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Synthesis of some Binuclear Oxomolybdenum(V), *O, O′*-Dialkyl (Alkylene) Dithiophosphate Complexes

R. RATNANI, G. SRIVASTAVA and R. C. MEHROTRA*

Department of Chemistry, University of Rajasthan, Jaipur-302 004 (India)

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Abstract

μ-Oxobis[oxobis(*O,O′*-dialkyl dithiophosphato)-molybdenum(V)], $Mo_2O_3[S_2P(OR)_2]_4$ (where R = Me, Et, Pr^n, Pr^i, Bu^i, Ph) and μ-oxobis[oxobis(*O,O′*-alkylene dithiophosphato)molybdenum(V)], $Mo_2O_3[S_2\overline{POGO}]_4$ (where G = $-CH_2CMe_2CH_2-$, $-CMe_2CMe_2-$, and $-CHMeCHMe-$) have been synthesized by the reactions of $MoO_2(acac)_2$ (acac = acetylacetone) with *O,O′*-dialkyl or alkylene dithiophosphoric acids. The reduction of molybdenum(VI) to molybdenum(V) appears to be quite facile in these reactions. The complexes have been characterized on the basis of elemental analyses and magnetic studies. Octahedral environment around molybdenums with chelating dithiophosphate moieties and *anti* terminal oxygens has been deduced on the basis of the IR and NMR (^1H, ^{13}C, ^{31}P) spectral studies.

Introduction

A variety of stable complexes of molybdenum, in different oxidation states, with 1,1-dithio ligands such as *N,N*-dialkyl dithiocarbamates [1, 2] and *O*-alkyl dithiocarbonates(xanthates) [2, 3] have been described in the literature. The chemistry of binuclear molybdenum(V) derivatives of the types, $Mo_2O_3(S_2CNR_2)_4$ and $Mo_2O_3(S_2COR)_4$ has been studied in detail.

O,O′-Dialkyl (and alkylene) dithiophosphoric acids also behave as versatile dithio ligands [4] and form a variety of complexes with transition [5] as well as non-transition [6] elements. A survey of the literature indicates the synthesis till now of only two molybdenum(V) dialkyl dithiophosphates [2, 7], $Mo_2O_3[S_2P(OR)_2]_4$; R = Et(II), Ph(VI), out of which the former [8] shows a centrosymmetric structure containing a linear Mo–O–Mo bridge with a mutually *anti* orientation of the two terminal oxo atoms. This is in contrast to the corresponding dithiocarbamato and xanthato derivatives in which the terminal oxo atoms are mutually *syn* oriented.

The nature of the alkyl group of the dialkyl dithiophosphato moieties has been found to have marked influence on the structural features of metal dialkyl dithiophosphates. In view of their relevance to the reported [9, 10] enzymatic oxidase and reductase activity, a novel interest has been created in these binuclear oxomolybdenum(V) derivatives by the observation of Newton and co-workers [11] that these appear to show the rather unusual property of dissociation into the corresponding Mo(VI) and Mo(IV) derivatives, which readily reunite on crystallization to give distinct Mo(V) species. The corresponding cyclic dithiophosphato derivatives of metals have received much less attention and these appear to be in general less labile in nature. In view of these features, a variety of new binuclear Mo(V) dithiophosphato derivatives, derived from both acyclic as well as cyclic dithiophosphoric acids has been isolated and their spectral properties have been investigated.

Experimental

Stringent precautions were taken to exclude moisture during experimental manipulations. Solvents (methanol, n-hexane, chloroform and dichloromethane) were dried by standard methods. Bis(acetylacetonato)dioxomolybdenum(VI) [12], dialkyl [13] and alkylene [14] dithiophosphoric acids were prepared by literature methods. Sulphur was estimated gravimetrically as barium sulphate (Messenger's method) and molybdenum was estimated by precipitation as molybdenum oxinate, $MoO_2(C_9H_6ON)_2$.

