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Ambident Nucleophiles.
Part IV[a]. Reactions of Di-isopropylphosphorothioate and Di-Isopropylphosphoroselenoate with Metal Ions

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Derivatives of the ambident nucleophiles $(Me_2CHO)_2POX^-$ *(X = S, Se) have been prepared with the following: V(IV), Cr(III), Mn(II), Fe(III), Co(II), Co(III), Ni(II), Cu(II), Zn(II), Zr(IV), Pd(II), Ag(I), Cd(II), Hg(II), Sn(II), Sn(IV), Pb(II), P(III), As(III), Sb(III), Bi(III), Se(II), Te(II), Th(IV), and U(VI). Structural deductions are made on the basis of* ^{31}P *n.m.r. and electronic spectra. When X = S,* $[(Me_2CHO)_2POS]_2$*,* $[(Me_2CHO)_2POS]_2Hg$ *and* $[(Me_2CHO)_2POS]_2Se$ *are the thiol isomers, and* $[(Me_2CHO)_2POS]_3P$ *is the thione isomer:* $[(Me_2CHO)_2POS]_2Te$ *exists in two forms having thiol and bidentate ligands, while all other derivatives contain bidentate (bridging or chelating) ligands. When X = Se, derivatives of Hg(II), As(III), Sb(III0, Bi(III), Se(II), and Te(II) are selenol isomers: all others contain bidentate* $(Me_2CHO)_2POSe$ *groups.*

Introduction

In previous papers [1, 2], the reactions of the (1, 3) ambident nucleophiles di-isopropylphosphorothioate, $(Me_2CHO)_2POS^-$ and di-isopropylphosphoroselenoate, $(Me_2CHO)_2POSe^-$, with some molecular halides were described. This investigation has now been extended to the reactions of these anions with metal ions, and the results are described here, with deductions of molecular constitution made in a number of cases from ^{31}P nuclear magnetic resonance spectra (δ_P and $^1J(PSe)$), and from electronic spectra.

Results and Discussion

Three principal methods have been employed for the preparation of metal ion derivatives of $(Me_2CHO)_2POS^-$ and $(Me_2CHO)_2POSe^-$: in method A (*cf.* Table III), halides of Sn(IV), P(III), As(III), Sb(III) or Bi(III) were treated with the sodium salt $(Me_2CHO)_2POX^-Na^+$ (X = S or Se throughout this paper) in nitromethane solution, to yield products which are solid in the cases of Sn(IV) and Bi(III) and involatile liquids in the cases of P(III) As(III) and Sb(III). Halides or nitrates of Zn(II), Hg(II), Ag(I), Pb(II), Zr(IV) and Th(IV) when treated in aqueous solution with $(Me_2CHO)_2POX^-Na^+$ immediately give readily filtrable precipitates of $[(Me_2CHO)_2POX]_nM$ (method B). A number of metals are not precipitated from aqueous solution by these anions: these include V(IV) (as vanadyl VO^{+2}), Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Pd(II), Sn(II) and U(VI) (as uranyl UO_2^{+2}). However if the mixed solutions are evaporated to dryness, the complexes can be extracted from the solid residue with acetone (method C). All of these derivatives prepared by methods A–C are miscible with, or are moderately soluble in, organic solvents. Attempts to prepare $(Me_2CHO)_2POSe$ derivatives of Fe(III), Cr(III), V(IV), Zr(IV) or U(VI) were unsuccessful, rapid loss of selenium occurring in each case: the corresponding derivatives of Co(II) and Ni(II) lost selenium within *ca.* 10 days, but the $(Me_2CHO)_2POSe$ derivatives of the p-block elements were in general much more stable. No crystallisable homogeneous derivatives of Al(III), Tl(I) or La(III) could be obtained with either ligand. Oxidation of $[(Me_2CHO)_2POS]_2Co$ with hydrogen peroxide yielded $[(Me_2CHO)_2POS]_3Co$. The complexes $[(Me_2CHO)_2POX]_2M$ (M = Co, Ni) all yielded crystalline adducts $[(Me_2CHO)_2POX]_2Mpy_2$ with pyridine.

