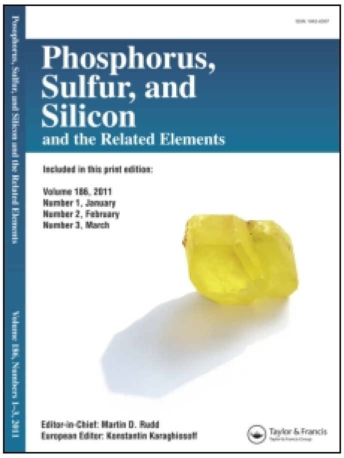

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Ratnani, R. , Srivastava, G. and Mehrotra, R. C.(1990) 'SYNTHESIS AND CHARACTERIZATION OF DICHLORODIMETHOXYMOLYBDENUM (V) 0,0'-DIALKY L(ALKYLENE) DITHIOPHOSPHATE COMPLEXES', Phosphorus, Sulfur, and Silicon and the Related Elements, 48: 1, 245 — 249

To link to this Article: DOI: 10.1080/10426509008045905

URL: http://dx.doi.org/10.1080/10426509008045905

Phosphorus, Sulfur, and Silicon, 1990, Vol. 48, pp. 245–249
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SYNTHESIS AND CHARACTERIZATION OF DICHLORODIMETHOXYMOLYBDENUM (V) 0,0′-DIALKYL(ALKYLENE) DITHIOPHOSPHATE COMPLEXES

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Dichlorodimethoxymolybdenum (V) 0,0′-dialkyl dithiophosphates, $MoCl_2(OMe)_2S_2P(OR)_2$ (where $R = Et, Pr^n, Pr^i, Bu^i$) and dichlorodimethoxymolybdenum (V), 0,0′-alkylene dithiophosphates, $MoCl_2(OMe)_2S_2\overline{POGO}$ (where $G = CH_2CMe_2CH_2$—, —CMe_2CMe_2—, —CHMeCHMe-) have been synthesized by the reactions of $MoCl_3$ $(OMe)_2$ with sodium (or ammonium) salts of the corresponding dithiophosphoric acids.

These complexes have been characterized on the basis of elemental analyses, ^{31}P NMR spectral data, magnetic studies and molecular weight determinations, which show their paramagnetic as well as dimeric nature. Based on these data, plausible structures containing hepta-coordinated molybdenum have been suggested for these compounds.

Key words: Dialkyl (alkylene) dithiophosphoric acid ligands; molybdenum (V) sulphur derivatives; phosphorus-31 NMR spectra; magnetic susceptibilities.

INTRODUCTION

Synthesis and various physicochemical properties of dialkyl (and alkylene) dithiophosphates of transition[1] as well as main group[2] elements have been extensively investigated and many of them show biological properties.[3,4] Much of the current interest in the co-ordination chemistry of molybdenum stems from attempts to prepare complexes, especially those of sulphur-containing ligands, which may serve as models for biological systems.[5,6] In continuation of our studies on the synthesis of binuclear oxomolybdenum (V)[7] and oxomolybdenum (IV)[8] 0,0′-dialkyl (alkylene) dithiophosphate complexes, we describe in the present paper, the synthesis and characterization of dichlorodimethoxymolybdenum (V) 0,0′-dialkyl (and alkylene) dithiophosphate complexes.

RESULTS AND DISCUSSION

Dichlorodimethoxymolybdenum (V) 0,0′-dialkyl (and alkylene) dithiophosphate complexes have been synthesized by the reactions of molybdenum trichloride dimethoxide with sodium or ammonium dialkyl (alkylene) dithiophosphate in equimolar ratio in benzene medium.

The above complexes (I–VII) of both acyclic and cyclic ligands are dark green viscous liquids and solids respectively, except the complex (VII), which is a green semi-solid. The yields obtained are in 85–97% range. The acyclic derivatives are

TABLE I

Synthesis of dichlorodimethoxymolybdenum (V) 0,0′-dialkyl(alkylene) dithiophosphate complexes

