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Another Bogus Isomer: *Sic Transit* "Green $Mo_2Cl_4(PMePh_2)_4$". The X-ray Crystal Structure Determination of $MoOCl_3(OPMePh_2)_2{\cdot}C_6H_6$

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The recent debunking[2] of one example (and by implication others) of so-called "bond-stretch" or "distortional" isomers involving M=O bonds has caused us to reconsider another case of alleged isomerism, namely the blue and green "isomers" of $Mo_2Cl_4(PMePh_2)_4$ reported by Carmona-Guzman and Wilkinson[3] and apparently supported by some more recent observations.[4,5]

This compound has been prepared in three ways, only two of which give the green "isomer". When $MoH_4(PMePh_2)_4$[3] or a mixture of $Mo(\eta^6\text{-}PhPMePh)(PMePh_2)_3 + MoCl_4L_2$ (L = THF, CH_3CN)[4] is the starting material, the initial product is green but recrystallization yields only a deep blue substance. This same deep blue substance is the initial and only product when $Mo_2(O_2CMe)_4$ is treated with $PMePh_2$ and Me_3SiCl.[5] A crystalline sample of the green "isomer" has never been obtained, whereas the blue compound has been crystallographically characterized and shown to have the expected staggered (D_{2d}) disposition of ligands about the Mo_2^{4+} core. Two different suggestions as to how the "green isomer" might differ from the blue one have been offered.[3,5]

We now report simple observations that reveal the true nature of the "green isomer". These results are based on more careful examinations of ^1H NMR spectra of the green material synthesized under slightly different conditions and a single-crystal diffraction study on material that crystallized out of a benzene solution of the green material. As a result of these studies, we can conclude that the "green isomer" is simply the blue $Mo_2Cl_4(PMePh_2)_4$ species contaminated with $MoOCl_3(OPMePh_2)_2$, $MoOCl_2(PMePh_2)_3$,[6] and possibly *trans*-$[MoCl_4(PMePh_2)_2]^-$,[7] the presence and amounts of which depend on the purity of the starting materials employed in the synthesis.

Experimental Section

The ^1H NMR spectra were obtained on a Gemini 300-MHz instrument. Samples of the "green $Mo_2Cl_4(PMePh_2)_4$" were prepared by the reaction of $Mo(\eta^6\text{-}PhPMePh)(PMePh_2)_3$ and either $MoCl_4(CH_3CN)_2$ or $MoCl_4(THF)_2$ in dry benzene as previously published.[4] A sample of $MoOCl_3(OPMePh_2)_2$ was prepared by an adaptation (use of $OPMePh_2$ instead of $OPPh_3$) of a published procedure.[8] The complex $MoOCl_2(PMePh_2)_3$ was prepared as published previously.[6]

Crystallographic Details

Crystals of a yellow substance were obtained by allowing slow precipitation from a concentrated benzene solution of the green material obtained by reacting $Mo(\eta^6\text{-}PhPMePh)(PMePh_2)_3$ and $MoCl_4(THF)_2$. A suitable crystal of approximate dimensions 0.4 × 0.2 × 0.2 mm was mounted on a glass fiber with epoxy resin in a random orientation. The data were collected using previously established procedures.[9] All calculations were performed on a VAX computer using MolEN.[10] Lorentz and polarization corrections were applied to the data as well as an empirical absorption correction based on three ψ scans.[11]

The structure, solved using direct methods, revealed that the crystal consisted of molecules of $MoOCl_3(OPMePh_2)_2$. From the outset, it was clear that there was disorder between the terminal oxo group and one cis chlorine ligand. The model presented below consisting of a 50% Cl and a 50% O atom at each site was derived after an analysis based on the refinement of site occupancies. Attempts to refine this disorder without constraints were not successful. This was also the case with a similar sort of disorder in $HB(Pz)_3MoOCl_2$.[12] The oxygen atoms were made to ride on the Mo atom with the stipulation that the Mo–O distance be approximately 1.7 Å. No constraints were applied to the disordered Cl atoms. Peaks indicative of a disordered benzene molecule (represented as two benzene molecules in the same plane rotated by 30°) were also apparent in a difference Fourier map. These were located near an inversion point and were adequately represented with six independent C atoms, each at 50% occupancy. H atoms were placed at calculated positions, with isotropic thermal parameters fixed at 1.2 times the current converged isotropic equivalent of the C atom to which they were attached.