IR spectra were recorded in KBr discs or nujol mulls in the range 4000–200 cm^{-1} using CsI cells. ^1H NMR spectra were recorded in deuterated chloroform/dimethyl sulfoxide using TMS as an internal standard. ^{13}C NMR spectra were scanned in chloroform using itself as an internal standard. ^{31}P NMR spectra were recorded in benzene/dichloromethane using H_3PO_4 as an external standard. All NMR spectra were recorded on a Jeol FX 90Q spectrometer.

Preparation of Complexes

The simple reactions of $MoCl_5$ with sodium (or ammonium) salts of the ligands in aqueous medium

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*Author to whom correspondence should be addressed.

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did give products approximating in composition to the purple $Mo_2O_3[S_2P(OR)_2]_4$ derivatives at lower temperatures, but these tended to be mixed with greenish yellow products of the composition $Mo_2O_4[S_2P(OR)_2]_2$, which appeared to be formed preferentially at higher temperatures.

An alternative route for synthesis of pure $Mo_2O_3[S_2P(OR)_2]_4$ derivatives was, therefore, reexplored [1] using the starting material $MoO_2(acac)_2$ which can be conveniently obtained by the reaction of ammonium molybdate with acetylacetone [12].

Binuclear oxomolybdenum(V) dialkyl and alkylene dithiophosphate complexes have been synthesized, during the course of these investigations, by the reactions in 1:2 molar ratio of bis(acetylacetonato)dioxomolybdenum(VI) with the corresponding dialkyl or alkylene dithiophosphoric acids in methanol medium at 0–5 °C. The colour changes immediately from initial yellow to dark purple on addition of the ligand to bis(acetylacetonato)dioxomolybdenum(VI) solution. The solution was stirred for one hour, when a dark purple product crystallized out, which was filtered, washed with methanol and n-hexane, followed by drying *in vacuo*. The products of acyclic and cyclic ligands could be recrystallized from benzene–n-hexane (1:1) and dichloromethane respectively.

Analytical and other relevant data are given in Table 1.

Results and Discussion

μ-Oxobis[oxobis(*O*,*O*′-dialkyl dithiophosphato)-molybdenum(V)] and μ-oxobis[oxobis(*O*,*O*′-alkylene dithiophosphato)molybdenum(V)] complexes have been synthesized by the reactions of bis(acetylacetonato)dioxomolybdenum(VI) with dialkyl (alkylene) dithiophosphoric acids in methanol at 0–5 °C.

$$MoO_2(acac)_2 \xrightarrow{HS_2P(OR)_2} Mo_2O_3[S_2P(OR)_2]_4$$

(where R = Me (compound **I**), Et (**II**), Pr^n (**III**), Pr^i (**IV**), Bu^i (**V**), Ph (**VI**)).

$$MoO_2(acac)_2 \xrightarrow{HS_2\overline{POGO}} Mo_2O_3[S_2\overline{POGO}]_4$$

(where G = $-CH_2CMe_2CH_2-$ (compound **VII**), $-CMe_2CMe_2-$ (**VIII**), $-CHMeCHMe-$ (**IX**)).

The above complexes **I**–**IX** of both acyclic and cyclic ligands crystallized out as dark purple solids leaving dithiophosphoryl disulphide in the mother liquor (as indicated by the ^{31}P NMR data). The yields obtained are in the 60–65% range. The acyclic derivatives **I**–**VI** are soluble in most common organic solvents, in contrast to the cyclic analogues **VII**–**IX** which are soluble only in CH_2Cl_2, DMSO and DMF and sparingly soluble in chloroform. The purple colour of the products points to +5 oxidation state for these complexes. This is further supported by the fact that these complexes gave with concentrated hydrochloric acid the characteristic green colour of the $MoCl_5^{2-}$ ion.

