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Preparation and Structure of Dichlorotetrakis(*o*-oxypyridine)dirhenium(III)

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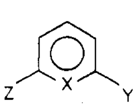
The reaction of $(N\text{-}n\text{-}Bu_4)_2Re_2Cl_8$ with 2-hydroxypyridine (Hhp) gives $Re_2(hp)_4Cl_2$, a red-brown solid, insoluble in most common solvents but slightly volatile. By use of a crystal grown by sublimation, the structure has been determined. The crystal contains $Re_2(hp)_4Cl_2$ molecules, each with a rigorous crystallographic inversion center and virtual C_{2h} symmetry, packed with normal van der Waals contacts in a unit cell belonging to space group $C2/c$ with the dimensions $a = 17.309$ (5) Å, $b = 9.345$ (3) Å, $c = 17.203$ (5) Å, $\beta = 128.85$ (2)°, and $V = 2167$ (1) $Å^3$. There are four molecules per unit cell. A total of 841 reflections with $I > 2\sigma(I)$ were used to refine 111 parameters to final discrepancy indices of $R_1 = 0.051$ and $R_2 = 0.059$ in a model that omits hydrogen atoms and allows for random twofold disorder in the orientation of one of the two crystallographically independent hp ligands. The distances and angles in the molecule are all approximately those expected by comparison to the $Re_2(O_2CR)_4Cl_2$ species (R = Ph, *t*-Bu) previously studied except for the Re–Re distance, 2.206 (2) Å, which is about 0.03 Å shorter than those in the carboxylates. This is a shortening effect quite comparable to that previously seen among Mo_2^{4+} compounds of analogous types.

Introduction

Several years ago[1,2] it was found that ligands of the general type **1** are prone to stabilize quadruply bonded dimetal units



1a, X = N, Y = O, Z = CH_3
b, X = N, Y = O, Z = H

with unusual properties, such as exceptionally short bonds, as in the case of Cr_2^{4+} complexes, or unique stability, as in the case of W_2^{4+}. One such ligand that has provided particularly interesting complexes,[2] of general formula M_2L_4, is **1a**, 2-oxy-6-methylpyridine. We have recently been using ligands of type **1** to see if we can obtain stable M_2L_4-type complexes with metal atoms outside of the Cr, Mo, and W group, where **1a** has featured prominently. For the Cr, Mo, and W series **1a** has been used instead of the simpler and considerably cheaper **1b** because there were early indications that unless the 6-position is blocked, intermolecular association leads to products that have poor solubility properties and are very difficult to obtain in the form of crystals suitable for X-ray structure determination.

In turning our attention to the preparation of a dirhenium compound, we have found that the preference is reversed, **1b** being suitable while **1a** is not. The reason for this difference is quite straightforward. The Re_2^{6+} unit tends to require coordination by a pair of axial ligands in addition to the four bridging bidentate ones, as in the well-known carboxylato compounds[3,4] $Re_2(O_2CR)_4X_2$. However, with **1a**, the 6-methyl groups interfere with the approach of axial ligands and we have been unable to synthesize $Re_2L_4X_2$ compounds when L = **1a**. With L = **1b**, however, the steric problem is avoided and we report here the preparation and structure of the $Re_2L_4X_2$ compound in which L = **1b** and X = Cl. We have previously used the symbol mhp to represent the anion **1a**; in a consistent way we use hp to represent the anion **1b**. Thus, the formula of the compound described here may be written $Re_2(hp)_4Cl_2$.

Experimental Section

Preparation of $Re_2(hp)_4Cl_2$. The tetrakis(2-hydroxypyridine) complex was prepared by heating, under N_2 at 150 °C, 0.25 g of tetra-*n*-butylammonium octachlorodirhenate, $(N\text{-}n\text{-}Bu_4)_2Re_2Cl_8$, and 1.0 g of 2-hydroxypyridine. During the 76-h reaction period the color changed from blue to red-brown, a color characteristic of the several known $Re_2(O_2CR)_4X_2$ compounds.[3,4] The solid product was separated by passing the reaction mixture through a warm glass frit and, after cooling, it was washed with CH_2Cl_2. The product is insoluble in most common solvents but slightly soluble in $CHCl_3$. Crystals suitable for X-ray diffraction were obtained by sublimation in an evacuated 25 × 0.7 cm Pyrex tube at 350 °C. Elemental analyses were performed by the Center for Trace Characterization, Texas A&M University.