Husebye has demonstrated [3] that dialkylphosphorodithioate ions react with selenium(IV) and tellurium(IV) in acid solution to yield complexes of Se(II) (yellow–orange) and Te(II) (orange–red) respectively:

$$4\,(RO)_2PS_2^- + MO_2 + 4H^+ \rightarrow$$
$$[(RO)_2PS_2]_2M + [(RO)_2PS_2]_2 + 2H_2O$$

(M = Se or Te).

Similar reactions appear to occur when $(Me_2CHO)_2POX^-$ react with Se(IV) or Te(IV) in aqueous acid media.

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[a] Part III: ref. 2.

TABLE I. Phosphorus NMR Data.

Compound	δ_P(/p.p.m.)	Compound	δ_P(/p.p.m.)	$^1J(PSe)$(Hz)
$(Me_2CHO)_2POS^-Na^+$ [a]	+53.72	$(Me_2(CHO)_2POSe^-Na^+$ [b]	+48.08	754.6
$[(Me_2CHO)_2POS]_2$	+18.39	$[(Me_2CHO)_2POSe]_2$ [b]	+11.70	515.9
$[(Me_2CHO)_2POS]_2Zn$	+41.63	$[(Me_2CHO)_2POSe]_2Zn$	+30.90	640.0
$[(Me_2CHO)_2POS]_4Zr$	+52.21			
$[(Me_2CHO)_2POS]_2Pd$	+37.08			
$(Me_2CHO)_2POSAg$	+40.09	$(Me_2CHO)_2POSeAg$	+27.19	547.0
$[(Me_2CHO)_2POS]_2Cd$	+44.88	$[(Me_2CHO)_2POSe]_2Cd$	+31.15	616.8[h]
$[(Me_2CHO)_2POS]_2Hg$	+28.64	$[(Me_2CHO)_2POSe]_2Hg$	+16.94	475.8
$[(Me_2CHO)_2POS]_2Sn$	+37.67[c]			
$(Me_2CHO)_2POSSnPh_3$ [a]	+33.66	$(Me_2CHO)_2POSeSnPh_3$ [b]	+16.45	479.7
$[(Me_2CHO)_2POS]_2SnPh_2$	+34.97	$[(Me_2CHO)_2POSe]_2SnPh_2$[b]	+24.35	545.9
$[(Me_2CHO)_2POS]_3SnPh$	+37.03[d]	$[(Me_2CHO)_2POSe]_3SnPh$[b]	+33.09	n.o.
$[(Me_2CHO)_2POS]_2Pb$	+42.82	$[(Me_2CHO)_2POSe]_2Pb$	+25.96	618.9
$[(Me_2CHO)_2POS]_3P$	+58.47	$[(Me_2CHO)_2POSe]_3Pb$	+58.25	874.2
$[(Me_2CHO)_2POS]_3As$	+37.05	$[(Me_2CHO)_2POSe]_3As$[b]	+12.44	473.3
$[(Me_2CHO)_2POS]_3Sb$	+35.29	$[(Me_2CHO)_2POSe]_3Sb$	+16.71	479.7
$[(Me_2CHO)_2POS]_3Bi$	+35.24	$[(Me_2CHO)_2POSe]_3Bi$	+15.25	505.2
$[(Me_2CHO)_2POS]_2Se$	+18.30[e]	$[(Me_2CHO)_2POSe]_2Se$	+7.87	482.8[i]
$[(Me_2CHO)_2POS]_2Te$	+18.53[f]	$[(Me_2CHO)_2POSe]_2Te$	+15.15	538.0[j]
	+47.41[g]			
$[(Me_2CHO)_2POS]_4Th$	+53.98	$[(Me_2CHO)_2POSe]_4Th$	+48.36	805.0
$[(Me_2CHO)_2POS]_2UO_2$	+43.99			