The reduction of Mo(VI) to Mo(V) in these reactions appears to be quite facile and in no case could the Mo(VI) derivative, $MoO_2[S_2P(OR)_2]_2$, be isolated even when the reaction of $MoO_2(acac)_2$ with dithiophosphoric acid was carried out in 1:2 or 1:<2 molar ratio, in which cases excess of the ligands was not available for reduction purposes.

Magnetic Measurements

Instead of showing moments of 1.73 BM expected for simple mononuclear Mo(V) derivatives, all these complexes show diamagnetic behaviour, which is in conformity with the suggested binuclear structure (see Fig. 1).

Infrared Spectral Studies

The assignments of relevant peaks (given in Table 2) have been made on the basis of literature published on various metal dialkyl and alkylene dithiophosphates [15] as well as molybdenum dithiocarbamates [10, 16] and dithiocarbonates [3]. A comparison of the spectra of the parent dithiophosphoric acids with those of the corresponding molybdenum derivatives reveal the following.

(a) The band due to νS–H at about 2500 cm^{-1} in the parent acids, disappears in the corresponding molybdenum complexes.

(b) The bands due to ν(P)–O–C and νP–O–(C) present in the region 1150–950 and 835–770 cm^{-1}, respectively, in the parent acids, do not show any change in the molybdenum complexes. In the cyclic derivatives the strong intensity band at ~950 cm^{-1}, attributed to ring vibrations (probably coupled with C–C stretching vibrations) [17, 18] also remarks unchanged on complexation.

(c) The band due to νP=S present at 670–630 cm^{-1} in the acyclic and at 690–670 cm^{-1} in the cyclic acids shows a small but notable shift ($\Delta\nu$ = 20–10 cm^{-1}) to lower frequencies in the molybdenum complexes indicating bidentate attachment of the ligand to the metal atom.

(d) New peaks of medium to strong intensity are present at 960 ± 10 and 770 ± 10 cm^{-1} and these may be assigned to ν_{as}Mo=O and ν_{as}Mo–O–Mo. Similarly, an additional peak present around 430 cm^{-1} may be assigned to δ Mo–O–Mo.

(e) The Mo–S stretching vibrations of weak to medium intensity are observed at 340 ± 10 cm^{-1}.

TABLE 1. Synthesis, properties and molecular weights of binuclear oxomolybdenum(V) dialkyl (alkylene) dithiophosphate complexes

Compound no.	Reactants (g)		Product[a]	Melting point (°C)	Elemental analyses (found/calc.) (%)		Molecular weight found (calc.)
	$MoO_2(acac)_2$	$HS_2P(OR)_2$ or $HS_2\overline{POGO}$ (R or G=)			Mo	S	
I	5.18	–Me (5.03)	$Mo_2O_3[S_2P(OMe)_2]_4$ (3.01)	123–124	22.2/22.1	29.6/29.5	
II	5.16	–Et (6.21)	$Mo_2O_3[S_2P(OEt)_2]_4$ (5.25)	123–124	19.9/19.6	26.3/26.2	503^c; 479^b (980)
III	2.29	$-Pr^n$ (3.02)	$Mo_2O_3[S_2P(OPr^n)_2]_4$ (2.38)	136	17.9/17.6	24.0/23.5	562^b (1093)
IV	2.60	$-Pr^i$ (3.42)	$Mo_2O_3[S_2P(OPr^i)_2]_4$ (2.75)	134	18.1/17.6	23.7/23.5	544; 534^c (1093)
V	2.68	$-Bu^i$ (3.99)	$Mo_2O_3[S_2P(OBu^i)_2]_4$ (2.91)	138	16.2/15.9	21.5/21.3	630, 617^c (1205)
VI	0.98	–Ph (1.69)	$Mo_2O_3[S_2P(OPh)_2]_4$ (1.17)	125	14.2/14.1	18.6/18.8	
VII	1.32	$-CH_2CMe_2CH_2-$ (1.60)	$Mo_2O_3[S_2\overline{POCH_2CMe_2CH_2O}]_4$ (1.37)	161–165 (decomp.)	18.8/18.7	24.7/24.9	
VIII	1.85	$-CMe_2CMe_2-$ (2.40)	$Mo_2O_3[S_2\overline{POCMe_2CMe_2O}]_4$ (1.91)	165–168 (decomp.)	17.9/17.7	23.9/23.6	
IX	2.39	–CHMeCHMe– (2.70)	$Mo_2O_3[S_2\overline{POCHMeCHMeO}]_4$ (2.23)	140–141	19.9/19.7	26.5/26.4	