All of the non-H atoms except for the C atoms defining the disordered benzene molecule and the two O atoms on Mo were refined with anisotropic thermal parameters. Some relevant crystallographic information is given in Table I. Final positional parameters and their estimated standard deviations for non-H atoms and selected bond lengths and bond angles are given in Tables II and III, respectively. An ORTEP representation of $MoOCl_3(OPMePh_2)_2$ is presented in Figure 1, and a view of the crystal packing of $MoOCl_3(OPMePh_2)_2{\cdot}C_6H_6$ is presented as supplementary material.

Results and Discussion

For one batch of green material obtained by the reaction of $Mo(\eta^6\text{-}PhPMePh)(PMePh_2)_3$ and $MoCl_4(CH_3CN)_2$ in benzene, the ^1H NMR spectrum revealed a broad resonance at δ −41 (in C_6D_6) in addition to other resonances in the δ 0–10 region attributed previously to H atoms in $Mo_2Cl_4(PMePh_2)_4$.[4] The resonance at δ −41 may indicate that *trans*-$[MoCl_4(PMePh_2)_2]^-$ was produced.[7a] However, we were unable to isolate this complex as a solid.[7b]

An ^1H NMR spectrum of a different batch of green material contained resonances (in addition to those due to $Mo_2Cl_4(PMePh_2)_4$) at δ 1.4, 1.6, and 2.2. These can be assigned to $MoOCl_3(OPMePh_2)_2$ (δ 1.6) and $MoOCl_2(PMePh_2)_3$ (δ 1.4 and 2.2 in a 1:2 ratio), according to the ^1H NMR spectra of authentic samples of these complexes synthesized by published procedures.[6,8]

On one occasion, the green material was recrystallized by first dissolving it in benzene, followed by filtration. This afforded a blue solution and small amounts of a yellow precipitate. Workup of the blue solution with hexanes yielded blue $Mo_2Cl_4(PMePh_2)_4$ as detailed previously.[4] An ^1H NMR spectrum of the yellow precipitate in CD_2Cl_2 was essentially featureless in the δ 0 to −50 range but did contain resonances indicative of $MoOCl_3(OPMePh_2)_2$ and $MoOCl_2(PMePh_2)_3$. Furthermore, these resonances were very broad, which would be indicative of other paramagnetic compounds. Unfortunately, we have not been able to isolate this (these) complex(es). Finally, we found no evidence to suggest that $MoCl_3(PMePh_2)_3$ was produced. However, this

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Table I. Crystallographic Data for $MoOCl_3(OPMePh_2)_2{\cdot}C_6H_6$

chem formula	$C_{32}H_{32}Cl_3MoO_3P_2$
fw	728.85
space group (No.)	$P2_1/c$ (14)
a	9.278(3) Å
b	15.605(6) Å
c	21.967(5) Å
β	106.90(2)°
V	3042.9(3) Å^3
Z	4
T	23 °C
λ, Å	0.710 73 Å
ρ_{calc}	1.59 g/cm^3
μ(Mo Kα)	8.2 cm^{-1}
$R(F_o)^a$	0.043
$R_w(F_o)^b$	0.064

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

Table II. Positional Parameters and Their Estimated Standard Deviations for $MoOCl_3(OPMePh_2)_2{\cdot}C_6H_6$[a]