[a] Ref. 1. [b] Ref. 2. [c] $^2J(PSn)$ 59.8 and 85.3 Hz. [d] $^2J(PSn)$ 64.3 and 87.1 Hz. [e] $^2J(PSe)$ 57.5 Hz. [f] $^2J(PTe)$ 50.7 Hz. [g] $^2J(PTe)$ 48.2 Hz. [h] $^2J(PCd)$ 36.5 Hz. [i] $^2J(PSe)$ 54.6 Hz. [j] $^2J(PTe)$ 61.1 Hz.

$$4\,(Me_2CHO)_2POX^- + M^{+4} \rightarrow$$

$$[(Me_2CHO)_2POX]_2M + [(Me_2CHO)_2POX]_2$$

The colours of the liquid products range from yellow $[(Me_2CHO)_2POS]_2Se$ to deep red $[(Me_2CHO)_2POSe]_2Te$, but all are unstable, losing selenium and/or tellurium very readily, even in the dark. The stability decreases $[(Me_2CHO)_2POS]_2Te$ > $[(Me_2CHO)_2POSe]_2Te$ > $[(Me_2CHO)_2POS]_2Se$ > $[(Me_2CHO)_2POSe]_2Se$. The products were too unstable for accurate microanalysis, but ^1H and ^{31}P nuclear magnetic resonance spectra were obtained: they are much less stable than the solid $[(RO)_2PS_2]_2M$ species. This reaction may be compared with the reactions of sulphur(II):

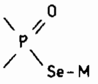
$$2(Me_2CHO)_2POX^- + SCl_2 \rightarrow$$

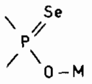
$$2Cl^- + [(Me_2CHO)_2POX]_2S \rightarrow X_xS_y$$

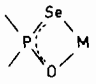
in which immediate deposition of Se_xS_y $(x + y = 8)$ occurs [2] when X = Se, and immediate deposition of S_8 when X = S: there was no evidence for the occurrence of isolable intermediates $[(Me_2CHO)_2POX]_2S$.

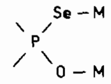
Information on the structures of a number of these derivatives can be obtained from ^{31}P nuclear magnetic resonance spectra and from electronic spectra.

Measurement of $^1J(PSe)$ in a number of phosphoroselenoates and phosphine selenides of known constitution has allowed [2] the generalisation to be postulated that phosphoroselenoates having $^1J(PSe) < 550$ Hz are of constitution (Ia).


(Ia)


(Ib)


(Ic)


(Id)

those having $^1J(PSe) > 850$ Hz are of constitution (Ib), while in those having 850 Hz $> {^1J(PSe)} >$ 550 Hz, the ligand is essentially anionic and probably bidentate: constitutions (Ic), with a chelating phosphoroselenoate, and (Id) with a bridging ligand, fulfil this requirement, but cannot be distinguished by this n.m.r. method. It was found [2] that infrared spectroscopy was not a reliable structural indicator for these compounds.

On the basis of this generalisation, constitutions may be deduced, from the observed values of $^1J(PSe)$, for most of the new $(Me_2CHO)_2POSe$ derivatives listed in Table I. Thus $[(Me_2CHO)_2POSe]_2Hg$, $[(Me_2CHO)_2POSe]_3Sb$, $[(Me_2CHO)_2POSe]_3Bi$, $[(Me_2CHO)_2POSe]_2Se$, and $[(Me_2CHO)_2POSe]_2Te$ all have

$^1J(PSe) < 550$ Hz and so are assigned the Se-bonded structure (Ia): the Sb(III) and Bi(III) derivatives thus resemble the As(III) analogue [2], but differ from the O-bonded $[(Me_2CHO)_2POSe]_3P$ [2]. The complexes of Zn(II), Cd(II), Pb(II) and Th(IV) all have 850 Hz > $^1J(PSe)$ > 550 Hz and so are assigned constitutions (Ic) or (Id). $(Me_2CHO)_2POSeAg$ has $^1J(PSe) = 547$ Hz, a value which does not allow a confident assignment of structure: however, it may be noted that the analogous $(C_3H_7)_2NCOSAg$ [4] and $(C_3H_7)_2NCS_2Ag$ [5] have been shown to be hexameric containing Ag_6 octahedra in which each silver atom is bonded to three ligand atoms (three sulphur in the dithiocarbamate, and two sulphur + one oxygen in the monothiocarbamate), suggesting that for $(Me_2CHO)_2POSeAg$, (Ic) or (Id) is more likely than (Ia).