[a] All the complexes are dark purple crystalline solids, obtained in 60–65% yield. [b] Molecular weight determined cryoscopically (in C_6H_6). [c] Molecular weight determined osmometrically (in $CHCl_3$ and C_6H_6).

TABLE 2. Some relevant spectral IR data (cm^{-1}) for binuclear oxomolybdenum(V) dialkyl (alkylene) dithiophosphate complexes

Compound no.	Complex	ν(P)–O–C	νP–O–(C)	Ring vibration	νP=S	νP–S	νMo=O	ν_{as}MoOMo	δ MoOMo	νMo–S
I	$Mo_2O_3[S_2P(OMe)_2]_4$	1017s	818s		640m	525s	964s	770m	420m	350w
II	$Mo_2O_3[S_2P(OEt)_2]_4$	1003s	810s		640s	528s	962w	775w	430m	340w
III	$Mo_2O_3[S_2P(OPr^n)_2]_4$	990s	810s		645s	542s	966m	750s	427w	326w
IV	$Mo_2O_3[S_2P(OPr^i)_2]_4$	980s	790s		667m	575m	965m	762w	419w	346w
V	$Mo_2O_3[S_2P(OBu^i)_2]_4$	1000s	800s		640s	560s	967s	765s	440w	324w
VII	$Mo_2O_3[S_2\overline{POCH_2CMe_2CH_2O}]_4$	1042s	816s	986s	675s	560s	970m	770m	430m	345m
VIII	$Mo_2O_3[S_2\overline{POCMe_2CMe_2O}]_4$	1010s	820s	925s	665m	580m	957w	775m	412w	351m
IX	$Mo_2O_3[S_2\overline{POCHMeCHMeO}]_4$	1035s	818s	935s	685s	612m	975m	763w	423w	339m

NMR Spectral Studies

The ^1H and ^{13}C NMR data (Tables 3 and 4) of molybdenum complexes are remarkably similar to those of the ligand dithiophosphoric acids, probably due to the large distance between the metal atom and these nuclei. The peak due to the S–H proton (present at δ 2.60–3.60 ppm in the spectra of dithiophosphoric acids) is expectedly absent in the corresponding molybdenum(V) complexes, showing the formation of the Mo–S bond by deprotonation.

The hydrogens attached to the α-carbon atoms of the alkoxy or glycoxy groups show coupling with phosphorus. The ^3J P–H values are in the range of 10–15 Hz and these do not appear to be much affected by replacement of the acid hydrogen by molybdenum. In the ^{13}C NMR spectra, the α-carbon atoms are deshielded by about 0.5–2.0 ppm. The ^1H and ^{13}C NMR spectra in general, are consistent with the four ligand moieties in each molecule of the complex being magnetically equivalent.

The ^{31}P chemical shifts for molybdenum(V) dialkyl (alkylene) dithiophosphate complexes increases to the extent of 12–22 ppm, with respect to the corresponding parent dithiophosphoric acids. A deshielding of this extent has been interpreted to be consistent with the bidentate behaviour of the dithiophosphate groups by different workers [19]. However, phosphorus chemical shifts, in general, depend on many factors (e.g. bond angle, steric effect, size of the ring and electronegativity of attached groups [20, 21]) and such correlations require more detailed studies.

