X-Ray Determination of Molecular Structures of Molybdenum(IV) Oxo-complexes. The Possibility of a New Type of Isomerism

By J. CHATT, LJUBICA MANOJLOVIĆ-MUIR,* and K. W. MUIR
(*School of Molecular Sciences, University of Sussex, Brighton* BN1 9QJ)

Summary Notable differences between corresponding bond lengths and interbond angles in the complexes blue *cis-mer*-[$MoOCl_2(PMe_2(Ph)_3$] and green *cis-mer*-[$MoOCl_2(PEt_2Ph)_3$] are caused by ligand repulsions; an explanation of the isomerism of *mer*-[$MoOCl_2(PMe_2Ph)_3$] is suggested in terms of the structures of the above complexes.

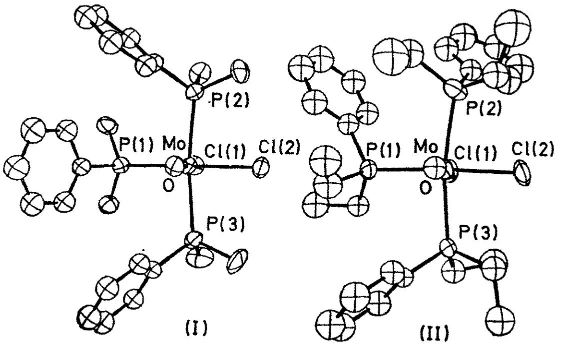
BUTCHER and CHATT recently described compounds of the type *mer*-[$MoOX_2L_3$] (X = halogen or pseudohalogen, and L = monotertiary phosphine).[1] Some are green, and others blue or blue-green, depending on X and L. The two series are also distinguishable by their i.r. spectra. In the green complexes the ν(Mo=O) band occurs at just under 946 cm^{-1}, whereas in the blue and blue-green complexes (except those with X = NCO) it occurs at frequencies higher than 946 cm^{-1}. One compound, *mer*-[$MoOCl_2(PMe_2Ph)_3$], was isolated in two isomeric forms, an unstable green one, with ν(Mo=O) at 943 cm^{-1}, and a stable blue one, with ν(Mo=O) at 954 cm^{-1}. The green form is irreversibly converted into the blue on gentle heating in solution.

Selected intramolecular distances (Å) *and angles* (°) *in* (I) *and* (II)

	(I)	(II)		(I)	(II)
Mo–O	1·676(7)	1·803(11)	Mo–P(1)	2·500(3)	2·521(5)
Mo–Cl(1)	2·551(3)	2·426(6)	Mo–P(2)	2·541(3)	2·582(6)
Mo–Cl(2)	2·464(3)	2·479(5)	Mo–P(3)	2·558(3)	2·556(6)
O–Cl(2)	3·333(8)	3·280(12)	Cl(1)–Cl(2)	3·405(4)	3·353(8)
O–P(1)	3·056(8)	3·185(12)	Cl(1)–P(1)	3·141(4)	3·233(6)
O–P(2)	3·086(8)	3·142(12)	Cl(1)–P(2)	3·581(4)	3·567(8)
O–P(3)	3·087(8)	3·117(14)	Cl(1)–P(3)	3·594(4)	3·549(8)
P(1)–P(2)	3·700(5)	3·856(6)	Cl(2)–P(2)	3·421(4)	3·407(9)
P(1)–P(3)	3·694(4)	3·666(8)	Cl(2)–P(3)	3·393(5)	3·403(5)
	(I)	(II)		(I)	(II)
Cl(1)–Mo–P(1)	76·9(1)	81·6(2)	P(1)–Mo–P(3)	93·8(1)	92·4(2)
P(1)–Mo–O	91·9(3)	93·4(4)	P(3)–Mo–Cl(2)	85·0(1)	85·0(2)
O–Mo–Cl(2)	105·7(3)	98·8(4)	P(2)–Mo–P(3)	171·2(1)	169·4(2)
Cl(2)–Mo–Cl(1)	85·5(1)	86·2(2)	O–Mo–P(2)	91·7(3)	89·7(4)
Cl(1)–Mo–O	168·8(3)	175·0(4)	P(2)–Mo–Cl(1)	89·4(1)	90·8(2)
Cl(2)–Mo–P(1)	162·4(1)	167·5(2)	Cl(1)–Mo–P(3)	89·4(1)	90·8(2)
Cl(2)–Mo–P(2)	86·2(1)	84·6(2)	P(3)–Mo–O	91·2(3)	89·6(4)
P(2)–Mo–P(1)	94·4(1	98·2(2			

An *X*-ray analysis of the blue isomer (I) has shown that it is a highly distorted octahedral complex, with a *cis*-configuration of chlorine atoms, and with the oxygen atom *trans* to chlorine.[2] It was therefore concluded[1] that the green isomer probably has a *trans*-arrangement of the chlorine atoms, with the oxygen atom *trans* to phosphine. However, the spectral properties of the two isomers are so similar that we decided to investigate this isomerism further.