atom	x	y	z	B, Å^2
Mo	0.39702(8)	0.22908(4)	0.16070(3)	4.50(2)
O(11)[b]	0.257	0.273	0.186	5.5(2)*
Cl(1)[b]	0.2640(5)	0.2195(3)	0.0590(2)	5.4(1)
O(22)[b]	0.291	0.222	0.083	9.9(4)*
Cl(2)[b]	0.2212(4)	0.2845(3)	0.1936(2)	6.1(1)
Cl(3)	0.3352(2)	0.0872(1)	0.1819(1)	5.07(5)
Cl(4)	0.4969(3)	0.3665(1)	0.1473(1)	5.35(5)
O(1)	0.5465(5)	0.2308(3)	0.2533(2)	3.8(1)
P(1)	0.5955(2)	0.2774(1)	0.31597(8)	3.48(4)
O(2)	0.5858(5)	0.1746(3)	0.1414(2)	4.7(1)
P(2)	0.7509(2)	0.1697(1)	0.15177(9)	3.80(5)
C(111)	0.5078(9)	0.3787(5)	0.3131(4)	5.4(2)
C(121)	0.5462(7)	0.2165(4)	0.3754(3)	3.4(2)
C(122)	0.5644(9)	0.2501(5)	0.4364(3q)	4.9(2)
C(123)	0.5210(9)	0.2054(6)	0.4813(4)	6.0(2)
C(124)	0.4621(9)	0.1251(6)	0.4682(3)	5.5(2)
C(125)	0.4461(9)	0.0896(5)	0.4104(4)	5.7(2)
C(126)	0.4882(8)	0.1348(5)	0.3625(3)	4.4(2)
C(131)	0.7943(8)	0.2918(4)	0.3402(3)	3.6(2)
C(132)	0.8875(9)	0.266(5)	0.3710(4)	4.9(2)
C(133)	1.0431(9)	0.2333(6)	0.3878(4)	6.2(2)
C(134)	1.104(1)	0.3066(6)	0.3740(4)	7.1(3)
C(135)	1.014(1)	0.3732(6)	0.3432(4)	7.4(3)
C(136)	0.8599(9)	0.3653(5)	0.3260(4)	5.2(2)
C(211)	0.8410(9)	0.2709(5)	0.1620(4)	5.8(2)
C(221)	0.7799(8)	0.1198(5)	0.0831(3)	3.9(2)
C(222)	0.8854(9)	0.1473(6)	0.0550(4)	5.5(2)
C(223)	0.902(1)	0.1047(6)	0.0015(4)	7.2(3)
C(224)	0.810(1)	0.0361(6)	−0.0221(4)	8.0(3)
C(225)	0.710(1)	0.072(7)	0.0070(5)	7.9(3)
C(226)	0.695(1)	0.0505(6)	0.0593(4)	6.1(2)
C(231)	0.8413(8)	0.1032(4)	0.2184(3)	3.8(2)
C(232)	0.7571(9)	0.0586(4)	0.2499(3)	4.3(2)
C(233)	0.827(1)	0.0061(5)	0.3001(4)	5.2(2)
C(234)	0.980(1)	−0.0015(5)	0.3196(4)	6.0(2)
C(235)	1.064(1)	0.0419(6)	0.2870(4)	6.4(2)
C(236)	0.9957(9)	0.0956(5)	0.2372(4)	5.3(2)
C(801)	0.121(2)	0.051(1)	0.5278(7)	5.0(4)*
C(802)	−0.014(2)	0.085(1)	0.5128(9)	7.2(5)*
C(803)	0.142(2)	−0.034(1)	0.5145(7)	5.0(4)*
C(901)	0.153(2)	0.009(1)	0.5264(7)	4.9(4)*
C(902)	−0.098(2)	0.075(1)	0.4991(8)	5.9(4)*
C(903)	0.059(2)	0.082(1)	0.5263(9)	7.8(5)*

[a] Starred values indicate that atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$. [b] Atom refined at 50% occupancy.

Table III. Selected Bond Lengths (Å) and Angles (deg) for $MoOCl_3(OPMePh_2)_2{\cdot}C_6H_6$[a]