As discussed above, the IR and multinuclear NMR (^1H, ^{13}C and ^{31}P) spectral data of the derivatives (both dialkyl as well as alkylene dithiophosphates) of molybdenum(V) indicate that the dithio moieties are uniformly bidentate, endowing an octahedral environment on both the molybdenums in all the derivatives described in this paper. These could have the *syn* (oxygens on the two molybdenums on the same side) or *anti* (the two oxygens being on the opposite site) structures. Although actual X-ray data particularly for the alkylene dithiophosphate derivatives would have provided definitive evidence (particularly in view of the reported *syn* structure for the analogous ethyldithiocarbonato [22] and dipropyl dithiocarbamato [23] derivatives, the dialkyl and alkylene dithiophosphates described in this paper may be expected to have the *anti* type structure (Fig. 1) similar to that of binuclear oxomolybdenum(V) diethyldithiophosphate [8].

The visible spectra of $Mo_2O_3[S_2P(OR)_2]_4$ complexes show an intense band at ~510 nm and a shoulder at ~370 nm. For comparison, the spectrum of the corresponding dithiocarbamate complex, $Mo_2O_3(S_2CNEt_2)_4$ was scanned and was also found to show bands at the same positions.

TABLE 3. ^{1}H and ^{31}P NMR spectral data (δ, ppm) for binuclear oxomolybdenum(V) dialkyl (alkylene) dithiophosphate complexes

Compound no.	Complex	^{1}H chemical shift[a]	^{31}P chemical shift[b]
I	$Mo_2O_3[S_2P(OCH_3)_2]_4$	3.81, d (J = 16 Hz) 3.97, d	103.15
II	$Mo_2O_3[S_2P(OCH_2CH_3)_2]_4$	1.38, t (J = 7 Hz), 24H ($-CH_3$) 3.88–4.55, m, 16H ($-OCH_2$)	97.90
III	$Mo_2O_3[S_2P(OCH_2CH_2CH_3)_2]_4$	0.98, t (J = 7 Hz), 24H ($-CH_3$) 1.30–2.06, m, 16H ($-CH_2$) 3.71–4.47, m, 16H ($-OCH_2$)	98.34
IV	$Mo_2O_3[S_2P(OCH(CH_3)_2)_2]_4$	0.89, d (J = 5 Hz), 48H ($-CH_3$) 0.94, d 3.08–3.48, m, 8H ($-OCH$)	94.13
V	$Mo_2O_3[S_2P(OCH_2CH(CH_3)_2)_2]_4$	0.94, d (J = 7 Hz) 48H ($-CH_3$) 1.01, d 1.74–2.19, m, 8H ($-CH$) 3.71–4.16, m, 16H ($-OCH_2$)	98.25
VI	$Mo_2O_3[S_2P(OC_6H_5)_2]_4$	6.95, s	101.14
VII	$Mo_2O_3[S_2\overline{POCH_2C(CH_3)_2CH_2O}]_4$	1.38, s, 24H ($-CH_3$) 3.75–4.33, d (J = 15 Hz), 16H ($-OCH_2$)	101.10
VIII	$Mo_2O_3[S_2\overline{POC(CH_3)_2C(CH_3)_2O}]_4$	1.58, s	106.7
IX	$Mo_2O_3[S_2\overline{POCH(CH_3)CH(CH_3)O}]_4$	1.34–1.78, d, 24H ($-CH_3$) 4.26–4.78, m, 8H ($-OCH$)	119.0

[a] In $CDCl_3$ except compound VII, in DMSO-d_6. [b] Compounds VII, VIII, IX in CH_2Cl_2, others in C_6H_6.

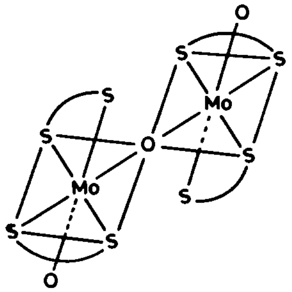

Fig. 1. Binuclear structure of oxomolybdenum(V) *O-O'*-dialkyl (alkylene) dithiophosphates.

