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A Novel Route to Molybdenum(V) 1,2-Bis(diphenylphosphine)ethane Complexes

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Presently all known Mo(V)–dppe complexes have been obtained from the nonaqueous media (dppe = 1,2-bis(diphenylphosphino)ethane). This communication reports data concerning their preparation from water solutions. It is well known that molybdenum cations in different oxidation states exist in water solutions. Molybdenum(V) exists in aqueous solutions for pH $\leqslant$ 7 [1]. The author has attempted the reaction of $MoOCl_5^{2-}$ anion with dppe in hydrochloric acid (c > 2*M*). As the result a bright green, moisture sensitive, amorphous compound(I) was obtained with $[dppeH_2]MoOCl_5$ formulation and μ_{eff} being 1.74 BM. After treating with dry methanol the compound (I) converted rapidly to a brown, air-stable compound (II) of $[MoOCl_3(dppe)]$ formulation, which was established by comparison with one of two isomers (red and brown) of $[MoOCl_3(dppe)]$ complex prepared earlier in a different way [2]. Similar method was employed to synthesize the corresponding complex with bipyridyl [3].

The magnetic moment of II being 1.62 BM is characteristic for a great number of Mo(V) monomeric complexes with other ligands [4]. Additionally, from the methanolic filtrate mauve crystals were separated after 4 days. The complex obtained is probably similar to the compound obtained by Butcher and Chatt [2]. The crystal form of I was obtained by slow air oxidation of Mo(III) and dppe solution in concentrated hydrochloric acid. Single crystals suitable for an X-ray crystalllography were not obtained. On the other hand, freshly prepared $[dppeH_2]MoOCl_5$ was treated with an excess of water affording an amorphous, air-stable dark violet, diamagnetic complex (III) with $[Mo_2O_{2.5}Cl_5(dppe)_2]$ formulation.

Characteristic bands in the IR and reflectance visible spectra are given in Table I.

TABLE I. Spectral Data.

C	Ir (cm^{-1})			Visible (×1000 cm^{-1})	
	νP–H	νMo=O	νM–Cl		
I	2400m	972vs	315s	21.70	13.50
II	–	953vs	337s 320s 274m	21.00	14.40
III	–	975s 942s	323s 299m 282vw	20.40 20.20^a	14.81 14.70^a

^{a}In chloroform.

The IR bands in the region 337–274 cm^{-1} were assigned to the Mo–Cl vibration and those in the region 975–942 cm^{-1} to the Mo=O [5, 6]. The additional band at 2400 cm^{-1} for I can be univocally assigned to the P–H stretching vibrations [7]. The compound III being diamagnetic should be at least dimeric. Levason *et al.* [5] describe compounds of $[MoClO(L-L)_2][MoCl_4O]$ type which show the stretching vibrations Mo=O at 980 and 940 cm^{-1} for the anion and cation respectively.

Such formulation cannot be used for the compound III because of its non-ionic character. The complex is insoluble in water, methanol and ethanol but is well soluble in chloroform, chlorobenzene, benzene and acetone. It can be assumed that bands of identical intensities at 975 and 942 cm^{-1} assigned to the Mo=O modes derive from sterically nonequivalent molybdenum atoms in the $[Mo_2O_{2.5}Cl_5(dppe)_2]$ unit. Thus they are in agreement with assignments made above.

Since complex III is very solvent sensitive the visible spectrum was recorded immediately after the chloroform solution was prepared. It was noticed that the solutions of III change colour from dark-violet to brown in few minutes. Possible Mo–O–Mo vibrations cannot be observed because the phosphine ligand gives very strong absorptions in the 680–760 cm^{-1} and 450–550 cm^{-1} region.

The reflectance visible spectra for all compounds synthesized are comparable with the spectrum of the red $[MoOCl_3(dppe)]$. Despite the small differences in absorption frequencies the shape of spectra of II and III is identical with that of the red isomer. Bands at *ca.* 21000 cm^{-1} are assigned to $^2B_1 \leftarrow {}^2B_2$ transitions and those in the region 16000–12000 cm^{-1} to $^2E \leftarrow {}^2B_2$ for octahedral d^1-electronic systems [4, 5].

From observations reported above the author concludes that the new compounds (I and III) were obtained from acidic aqueous solutions and that a relatively fast easy method of preparation of II was elaborated.

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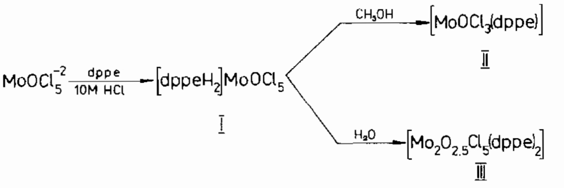
The complexes in question exhibit very interesting catalytic properties in the reactions of decomposition of organic hydroperoxides and olefin epoxidation.

Further investigations on the preparation of this type of complexes with molybdenum in other oxidation states in aqueous solutions are in progress.



Experimental

The IR spectra were obtained on a Perkin-Elmer 180 spectrophotometer (KBr discs). The reflectance visible spectra were recorded on a Beckmann 5240 spectrophotometer (MgO discs). The magnetic measurements were performed on a Gouy's balance (Cahn) Ventron Model RM-2 with ±0.5 B.M. accuracy.

Molybdenum was determined by the gravimetric method using 8-hydroxyquinoline [8].

[dppeH$_2$]MoOCl$_5$, Green Compound (I)

To a 0.05 molar solution of dppe in concentrated hydrochloric acid a 0.003 molar solution of Mo(V) [9] was added dropwise, during continuous stirring. Immediately a bright-green precipitate was formed. On addition the colour changed to brown-green. The precipitate was filtered, washed with concentrated HCl and dried in vacuum. *Anal.*: Calc. Mo: 13.92%; Cl: 25.74%; C: 45.25%; H: 3.48%. Found, Mo: 13.46%; Cl: 24.97%; C: 44.66%; H: 4.31%.

[MoOCl$_3$(dppe)], Brown Compound (II)

The complex was prepared from the compound I by treating with an excess of dry methanol at room temperature. As a result a brown complex was obtained which, after drying in vacuum, analysed satisfactorily. *Anal.*: Calc. Mo: 15.57%; Cl: 17.27%; C: 50.60%; H: 3.89%. Found, Mo: 15.52%; Cl: 17.17%; C: 49.87%; H: 4.24%.

[Mo$_2$O$_{2.5}$Cl$_5$(dppe)$_2$], Violet Compound (III)

The compound [dppeH$_2$]MoOCl$_5$ prepared as above was filtered on a synthetic glass and washed subsequently with several portions of conc. HCl, excess of water and again with small amounts of conc. HCl and water during continuous stirring of the precipitate. The dark-violet complex obtained was dried in a vacuum for 6 hours at room temperature. *Anal.*: Calc. Mo: 15.90%; Cl: 14.71%; C: 51.73%; H: 3.98%. Found, Mo: 15.30%; Cl: 14.59%; C: 52.05%; H: 4.35%.

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Erratum

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A ^{117}Sn and ^{31}P NMR Study of Trans-[$Pt(SnCl_3)_nCl_{2-n}(P(CH_2CH_3)_3)_2$] (n = 1,2) in Acetone: the Effect of Solvent

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Please note the principal author's correct initials (K. R. as opposed to the erroneously published B. R.). The same error should be corrected in the Author Index on p. 292 of the volume.