Anal. Calcd for $Re_2Cl_2O_4N_4C_{20}H_{16}$: N, 6.84; C, 29.32; H, 1.97. Found: N, 6.93; C, 28.7; H, 1.98.

X-ray Crystallographic Studies.[5,6] A red crystal having the approximate dimensions 0.25 × 0.15 × 0.10 mm was attached with epoxy cement to a glass fiber. The optical clarity of the crystal was good and it extinguished cleanly under crossed polarizers. This coupled with narrow widths at half-height for the ω scans of several reflections indicated the crystal to be suitable for X-ray diffraction studies. Autoindexing on 15 intense centered reflections produced a unit cell of the monoclinic system with the dimensions $a = 17.309$ (5) Å, $b = 9.345$ (3) Å, $c = 17.203$ (5) Å, $\beta = 128.85$ (2)°, and $V = 2167$ (1) $Å^3$. The observed volume corresponds with expectation for $Z = 4$. Systematic absences of hkl, $h + k \neq 2n$, and $h0l$, $l \neq 2n$, were observed thereby indicating that the space group is either Cc or $C2/c$.

Data were collected on a Syntex $P\bar{1}$ diffractometer by procedures previously reported. The linear absorption coefficient of 121 cm^{-1} necessitated an absorption correction. This was made by an empirical method in which a ψ scan was obtained for four reflections near $\chi = 90°$. Each reflection was measured at 10° intervals from $\psi = 0$ to $\psi = 350°$. The normalized transmission factors so obtained varied from 1.00 to 0.80. Of the 1605 reflections collected only those 841 having $I > 2\sigma(I)$ were used to solve and refine the structure.

Neither statistical tests on the data nor a three-dimensional Patterson function enabled us to differentiate between two possible space groups. As a matter of convenience we first considered the centric $C2/c$. The location of one Re atom was refined producing discrepancy indices of

$$R_1 = \sum||F_o| - |F_c|| / \sum|F_o| = 0.18$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.23$$

The remaining 15 nonhydrogen atoms were easily located by subsequent refinement and difference Fourier maps. When further refinement was undertaken, however, one of the two crystallographically independent ligands of the asymmetric unit appeared to be disordered in such a way that it behaved as a superposition of two possible orientations, and the O and N atoms had to be treated as the resultant contribution of each atom at 50% occupancy. An attempt to eliminate the need for the postulation of disorder by refinement in the space group Cc was made but proved to be unsuccessful, and we returned to $C2/c$ to complete the refinement. The other ligand pair showed no indication of disorder. Final refinement on the positional and isotropic thermal parameters of the 20 atoms gave $R_1 = 0.068$ and $R_2 = 0.081$. Three cycles of least-squares refinement employing anisotropic thermal parameters then reduced R_1 to 0.051 and R_2 to 0.059. The estimated standard deviation of an observation of unit weight after the final cycle was 1.08. None of the 111 varied parameters shifted more than 0.04σ. A final difference map revealed only peaks presumably associated with the hydrogen atoms on the ligands and ghosts of the heavy metal atom. A list of observed and calculated structure factors is available as supplementary material.

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Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations[a, b]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Re	0.47176 (6)	0.0703 (1)	0.02868 (6)	3.96 (2)	4.87 (4)	3.93 (2)	1.00 (4)	1.70 (2)	−0.60 (4)
Cl	0.5893 (4)	0.2522 (8)	0.4107 (4)	7.2 (2)	6.3 (4)	7.5 (2)	−1.0 (2)	4.6 (1)	1.5 (2)
O(1)	0.4923 (9)	−0.244 (2)	0.0109 (9)	6.6 (5)	3.9 (7)	6.2 (5)	0.8 (5)	4.0 (3)	−1.1 (5)
O(2)	0.3935 (12)	−0.071 (2)	−0.1675 (10)	8.2 (8)	5.3 (9)	4.1 (6)	0.9 (8)	1.4 (5)	1.2 (8)
N(1)	0.334 (1)	0.067 (2)	−0.106 (1)	3.5 (9)	3.6 (9)	7.7 (8)	0.4 (7)	2.2 (4)	1.0 (9)
N(2)	0.431 (1)	−0.103 (2)	0.066 (1)	8.3 (6)	6 (1)	5.6 (5)	0.4 (7)	5.2 (4)	−0.1 (7)