It may be pointed out that visible spectral data [2, 10, 11] for $Mo_2O_3[S_2P(OEt)_2]_4$ as well as several $Mo_2O_3(dtc)_4$ (dtc = dithiocarbamate) complexes have been reported in the literature which correspond to a dissociation of the binuclear molybdenum(V) complex into mononuclear molybdenum(VI) and molybdenum(IV) complexes.

$$Mo_2O_3[S_2P(OR)_2]_4 \rightleftharpoons MoO_2[S_2P(OR)_2]_2 + MoO[S_2P(OR)_2]_2$$

On addition of CH_2Cl_2 to a mixture of $Mo_2O_3[S_2P(OEt)_2]_4$ and $MoO(S_2CNEt_2)_2$ in equimolar ratio, an unsymmetrical complex $(Et_2NCS_2)_2OMo{-}O{-}MoO[S_2P(OEt)_2]_2$ is formed. Newton and coworkers [11] have obtained chemical evidence as well for the above dissociation. As indicated below, our observations further support the above dissociation. (a) The molecular weight data measured osmometrically (in $CHCl_3$ and C_6H_6) as well as cryoscopically (in C_6H_6) (Table 1) of $Mo_2O_3[S_2P(OR)_2]_4$ complexes correspond to about one half of the calculated value thus showing that the Mo(V) complex breaks down into two species. (For comparison, the molecular weights of a few binuclear oxomolybdenum(V) dialkyl dithiocarbamate complexes have also been determined in chloroform and also in benzene, indicating about half the values of calculated values.) (b) The conductance measurements in chloroform and benzene solutions of the various $Mo_2O_3[S_2P(OR)_2]_4$

TABLE 4. ^{13}C NMR spectral data for binuclear oxomolybdenum(V) dialkyl (alkylene) dithiophosphate complexes

Compound no.	Complex	^{13}C chemical shift, δ (ppm)						
		–CH3	–CH2	–CH	–C	–OCH3	–OCH2	–OCH
I	$Mo_2O_3[S_2P(OCH_3)_2]_4$					54.72, s		
II	$Mo_2O_3[S_2P(OCH_2CH_3)_2]_4$	15.88, s					64.63, s	
III	$Mo_2O_3[S_2P(OCH_2CH_2CH_3)_2]_4$	10.19, s	23.46, s				69.99, s	
IV	$Mo_2O_3[S_2P(OCH(CH_3)_2]_4$	23.54, s						73.78, s
V	$Mo_2O_3[S_2P(OCH_2CH(CH_3)_2)_2]_4$	18.69, s		28.71, d (*J* = 4.89 Hz)			74.11, d (*J* = 2.45 Hz)	
VII	$Mo_2O_3[S_2\overline{POCH_2C(CH_3)_2CH_2O}]_4$	21.33, s			32.43, s		79.27, d (*J* = 10.98 Hz)	
IX	$Mo_2O_3[S_2\overline{POCH(CH_3)CH(CH_3)O}]_4$	17.84, d (*J* = 6.10 Hz)						83.87, d (*J* = 21.98 Hz)
VI	$Mo_2O_3[S_2P(OC_6H_5)_2]_4$	150.23, s(i)	121.57, s(o)	129.64, s(m)	126.01, s(p)			

complexes indicate the non-ionic nature of the species present. (c) Confirming the observations of Newton *et al.*, we have also observed that on addition of dichloromethane to a mixture of $MoO_2(dtc)_2$ and $MoO(dtp)_2$, unsymmetrical dinuclear molybdenum(V) derivatives containing both dithiophosphato as well as dithiocarbamato groups are obtained. This behaviour is shown even by cyclic dithiophosphates, e.g.

$$MoO_2(S_2CNEt_2)_2 + MoO(S_2\overline{POCH_2CMe_2CH_2O})_2 \longrightarrow$$
$$(Et_2NCS_2)_2OMo{-}O{-}MoO(S_2\overline{POCH_2CMe_2CH_2O})_2$$

The above purple coloured compound is identified by IR and analysis. Calc.: Mo, 20.6; S, 27.6. Found: Mo, 20.8; S, 27.5%.