A second generalisation, concerning ^{31}P chemical shifts, may also be made for phosphoroselenoates: if the Ag(I) species is excluded as ambiguous, then for all those species reported here and previously [2], those of constitution (Ia) have $\delta_P < +24$ p.p.m., those of constitution (Ib) have $\delta_P > +58$ p.p.m., while those having constitution (Ic) and (Id) fall in the range $+58$ p.p.m. $> \delta_P > +24$ p.p.m. This then suggests that $(Me_2CHO)_2POSeAg$, for which $\delta_P = +27.19$ p.p.m. is best assigned constitution (Ic) or (Id), of which (Id) is the more plausible, in view of the usual behaviour of the d^{10} Ag(I) ion, when two-coordinate, in adopting a linear configuration.

Chemical shift data for phosphorothioates are rather less abundant than for phosphoroselenoates: however, it appears [6, 7] that, in the absence of benzenoid groups, those with S-bonded structures analogous to (Ia) have $\delta_P < +30$ p.p.m., and that those with O-bonded structures analogous to (Ib) have $\delta_P > +58$ p.p.m. On this basis, S-bonded constitutions are assigned to $[(Me_2CHO)_2POS]_2$, $[(Me_2CHO)_2POS]_2Hg$ and $[(Me_2CHO)_2POS]_2Se$, and an O-bonded constitution to $[(Me_2CHO)_2POS]_3P$: $[(Me_2CHO)_2POS]_2Te$ appears to exist (in $CDCl_3$ solution) in two forms, (Ia) and (Ic) (relative abundance approximately 1:2), having δ_P of +18.53 and +47.41 p.p.m. respectively: constitutions of types (Ic) and (Id) are assigned to the remainder. This implies that the O-bonded constitution originally assigned [1] to $(Me_2CHO)_2POSSnMe_3$ and to $(Me_2CHO)_2POSSnPh_3$ should be revised to one having a bidentate and probably chelating $(Me_2CHO)_2POS$ ligand (Ic), although $(Me_2CHO)_2POSeSnPh_3$ is of type (Ia) [2]. The remaining species in Table I all display a structural correspondence between the analogous phosphorothioate and phosphoroselenoate with the exception of the derivatives of Te(II), and of As(III), Sb(III) and Bi(III) which are Se-bonded (Ia) in the latter case but appear to contain bidentate ligands in the former. Jorgensen [8] regarded the analogous $[(EtO)_2PS_2]_3Bi$ as containing an octahedral BiS_6 chromophore, and $[(Me_2CHO)_2PS_2]_3Bi$ was subsequently shown [9] to contain chelating ligands, the whole BiS_6 group being slightly trigonally distorted, having three Bi–S distances of 2.70 Å and three of 2.87 Å. The analogous xanthates $[EtOCS_2]_3As$ [10] and $[EtOCO_2]_3Sb$ [11] also contain bidentate chelating ligands but the differences between the two types of M–S distance are rather greater, being 0.68 and 0.48 Å in the arsenic and antimony derivatives respectively, compared with 0.17 Å in the bismuth compound. This difference in coordination between the $(Me_2CHO)_2POS$ derivatives, type (Ic), and the $(Me_2CHO)_2POSe$ derivatives, type (Ia), of As(III), Sb(III) and Bi(III) can probably be confirmed definitively only by X-ray analysis.