atom	x	y	z	B, A^2	atom	x	y	z	B, A^2
C(1)	0.454 (1)	−0.239 (3)	0.053 (1)	4.6 (5)	C(8)	0.156 (2)	0.054 (6)	−0.309 (3)	4.8 (10)
C(2)	0.425 (2)	−0.363 (3)	0.074 (2)	6.3 (6)	C(9)	0.162 (3)	0.120 (5)	−0.244 (3)	4.9 (11)
C(3)	0.382 (2)	−0.361 (4)	0.121 (2)	8.6 (8)	C(10)	0.246 (3)	0.129 (5)	−0.144 (3)	5.4 (11)
C(4)	0.360 (2)	−0.215 (4)	0.139 (2)	8.5 (8)	C(7)*	0.204 (3)	−0.001 (6)	−0.265 (3)	5.5 (11)
C(5)	0.390 (1)	−0.096 (3)	0.116 (1)	6.2 (6)	C(8)*	0.186 (3)	−0.049 (6)	−0.344 (3)	5.5 (11)
C(6)	0.316 (2)	0.003 (3)	−0.182 (2)	7.1 (7)	C(9)*	0.259 (3)	−0.123 (5)	−0.341 (3)	5.3 (11)
C(7)	0.240 (2)	−0.010 (5)	−0.288 (2)	4.4 (10)	C(10)*	0.350 (3)	−0.141 (7)	−0.257 (4)	7.9 (15)

[a] The form of the anisotropic thermal parameter is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. [b] Carbon atoms with asterisks and those with corresponding numbers are half atoms because of the disorder. See text and Figure 2.

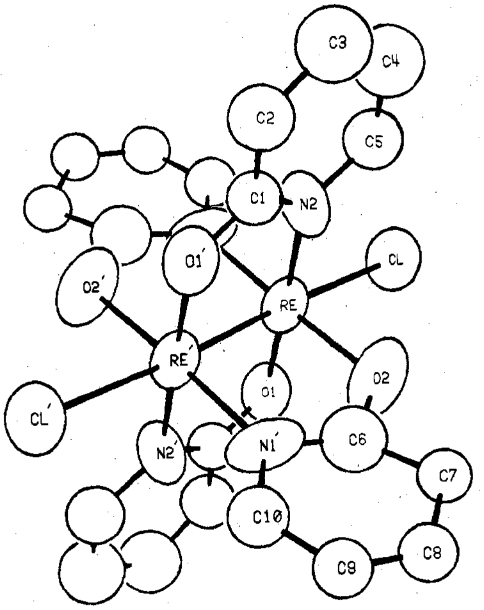

Figure 1. An ORTEP projection of the molecule, showing the atomic numbering. Primed atoms are related to unprimed ones with the same number by the inversion center at the midpoint of the Re–Re′ bond.

Results and Discussion

The positional and thermal parameters of all atoms are listed in Table I. With four molecules in the unit cell in space group $C2/c$, the asymmetric unit is only half of the molecule and the two halves are related by a crystallographic inversion center. The Re atom, the Cl atom, and the seven atoms, N(2), C(1)–C(5), O(1), making up one symmetry-related pair of hp ligands are well-defined, undisordered atoms. The other symmetry-related pair of hp ligands, consisting of N(1), C(6)–C(10), O(2), are disordered. Figure 1 shows the molecule with one orientation of the disordered ligands and defines the numbering scheme. Figure 2 shows the disorder. In refining the atoms of this disordered ligand O(2)/N(1), N(1)/O(2), and C(7)–C(10) were treated as half atoms while C(6) was treated as a single, full carbon atom; even though this is not entirely correct physically, the two half-occupied positions for C(6) would be too close together to be resolved.