Compd. no.	Reactants (in gms)		Product**	Yield %	NH_4Cl/ NaCl found (calcd)	Elemental analyses Found (calcd) %		
	$MoCl_3(OMe)_2$	$NH_4S_2P(OR)_2$ or $NH_4S_2\overline{POGO}$				Mo	S	Cl
I	1.03	0.80	$MoCl_2(OMe)_2S_2P(OEt)_2$ 1.52	93.3	0.20 (0.21)	23.52 (23.10)	15.59 (15.45)	16.4 (17.07)
II	0.92	0.83	$MoCl_2(OMe)_2S_2P(OPr^n)_2$ 1.5	97.1	0.21 (0.20)	21.9 (21.69)	14.64 (14.50)	16.13 (16.03)
III	0.78	0.69	$MoCl_2(OMe)_2S_2P(OPr^i)_2$ 1.19	90.6	0.14 (0.16)	21.97 (21.69)	14.83 (14.50)	14.70 (16.03)
IV	0.70	0.68	$MoCl_2(OMe)_2S_2P(OBu^i)_2$ 1.17	95.3	0.15 (0.16)	21.07 (20.75)	13.56 (13.87)	15.34 (15.34)
V	0.97	0.81*	$MoCl_2(OMe)_2S_2\overline{POCH_2CMe_2CH_2O}$ 1.29	82.3	0.22 (0.22)	22.40 (22.51)	15.21 (15.05)	16.26 (16.64)
VI	0.96	0.85*	$MoCl_2(OMe)_2S_2\overline{POCMe_2CMe_2O}$ 1.25	88.8	0.22 (0.21)	22.20 (21.79)	14.83 (14.57)	15.69 (16.10)
VII	0.62	0.47	$MoCl_2(OMe)_2S_2\overline{POCHMeCHMeO}$ 0.92	95.4	0.12 (0.13)	23.35 (23.28)	15.34 (15.56)	16.75 (17.21)

** Compounds I–IV, green viscous liquids; V and VI, green solids, and VII, green semi-solid.

* Na salts.

$$MoCl_3(OMe)_2 + MS_2P(OR)_2 \longrightarrow MoCl_2(OMe)_2S_2P(OR)_2 + MCl$$

$$MoCl_3(OMe)_2 + MS_2\overline{POGO} \longrightarrow MoCl_2(OMe)_2S_2\overline{POGO} + MCl$$

[where R = Et (compound No. I), Pr^n (II), Pr^i (III),
Bu^i (IV); G = $-CH_2CMe_2CH_2-$ (V),
$-CMe_2CMe_2-$ (VI), $-CHMeCHMe-$ (VII),
M = NH_4 or Na].

freely soluble in most of the common organic solvents, but the cyclic derivatives are only sparingly soluble. The solubility in general, however, is markedly decreased on storage of the products for a few weeks. The molecular weights (Table II) of all the acyclic derivatives determined osmometrically in benzene indicated, the dimeric nature of these products. However, m.w.'s of cyclic derivatives could not be obtained due to their limited solubility in most of the organic solvents.

MAGNETIC MOMENTS

These molybdenum derivatives are paramagnetic with magnetic moments (Table II) in the range of 1.10–1.18 B.M. at *ca.* 301 K, which is lower than the

TABLE II

Molecular weights, magnetic moments and ^{31}P NMR spectral data for dichlorodimethoxymolybdenum (V) 0,0′-dialkyl (alkylene) dithiophosphate complexes

Compd. no.	Compound	Molecular weights* found (calcd)	Magnetic moments	^{31}P chemical shift * (Δδ ppm)
I	$MoCl_2(OMe)_2S_2P(OEt)_2$	814.7 (415.2)	1.15	112.69 (26.69)
II	$MoCl_2(OMe)_2S_2P(OPr^n)_2$	876.2 (442.2)	1.10	113.39 (30.98)
III	$MoCl_2(OMe)_2S_2P(OPr^i)_2$	881.4 (442.2)	1.10	109.1 (26.17)
IV	$MoCl_2(OMe)_2S_2P(OBu^i)_2$	947 (462.3)	1.18	113.48 (26.69)
V	$MoCl_2(OMe)_2S_2\overline{POCH_2CMe_2CH_2O}$	—	—	112.76** (35.69)
VI	$MoCl_2(OMe)_2S_2\overline{POCMe_2CMe_2O}$	—	—	129.3** (36.91)
VII	$MoCl_2(OMe)_2S_2\overline{POCHMeCHMeO}$	—	—	128.18 (32.68)

Δδ = shift in the position of ^{31}P absorption in the derivatives compared to the free dithiophosphoric ligands.
* in C_6H_6.
** in CH_2Cl_2.

theoretically calculated value of 1.73 B.M. for one unpaired electron. Although other possibilities can not be ruled out, the observed low values may be ascribed to a weak interaction of the unpaired electrons in the dimeric complex species.

^{31}P NMR spectral study

Proton-decoupled ^{31}P NMR spectra (Table II) of dichlorodimethoxymolybdenum (V) dialkyl (alkylene) dithiophosphate complexes show deshielding to the extent of 25–35 ppm, with respect to the corresponding parent acyclic and cyclic dithiophosphoric acids; this type of deshielding has been interpreted by Glidewell[9] to indicate the bidentate nature of dithiophosphate groups. However, in view of the influence of paramagnetism, it is difficult to derive a definite conclusions on the basis of ^{31}P data of these derivatives.