We have not yet been able to obtain crystals of the green isomer suitable for accurate *X*-ray analysis, and we have therefore determined the molecular structure of the green complex *mer*-[$MoOCl_2(PEt_2Ph)_3$] (II), for which ν(Mo=O) = 940 cm^{-1}. The crystals of this compound were kindly supplied by Dr. A. V. Butcher. They are monoclinic, space group $P2_1/c$, $a = 12{\cdot}238$, $b = 14{\cdot}818$, $c = 21{\cdot}687$ Å, $\beta = 121{\cdot}28°$. The structure has been refined by full-matrix least-squares to an R-value of 0·087, based on 2283 independent reflections measured on a four-circle diffractometer. We find, as expected, that the molybdenum atom again exhibits distorted octahedral co-ordination with a *mer*-arrangement of the phosphorus atoms; surprisingly, the chlorine atoms are again *cis* to each other and the oxygen atom is again *trans* to chlorine.



Molecular structures of cis-mer-[$MoOCl_2(PR_2Ph)_3$] (I; R = Me; II; R = Et) *viewed along the normal to the plane* Mo, Cl(2), P(2)

The molecules of (I) and (II) are shown in the Figure, and selected intramolecular distances and angles are listed in the Table. These show interesting differences in the molecular geometries.

1. The Mo=O bond is 0·127(13) Å shorter in (I) than in (II), while the Mo–Cl(1) bond is 0·125(7) Å longer; the other bond lengths involving molybdenum are similar in both complexes. The higher ν(Mo=O) occurs in (I); however, the small difference between ν(Mo=O) in the green and blue compounds suggests that the oxygen is about equally strongly held in both.

2. The distortions from ideal octahedral geometry are also different. They are most noticeable in the plane defined by the atoms O, Cl(1), Cl(2), and P(1). Thus, in (I) the angles O–Mo–Cl(2) and P(1)–Mo–Cl(1) are respectively 105·7(3) and 76·9(1)°, whereas the corresponding angles in (II) are 98·8(4) and 81·6(2)°.

3. The atoms in the co-ordination sphere of molybdenum in each complex are arranged so as to prevent unacceptably close contacts between the ligand atoms bound to molybdenum. Thus, in (II) the O · · · Cl(2) contact, evidently a minimal one in view of the angle the two atoms subtend at molybdenum, is 3·28 Å, while in (I) the corresponding contact is 3·33 Å, although the Mo=O distance is shorter. The shortest Cl · · · P contact in either compound is that of 3·14 Å between Cl(1) and P(1) in (I); the comparable contact in (II) is longer, though the Mo–Cl(1) bond is shorter.

4. The organic substituents on the phosphorus atoms in (I) and (II) (see Figure) are in a different orientation with respect to the molybdenum co-ordination polyhedron.

The differences between the two complexes are best rationalised in terms of ligand repulsions. The closer intramolecular contacts between either O, or Cl(1), and the carbon atoms of the phosphines are not sensitive to changes in the Mo=O and Mo–Cl(1) bond lengths. It thus appears that the geometry of the molybdenum co-ordination polyhedron in these very similar complexes is determined by a balance of the bonding forces between the metal and its ligands and the repulsive forces between the ligand atoms bound directly to the metal.

Bright and Ibers have suggested that the unusually long Re–N and Re–Cl (*trans* to N) distances in *cis-mer*-[$ReNCl_2(PEt_2Ph)_3$] may be due to steric requirements of the ligands.[3] Since the molecular geometry of the nitrido-complex is very closely related to those of the above oxo-complexes, our results strongly support their suggestion.

The molecular structure of (II) raises another possibility for the configuration of the green isomer of *mer*-[$MoOCl_2(PMe_2Ph)_3$], and, therefore, the nature of isomerism in the latter complex becomes even more intriguing. It may be that it is a new type of isomerism, involving two equilibrium arrangements of ligands, which differ in the distortions of the highly strained co-ordination polyhedron of the metal. We suggest that it may be called distortional isomerism, and that green and blue [$MoOCl_2(PMe_2Ph)_3$] are distortional isomers of *cis-mer*-[$MoOCl_2\ (PMe_2Ph)_3$].

We gratefully acknowledge the financial support of this work by the S.R.C.

(*Received, March 4th,* 1971; *Com.* 177.)

---

[1] A. V. Butcher and J. Chatt, *J. Chem. Soc. (A)*, 1970, 2652.
[2] Lj. Manojlović-Muir, *Chem. Comm.*, 1971, 147.
[3] D. Bright and J. A. Ibers, *Inorg. Chem.*, 1969, 8, 709.