	Bond Distances		
Mo–O(11)	1.6935(8)	Cl(1)–O(22)	0.516(4)
Mo–Cl(1)	2.222(4)	O(1)–P(1)	1.505(5)
Mo–O(22)	1.7078(7)	P(1)–C(111)	1.770(8)
Mo–Cl(2)	2.148(5)	P(1)–C(121)	1.779(7)
Mo–Cl(3)	2.368(2)	P(1)–C(131)	1.779(7)
Mo–Cl(4)	2.388(2)	O(2)–P(2)	1.484(5)
Mo–O(1)	2.103(4)	P(2)–C(211)	1.771(8)
Mo–O(2)	2.098(5)	P(2)–C(221)	1.786(8)
O(11)–Cl(2)	0.455(5)	P(2)–C(231)	1.791(7)
C(801)–C(802)	1.32(3)	C(901)–C(903)	1.44(3)
C(801)–C(803)	1.38(2)	C(902)–C(903)	1.41(3)
	Bond Angles		
O(11)–Mo–Cl(1)	95.9(1)	Cl(3)–Mo–O(1)	87.2(1)
O(11)–Mo–O(22)	94.78(3)	Cl(3)–Mo–O(2)	85.7(2)
O(11)–Mo–Cl(3)	93.45(7)	Cl(4)–Mo–O(1)	86.4(1)
O(11)–Mo–Cl(4)	92.27(1)	Cl(4)–Mo–O(2)	87.8(2)
O(11)–Mo–O(1)	91.7(1)	O(1)–Mo–O(2)	81.1(2)
O(11)–Mo–O(2)	172.8(1)	Mo–O(11)–Cl(2)	177.7(5)
Cl(1)–Mo–Cl(2)	96.4(2)	Mo–O(22)–Cl(1)	174.5(6)
Cl(1)–Mo–Cl(3)	92.2(1)	Mo–O(1)–P(1)	146.0(3)
Cl(1)–Mo–Cl(4)	93.4(1)	O(1)–P(1)–C(111)	112.7(3)
Cl(1)–Mo–O(1)	172.4(2)	O(1)–P(1)–C(121)	109.9(3)
Cl(1)–Mo–O(2)	91.2(2)	O(1)–P(1)–C(131)	110.2(3)
O(22)–Mo–Cl(2)	95.3(1)	C(111)–P(1)–C(121)	106.8(4)
O(22)–Mo–Cl(3)	91.76(5)	C(111)–P(1)–C(131)	108.9(3)
O(22)–Mo–Cl(4)	93.96(6)	C(121)–P(1)–C(131)	108.2(3)
O(22)–Mo–O(1)	173.5(1)	Mo–O(2)–P(2)	151.1(3)
O(22)–Mo–O(2)	92.4(1)	O(2)–P(2)–C(211)	113.7(4)
Cl(2)–Mo–Cl(3)	93.4(1)	O(2)–P(2)–C(221)	107.2(3)
Cl(2)–Mo–Cl(4)	92.3(1)	O(2)–P(2)–C(231)	111.9(3)
Cl(2)–Mo–O(1)	91.2(2)	C(211)–P(2)–C(221)	108.4(4)
Cl(2)–Mo–O(2)	172.3(2)	C(211)–P(2)–C(231)	108.7(3)
Cl(3)–Mo–Cl(4)	171.55(7)	C(221)–P(2)–C(231)	106.8(3)
C(802)–C(801)–C(803)	121.(2)	C(901)–C(903)–C(902)	119.(2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

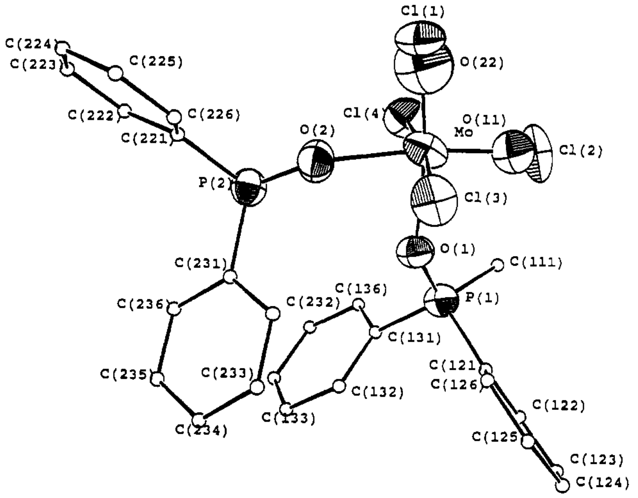

Figure 1. ORTEP representation of $MoOCl_3(OPMePh_2)_2{\cdot}C_6H_6$ without the C_6H_6 molecule of solvation. The ellipsoids represent thermal displacements and are drawn at the 50% probability level. Carbon atoms and the disordered O atoms are represented by spheres of arbitrary size.

complex may be the contaminant in the green $Mo_2Cl_4(PMePh_2)_4$ produced by reacting $MoH_4(PMePh_2)_4$ with HCl.[3] All spectra are available as supplementary material.