The molecular symmetry is C_{2h}. In each molecule nitrogen atoms on the same rhenium atom are cis to each other. This property is unaffected by the disorder since ring orientations are reversed in pairs. The molecules are packed in the cell with normal van der Waals contacts with no unusual packing features, as may be seen in Figure 3.

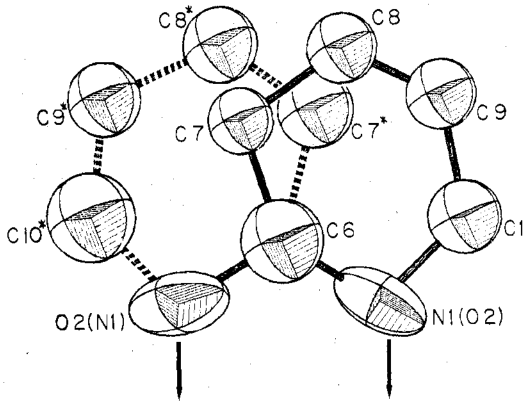

Figure 2. An ORTEP drawing showing the way in which one of the two crystallographically independent hp ligands is disordered.

Table II. Bond Distances (Å) and Angles (deg)[a]

Re–Re′	2.206 (2)	C(6)–O(2)	1.38 (4)
–Cl	2.545 (7)	–N(1)	1.30 (4)
–O(1)	2.00 (2)	–C(7)	1.43 (7)
–O(2)	2.04 (2)	C(3)–C(4)	1.49 (5)
–N(1)	2.03 (2)	–C(2)	1.42 (4)
–N(2)	2.03 (2)	C(5)–N(2)	1.41 (4)
C(1)–O(1)	1.26 (3)	–C(4)	1.38 (5)
–N(2)	1.39 (4)	C(8)–C(7)	1.39 (7)
–C(2)	1.39 (4)	–C(9)	1.23 (7)
		C(10)–N(1)	1.35 (5)
		–C(9)	1.23 (7)
Re′–Re–Cl	174.6 (2)	O(2)–C(6)–N(1)′	117 (3)
–O(1)	90.6 (5)	–C(7)	102 (3)
–O(2)	91.3 (6)	N(1)–Re–Cl	89.1 (6)
–N(1)	90.9 (6)	–N(2)	87.2 (9)
–N(2)	90.6 (6)	–C(6)–C(7)	140 (3)
O(1)–Re–Cl	84.1 (5)	–C(10)–C(9)	123 (4)
–O(2)	89.0 (6)	N(2)–Re–Cl	94.8 (6)
–N(1)	89.1 (6)	–C(1)–C(2)	122 (2)
–N(2)	94.8 (6)	–C(5)–C(4)	124 (3)
O(1)–C(1)–N(2)′	116 (3)	C(3)–C(2)–C(1)	123 (3)
–C(2)	121 (2)	–C(4)–C(5)	120 (3)
O(2)–Re–Cl	89.0 (6)	C(2)–C(3)–C(4)	114 (2)
–N(1)	176.6 (8)	C(8)–C(7)–C(6)	106 (4)
–N(2)	90.1 (9)	–C(9)–C(10)	126 (5)
		C(7)–C(8)–C(9)	120 (5)

[a] Primed atoms are the symmetry-related counterpart of the corresponding unprimed atom.

The disordered arrangement of two of the rings has an interesting but readily understandable effect on the apparent position of the chorine atom. This is easily appreciated with the help of Figure 4. The ortho hydrogen atom of the pyridine

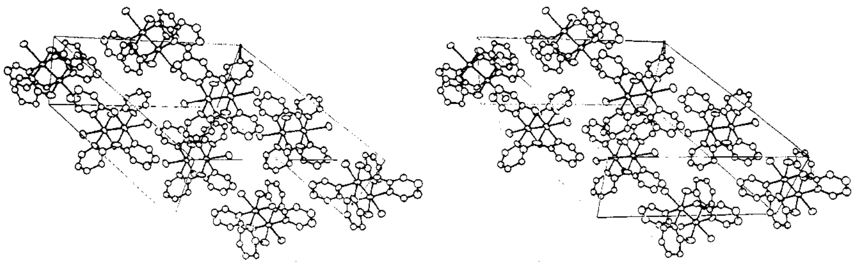

Figure 3. An ORTEP stereoview of the unit cell showing the molecular packing.