$[(Me_2CHO)_2PS_2]_2M$ (M = Zn, Cd) both form [12] dimeric units in which two of the ligands are of type (Ic) and two of type (Id), while $[(Me_2CHO)_2PS_2]_2Hg$ contains essentially two-coordinate mercury in the solid state, and is monomeric in benzene [13]. Structures of the same type for the $Me_2CHO)_2POX$ derivatives would be consistent with the n.m.r. data. $[(Me_2CHO)_2PS_2]_2Pb$ forms infinite chains in the solid state [14] in which the lead is six-coordinate, being of the form AB_6E *i.e.* pentagonal bipyramidal with an equatorial lone pair, while in solution in benzene a monomer–dimer equilibrium obtains: certainly the existence of bidentate ligands is consistent with the n.m.r. parameters for $[(Me_2CHO)_2POX]_2Pb$: $[(Me_2CHO)_2POS]_2Sn$ may be similar. Crystalline $[(MeO)_2PS_2]_2Te$ contains [15] approximately square planar TeS_4 groups in which two short (intramolecular) Te–S distances subtend an angle of 98.3° at tellurium with two longer (intermolecular) distances subtending an angle of 85.5°: $[(Me_2CHO)_2POX]_2M$ (M = Se, Te) may contain (in solution) XMX angles of *ca.* 90°, while the (Ic) form of $[(Me_2CHO)_2POS]_2Te$ may contain square-planar tellurium. In $[Et_2NCS_2]_4Th$, the S_8 coordination polyhedron is a distorted dodecahedron [16], and the O_4X_4 polyhedra in $[(Me_2CHO)_2POX]_4Th$ may be similar.

In Table II are summarised the electronic absorption data: in general both the qualitative colours, and the quantitative absorption frequencies resemble those of metal derivatives of dialkylphosphorodithioates [8], and this similarity has been used to make structural deductions for $(Me_2CHO)_2POX$ complexes of those metals whose phosphorodithioate derivatives have been structurally characterised. Violet $[(EtO)_2PS_2]_2Ni$ contains the square planar NiS_4 chromophore as shown both by electronic spectroscopy [8], and by X-ray analysis [17, 18]; and pale green $[(EtO)_2PS_2]_2Nipy_2$ contains the *trans*-octahedral NiS_4N_2 chromophore [8, 19]: consequently square planar and *trans*-octahedral configurations are assigned to purple $[(Me_2CHO)_2POS]_2Ni$ and turquoise $[(Me_2CHO)_2POS]_2Nipy_2$ respectively. Similarly the deep orange $[(Me_2CHO)_2POS]_2Pd$ is also assigned a square planar configura-

TABLE II. Visible and Ultra-Violet Absorption.

Compound	ν (/kK)	ϵ(/m^2 mol^{-1})
L = $(Me_2CHO)_2POS$		
LNa	44.3	0.32
L_2VO	41.8, 39.4, 16.7	1.2, 1.4, 0.11
L_3Cr	39.9, 21.8, 15.6, 14.7	1.9, 0.13, 0.11, 0.10
L_2Mn	43.5, 40.0, 36.8	0.14, 0.07, 0.05
L_3Fe	44.3, 28.6, 27.4	2.1, 0.17, 0.15
L_2Co	42.7, 37.7, 16.5	0.97, 1.2, 0.11
L_3Co	39.7, 12.7	3.7, 0.22
L_2Ni	43.9, 37.8, 22.2	0.6, 0.7, 0.01
L_2Cu	41.2, 35.7	3.5, 1.9
L_2Zn	45.7	0.78
L_4Zr	42.7	0.79
L_2Pd	43.7, 35.2, 32.6	4.7, 7.5, 8.0
LAg	42.4, 38.6	2.9, 2.7
L_2Cd	41.7	2.7
L_2Hg	46.7, 42.9	16.7, 12.7
L_2Sn	45.5	3.5
L_2Pb	43.7, 39.1, 34.1	8.6, 6.9, 2.7
L_3Bi	42.9, 37.7, 30.3	4.3, 4.1, 1.9
L_4Th	46.7, 36.5	3.6, 0.66
L_2UO_2	42.9, 37.7, 30.3	0.8, 0.74, 0.34
L = $(Me_2CHO)_2POSe$		
L_2Co	40.7, 36.4, 29.0, 16.7	2.0, 0.57, 0.20, 0.09
L_2Ni	41.5, 32.9, 18.2	2.5, 0.40, 0.12
L_2Cd	39.1	2.9
L_2Pb	42.9, 38.5, 31.7	9.7, 7.9, 4.0

tion with chelating ligands ($[(EtO)_2PS_2]_2Pd$ is orange [8]), consistent with its chemical shift, δ_P = +37.08 p.p.m. Blue $[(EtO)_2PS_2]_2Co$ contains [20] the tetrahedral CoS_4 chromophore while dark brown $[(EtO)_2PS_2]_3Co$ contains the octahedral chromophore CoS_6; hence blue $[(Me_2CHO)_2POS]_2Co$ is regarded as tetrahedral and green–black $[(Me_2CHO)_2POS]_3Co$ as approximately octahedral.