An attempt to grow crystals from a benzene solution of the green material resulted in crystals of a yellow impurity. As is illustrated in Figure 1, this yellow impurity turned out to be the compound $MoOCl_3(OPMePh_2)_2$. The crystal displayed a type of disorder that is often seen in oxo/chloro complexes where the M–O and cis M–Cl bonds can be interchanged while leaving the arrangement of the other ligands unaltered. Such a disorder was previously observed in the structure of the related complex $MoOCl_3(OPh_3)_2$[13] although, in that case, the compound crystallized so that two molecules constituted the asymmetric unit, one of them showing the disorder and the other molecule being completely ordered.

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The structure of $MoOCl_3(OPMePh_2)_2$ can best be described as distorted octahedral around the Mo atom with cis $OPMePh_2$ groups, a set of mutually trans Cl ligands, and the disordered cis O and Cl atoms constituting the core geometry. This arrangement results in a pseudo-C_2 axis along the midpoints of the O(11)···O(22) and O(1)···O(2) edges. After careful consideration of site occupancy factors and thermal parameters, the disordered O and Cl atoms were represented by a 50% Cl and a 50% O atom at each site. The Cl atoms at 50% occupancy at each site refined freely but the 50% O atoms had to be constrained. We do not believe that the Mo–Cl(1) and Mo–Cl(2) distances of 2.222(4) and 2.148(5) Å, respectively, can be taken at face value. They are shorter than expected because of the disordered arrangement of the cis O and Cl atoms. As a further consequence of the disorder, the Mo to O atom distances (on the $OPMePh_2$ ligands) are equal (2.103(4), 2.098(5) Å) as was the case with $MoOCl_3(OPPh_3)_2$.[13] The Mo–Cl(3) and Mo–Cl(4) distances of 2.368(2) and 2.388(1) Å, respectively, are within the range 2.359(3)–2.383(2) Å found for similar bonds in related structures.[13] It is of interest that in the structure of $MoOCl_3(OPMePh_2)_2$ the Mo–O–P angles of 146.0(3) and 151.1(3)° are significantly different, and both values are much smaller that the corresponding ones found for the disordered molecule in the structure of $MoOCl_3(OPPh_3)_2$ of 164.9(8) and 165.3(8)°.[13] The smaller Mo–O–P angles in $MoOCl_3(OPMePh_2)_2$ may well be due to reduction in steric crowding, but since one of the angles in the ordered form of $MoOCl_3(OPPh_3)_2$ was established as 145.6(7)°, this may not be the only reason.

In conclusion, we propose that the "green isomer" of $Mo_2Cl_4(PMePh_2)_4$ is simply the authentic and well-characterized[5] blue compound contaminated with $MoOCl_3(OPMePh_2)_2$, $MoOCl_2(PMePh_2)_3$, possibly *trans*-$[MoCl_4(PMePh_2)_2]^-$, and perhaps still other paramagnetic compounds. It may be noted that the "green isomer" was obtained only when mononuclear starting materials were used but not when $Mo_2(O_2CMe)_4$ was used. The origin of the oxo contaminants may well be adventitious H_2O or contamination of the starting material, $MoCl_5$, by $MoOCl_3$. We also note that the complex $WOCl_2(PMePh_2)_3$ was produced in the synthesis of the heteronuclear quadruply bonded complex $MoWCl_4(PMePh_2)_4$, where the starting materials were $Mo(\eta^6\text{-}PhPMePh)(PMePh_2)_3$ and $WCl_4(PPh_3)_2$.[4a]

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Supplementary Material Available: Figures depicting ^1H NMR spectra of $Mo_2Cl_4(PMePh_2)_4$ and all the various impurities and tables of crystal data, positional parameters, bond distances, bond angles, and anisotropic thermal parameters for $MoOCl_3(OPMePh_2)_2{\cdot}C_6H_6$ (20 pages). Ordering information is given on any current masthead page.