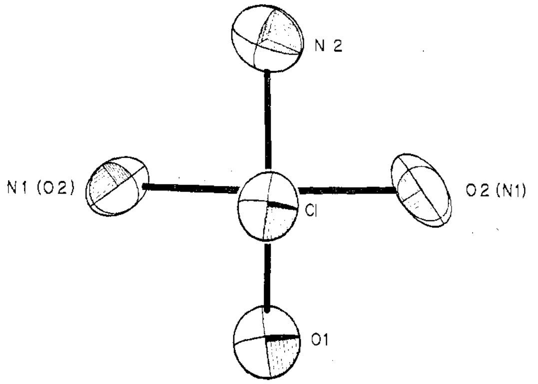

Figure 4. A view of one end of the molecule seen along the extension of the Re–Re bond, showing how the Cl atom is displaced from the extension of the Re–Re bond axis.

ring tends to push the Cl atom off of the direct extension of the Re–Re axis toward the opposite ligand which is bound by an oxygen atom and therefore leaves space for the Cl atom to more over. Thus, as seen in Figure 4, the Cl atom is displaced away from N(2) and toward O(1). While a similar displacement should occur from N(1) toward O(2) in each individual molecule, the random arrangement of N(1) and O(2) leads to a cancellation of this when it is averaged over many molecules, leading to the result depicted in Figure 4.

A point worthy of note is that the C_{2h} structure, i.e., the cis arrangement of nitrogen atoms, is in contrast to the noncentric, D_{2h} arrangement in which nitrogen atoms are trans that is found in all of the mhp[2,7] and the hydroxypyrimidine compounds[8] of Cr_2, Mo_2, W_2, and MoCr. A trans arrangement is also found in $Mo_2(OSCCH_3)_4$,[9] but there is precedent for the cis configuration in the Cr_2 and Mo_2 compounds with 2,6-dimethoxyphenyl ligands[1,10] and related ones.[11]

The bond distances and angles, Table II, within the molecule are all about as expected, except for the Re–Re distance, when compared with previous results for $Re_2(O_2CR)_4Cl_2$ molecules. In the benzoate[3b] the Re–Re distance is 2.235 (2) Å and in the pivalate it is 2.236 (1) Å. Thus, the hp ligand causes the metal–metal bond to be about 0.03 Å shorter than it is with carboxylato ligands. This situation exactly parallels that for Mo_2^{4+} compounds where, for example, the metal–metal distance in $Mo_2(mhp)_4$[2] is 2.065 (1) Å while those in $Mo_2(O_2CR)_4$ compounds are usually in the range 2.09–2.10 Å.[12]

It is interesting that the Re–O and Re–N distances are essentially equal here, whereas in the $M_2(mhp)_4$ molecules with M = Cr, Mo, and W, they differ significantly. Also, in this case the M–M–N and M–M–O angles are essentially equal, with mean values of 90.8 and 91.0°, respectively. This presumably reflects the fact that the Re–Re distance, which is considerably longer than Cr–Cr, Mo–Mo, and even W–W distances in $M_2(mhp)_4$ molecules, is practically equal to the preferred "bite" of the ligand. Finally, we may note that the weak axial Re–Cl bonds are slightly longer here, 2.55 (1) Å, compared to those of 2.49 (1) and 2.477 (3) Å found in the benzoate[3b] and pivalate,[4] respectively. Whatever the casual relationship, if any, we have once again the persistent inverse relationship between the M–M and $M–L_{ax}$ bond lengths.[13]

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Registry No. $Re_2(hp)_4Cl_2$, 69927-33-9; $(N\text{-}n\text{-}Bu_4)_2Re_2Cl_8$, 14023-10-0.

Supplementary Material Available: A table of observed and final calculated structure factors (4 pages). Ordering information is given on any current masthead page.

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