While the constitutions of a number of these $(Me_2CHO)_2POX$ derivatives can be securely deduced from the n.m.r. or optical properties, plausible structures for others can only be inferred or suggested from the structures of similar species known from X-ray analysis. Thus $[(EtO)_2PS_2]_3Cr$ exhibits [21] approximately octahedral coordination, so that $[(Me_2CHO)_2POS]_3Cr$ may reasonably be supposed to be nearly octahedral. $(Et_2NCS_2)_2Mn$ is square planar [22], so that $[(Me_2CHO)_2POS]_2Mn$ may be also: in $[(C_3H_7)_2NCS_2]_2$ Cu the square planar molecules are [23] weakly associated into dimers. Several tris(dithiocarbamate) derivatives of iron(III), $(R_2NCS_2)_3Fe$, have been structurally characterised: these adopt configurations between octahedral and trigonal prismatic and can be characterised by an angle of twist, θ, about the triad axis (for an octahedron θ = 60°, for a trigonal prism θ = 0°). The angle of twist is generally around 40°, thus: $(C_4H_8NCS_2)_3Fe$ [24], 40.4°; $(Et_2NCS_2)_3Fe$ [25], 37.6 at 297 K and 40.5° at 79 K; $(PhMeNCS_2)_3Fe$ [24], 38.6°. Consequently a non-octahedral configuration is expected in $[(Me_2CHO)_2POS]_3Fe$: whatever the angle of twist (other than θ = 0°) two enantiomeric pairs of isomers are expected.

Experimental

N.m.r. spectra were recorded ($CDCl_3$ solution) using Varian Associates instruments: EM-360, CFT-20, XL-100. Electronic spectra were recorded (Me_2CHOH solution) using a Perkin–Elmer model 402. Nitromethane was dried over flamed-out molecular sieve.

Preparation of Derivatives $[(Me_2CHO)_2POX]_nM$

Method A

Stoichiometric quantities of a molecular halide and the salt $(Me_2CHO)_2POX^-Na^+$ were mixed in nitromethane solution: the sodium halide precipitate which formed either at room temperature or on brief reflux was removed by filtration or centrifugation,

TABLE III. Preparative Methods and Microanalytical Data.