STRUCTURE

Phosphorus-31 NMR spectra show magnetic equivalence of the phosphorus nuclei in the dimeric complexes. Out of chloride, alkoxy and dithiophosphato linkages, alkoxy bridging seems to be preferred in general.[10] In view of the well established[11] tendency of dithiophosphato moieties (L) in general to attach to transition metal centres in a bidentate chelating (rather than monodentate or bidentate bridging) manner, a plausible structure of the following type (Figure 1) may be suggested as one of the possible isomeric forms for the new derivatives, $[MoCl_2(OMe)_2L]_2$:

Further replacement of chlorine in the above derivatives does not appear to proceed in a straightforward manner and is accompanied with the formation of bis [dialkyl (alkylene) thiophosphoryl] disulphide.

EXPERIMENTAL

Stringent precautions were taken to exclude moisture during experimental manipulations. Solvents (methanol, benzene etc.) were dried by standard methods. Trichlorodimethoxymolybdenum (V),[12]

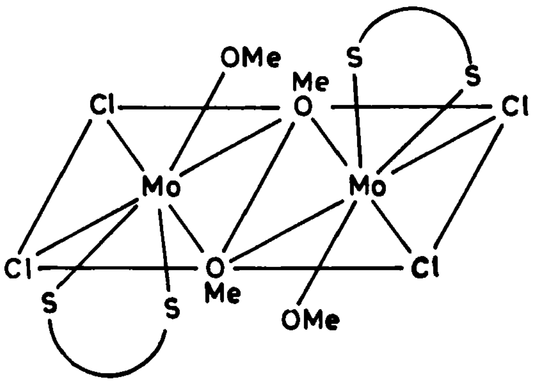

FIGURE 1.

dialkyl[13] and alkylene[14] dithiophosphoric acids were prepared by the methods reported in the literature. Sulphur, molybdenum and chloride were estimated gravimetrically as barium sulphate (Messenger's method), molybdenum oxinate and Volhard's method respectively.

Magnetic susceptibility measurements were made on a Gouy balance (Bruker Magnetic balance, Model no. B.E. 70B8) using $Hg[Co(CNS)_4]$ as standard. The magnetic moments, $\mu_e = 2.84\sqrt{\chi_M^{corr}T}$ (where χ_{corr}^{M} is the observed molar susceptibility after correction for the diamagnetism of the constituent atoms). Molecular weights were determined on a Knauer Vapour Pressure Osmometer in benzene solutions. ^{31}P NMR spectra were recorded in benzene using H_3PO_4 as an external standard. NMR spectra were recorded on Jeol FX 90Q spectrometer.

Methods of preparation

(*a*) *Trichlorodimethoxymolybdenum (V), $MoCl_3(OMe)_2$.* Molybdenum pentachloride (2.60 g), added cautiously to cold (*ca* −40°C) methanol (30 ml), caused a vigorous reaction and a green coloured solution was obtained. The excess of alcohol was removed under reduced pressure at room temp. (35°C) leaving a brown solid, $MoCl_3(OMe)_2$ (2.51 g) [Found: Mo, 40.1; Cl, 36.8; Calcd. for $MOCl_3(OMe)_2$: Mo, 40.2; Cl, 36.2)].

(*b*) *Dichlorodimethoxymolybdenum (V) 0,0′-diethyldithiophosphate, $MoCl_2(OMe)_2S_2P(OEt)_2$.* A solution of trichlorodimethoxymolybdenum (V) (1.03 g) in benzene (40 ml) was added to an equimolar amount of ammonium salt of diethyl dithiophosphoric acid (0.80 g) and the solution was stirred for two hours at room temperature, during which the colour changed to green from initial brown. The precipitated ammonium chloride (0.20 g) was filtered out and the solvent was removed under reduced pressure at room temperature, yielding a green coloured viscous compound, identified as $MoCl_2(OMe)_2S_2P(OEt)_1$ (1.52 g, 93.3%).

Similarly, the other alkyl (Pr^n, Pr^i and Bu^i) derivatives were prepared, following the same reaction conditions (Table I).

(*c*) *Dichlorodimethoxymolybdenum (V) 0,0′-alkylene dithiophosphate, $MoCl_2(OMe)_2S_2\overline{POGO}$.* A procedure, similar to that for the open chain complexes, gave green coloured solid compound, identified as $MoCl_2(OMe)_2S_2POGO$.

ACKNOWLEDGEMENT

One of the authors (R. Ratnani) is thankful to the State Government of Rajasthan, Jaipur and U.G.C., New Delhi for financial assistance under Special Assistance Programme.

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