It may be pointed out that NMR spectral studies give no idea of the above dissociation; this is probably due to fast exchange.

As indicated earlier the crystal structure of one of the open chain derivatives $Mo_2O_3[S_2P(OEt)_2]_4$ has already been reported and this showed the groups being *anti* oriented. Attempts to get suitable crystals of other compounds in this series (particularly the alkylene dithiophosphate) for X-ray diffraction study have so far been unsuccessful. However, the similarity of other physicochemical data of all these derivatives are in accordance with the structure suggested in Fig. 1.

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References

1 G. J.-J. Chen, J. W. McDonald and W. E. Newton, *Inorg. Chem.*, *15* (1976) 2612.
2 R. N. Jowitt and P. C. H. Mitchell, *J. Chem. Soc. A*, (1970) 1702.
3 W. E. Newton, J. L. Corbin and J. W. McDonald, *J. Chem. Soc., Dalton Trans.*, (1974) 1044.
4 I. Haiduc, *Rev. Inorg. Chem.*, *3* (1981) 353.
5 J. R. Wasson, G. M. Wolterman and H. J. Stocklosa, *Topics Curr. Chem.*, *35* (1973) 65; *Chem. Abstr.*, *78* (1973) 118588m.
6 R. C. Mehrotra, G. Srivastava and B. P. S. Chauhan, *Coord. Chem. Rev.*, *55* (1984) 207.
7 G. Spengler and W. Weber, *Chem. Ber.*, *92* (1959) 2163; *Chem. Abstr.*, *54* (1960) 873e.
8 J. R. Knox and C. K. Prout, *Acta Crystallogr., Sect. B*, *25* (1969) 2281; *Chem. Abstr.*, *72* (1970) 26084s.
9 P. W. Schneider, D. C. Bravard, J. W. McDonald and W. E. Newton, *J. Am. Chem. Soc.*, *94* (1972) 8640.

10 W. E. Newton, J. L. Corbin, D. C. Bravard, J. E. Searles and J. W. McDonald, *Inorg. Chem.*, *13* (1974) 1100.

11 G. J.-J. Chen, J. W. McDonald and W. E. Newton, *Inorg. Nucl. Chem. Lett.*, *12* (1976) 697.

12 H. Gehrke Jr. and J. Veal, *Inorg. Chim. Acta, 3* (1969) 623.

13 B. P. Singh, G. Srivastava and R. C. Mehrotra, *J. Organomet. Chem.*, *171* (1979) 35.

14 H. P. S. Chauhan, C. P. Bhasin, G. Srivastava and R. C. Mehrotra, *Phosphorus Sulphur, 15* (1983) 99.

15 J. S. Yadav, R. K. Mehrotra and G. Srivastava, *Polyhedron, 6* (1987) 1687.

16 W. E. Newton and J. W. McDonald, *J. Less-Common Met.*, *51* (1977) 51.

17 J. Cason, W. N. Baxter and W. DeAcetis, *J. Org. Chem.*, *24* (1959) 247.

18 R. A. Y. Jones and A. R. Katritzky, *J. Chem. Soc.*, (1960) 4376.

19 C. Glidewell, *Inorg. Chim. Acta, 25* (1977) 159.

20 L. D. Quin, *The Heterocyclic Chemistry of Phosphorus*, Wiley Interscience, New York, 1981.

21 D. W. Meek and T. J. Mazance, *Acc. Chem. Res.*, *14(a)* (1981) 266; *Chem. Abstr.*, *95* (1981) 114209s.

22 A. B. Blake, F. A. Cotton and J. S. Wood, *J. Am. Chem. Soc.*, *86* (1964) 3024.

23 L. Ricard, J. Estienne, P. Karagiannidis, P. Toledano, A. Mitchell and R. Weiss, *J. Coord. Chem.*, *3* (1974) 277.