Crystallographic Data Centre, Cambridge, April 1997.

17 R. Mattes and H. Weber, *Z. Anorg. Allg. Chem.*, 1981, **474**, 216.

18 (*a*) P. J. Blower, J. R. Dilworth, J. P. Hutchinson, T. Nicholson and J. Zubieta, *J. Chem. Soc.*, *Dalton Trans.*, 1986, 1339; (*b*) W. Clegg, S. Boyde and C. D. Garner, *Acta Crystallogr.*, *Sect. C*, 1988, **44**, 172.

19 L. R. Gray, D. J. Gulliver, W. Levason and M. Webster, *Acta Crystallogr.*, *Sect. C*, 1983, **39**, 877.

20 M. Pfeffer, E. P. Urriolabeitia, A. de Cian and J. Fischer, *J. Organomet. Chem.*, 1995, **494**, 187.

21 J. Singh, A. K. Powell, S. E. M. Clarke and P. J. Blower, *J. Chem. Soc.*, *Chem. Commun.*, 1991, 1115.

22 I. G. Dance, A. G. Wedd and I. W. Boyd, *Aust. J. Chem.*, 1978, **31**, 519.

23 A. C. McDonell, T. W. Hambley, M. R. Snow and A. G. Wedd, *Aust. J. Chem.*, 1983, **36**, 253; T. Nicholson, P. Lombardi and J. Zubieta, *Polyhedron*, 1987, **6**, 1577; G. Matsubayashi, T. Maikawa and M. Nakano, *J. Chem. Soc.*, *Dalton Trans.*, 1993, 2995; R. Hubener and U. Abram, *Acta Crystallogr.*, *Sect. C*, 1993, **49**, 1068; J. R. Dilworth, J. Hu, J. R. Miller, D. L. Hughes, J. A. Zubieta and Q. Chen, *J. Chem. Soc.*, *Dalton Trans.*, 1995, 3153.

24 P. L. Dahlstrom, J. R. Hyde, P. A. Vella and J. Zubieta, *Inorg. Chem.*, 1982, **21**, 927; V. Sanz, T. Picher, P. Palanca, P. Gomez-Romero, E. Llopis, J. A. Ramirez, D. Beltran and A. Cervilla, *ibid.*, 1991, **30**, 3113; D. Coucouvanis, S. Al-Ahmad, C. G. Kim, P. E. Mosier and J. W. Kampf, *ibid.*, 1993, **32**, 1533; C. G. Kim and Coucouvanis, *ibid.*, 1993, **32**, 1881; S. G. Jonasdottir, C. G. Kim and D. Coucouvanis, *ibid.*, 1993, **32**, 3591.

25 J. R. Dilworth, W. Hussain, A. J. Hutson, C. J. Jones and F. S. McQuillan, *Inorg. Synth.*, 1996, **3**, 257.

26 R. B. King, *Inorg. Chem.*, 1967, **6**, 30.

27 TEXSAN, version 1.6, Single Crystal Structure Analysis Software, Molecular Structure Corporation, Houston, TX, 1993.

28 G. M. Sheldrick, SHELXL 93, Program for Crystal Structure Refinement, University of Göttingen, 1993.

29 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

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