Compound	Colour	Method	Found (%)		Calculated (%)	
			C	H	C	H
L = $(Me_2CHO)_2POS$						
L_2VO	Blue	C	31.1	6.4	31.2	6.1
L_3Cr	Deep green	C	33.6	6.9	33.6	6.6
L_2Mn	Pale green	C	32.3	6.7	32.1	6.3
L_3Fe	Orange–red	C	33.3	5.9	33.4	6.5
L_2Co	Blue	C	31.7	6.5	31.8	6.2
L_3Co	Green–black	D	33.7	6.6	33.2	6.5
L_2Copy_2[a]	Pink	D	43.1	6.4	43.2	6.3
L_2Ni	Purple	C	30.0	6.6	31.8	6.2
L_2Nipy_2[b]	Turquoise	D	43.3	6.4	43.2	6.3
L_2Cu	Orange	C	31.7	5.9	31.5	6.2
L_2Zn	White	B	32.3	6.4	31.4	6.1
L_4Zr	White	B	31.7	6.3	32.8	6.4
L_2Pd	Deep Orange	C	28.8	6.6	28.8	5.6
LAg	White	B	23.7	4.9	23.6	4.6
L_2Cd	White	B	28.5	5.8	28.4	5.6
L_2Hg	White	B	24.1	4.9	24.2	4.7
L_2Sn	Pale yellow	C	28.7	5.8	28.1	5.5
L_2SnPh_2	White	A	44.6	5.9	43.2	5.7
L_3SnPh	White	A	37.1	5.8	36.6	6.0
L_2Pb	White	B	24.8	4.9	24.0	4.7
L_3P	Pale yellow	A	34.6	7.1	34.7	6.8
L_3As	Pale yellow	A	33.1	6.5	32.4	6.4
L_3Sb	Pale yellow	A	29.7	6.0	29.8	5.9
L_3Bi	Yellow	A	27.6	5.6	27.0	5.3
L_4Th	White	B	28.0	5.1	28.2	5.5
L_2UO_2	Orange	C	22.3	4.6	21.7	4.3
L = $(Me_2CHO)_2POSe$						
L_2Co	Blue	C	26.5	5.7	26.3	5.2
L_2Copy_2[c]	Orange–pink	D	38.1	5.7	37.5	5.4
L_2Ni	Orange–red	C	26.7	5.4	26.4	5.2
L_2Nipy_2[d]	Blue	D	37.1	5.1	37.5	5.4
L_2Zn	White	B	25.7	5.5	26.0	5.1
LAg	White	B	20.7	4.0	20.5	4.0
L_2Cd	White	B	23.7	5.1	24.0	4.7
L_2Hg	White	B	21.1	4.4	20.9	4.1
L_2Pb	White	B	20.2	4.3	20.7	4.1
L_3Sb	Yellow	A	26.7	5.6	25.3	5.0
L_3Bi	Yellow	A	22.9	4.7	23.0	4.5
L_4Th	White	B	24.4	4.3	23.9	4.7

[a] N found 4.6%, calculated 4.6%. [b] N found 4.8%, calculated 4.6%. [c] N found 4.3%, calculated 4.0%. [d] N found 4.4%, calculated 4.0%.

and evaporation of the solvent then yielded the product.

Method B

Stoichiometric quantities of the sodium salt and a metal salt (usually a nitrate or halide) were mixed in aqueous solution. The precipitate was filtered, washed and dried, and then recrystallised from carbon tetrachloride.

Method C

Stoichiometric quantities of the sodium salt and a metal salt were mixed in aqueous solution. The solution was evaporated to dryness and extracted with Analar acetone: the extract was filtered and evaporated, and the resulting product recrystallised from diethyl ether.

Method D

Miscellaneous methods, which are detailed below.

Preparation of $[(Me_2CHO)_2POS]_3Co$

$[(Me_2CHO)_2POS]_2Co$ (0.85 g, 1.87×10^{-3} mol) was dissolved in absolute ethanol (20 ml) to give an indigo solution. 1.0 ml of 6% hydrogen peroxide solution was added dropwise, and the solution turned brown. The solvent was evaporated and the dark oil remaining was extracted with diethyl ether: after filtration, evaporation yield the green–black product.

Preparation of $[(Me_2CHO)_2POX]_2Mpy_2$ *(M = Co, Ni)*

$[(Me_2CHO)_2POX]_2M$ was dissolved in the minimum volume of absolute ethanol, and an excess of pyridine added: slow evaporation yielded crystals of $[(Me_2CHO)_2POX]_2Mpy_2$.

Preparation of $[(Me_2CHO)_2POS]_2Se$ *and Related Species*

SeO_2 (0.3 g, 2.7×10^{-3} mol) was dissolved in 20 ml of ice-cold 3*M* hydrochloric acid: an ice-cold solution of $(Me_2CHO)_2POS^-Na^+$ (2.3 g, 10.4×10^{-3} mol) in 20 ml water was stirred in: the aqueous layer was decanted off, and the organic phase taken up in benzene, washed with water and dried: evaporation at low temperature and reduced pressure yielded yellow $[(Me_2CHO)_2POS]_2Se$. Similarly prepared were orange $[(Me_2CHO)_2POSe]_2Se$, red $[(Me_2CHO)_2POS]_2Te$ and deep-red $[(Me_2CHO)_2POSe]_2Te$: ^1H and ^{31}P n.m.r. spectra recorded immediately after preparation indicated the absence of proton- or phosphorus-containing impurities (Table III).

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