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Ionic cluster dithiophosphinates $[Mo_3S_4(R_2PS_2)_3py_3]^+[MI_3]^-$ ($M=Zn\cdot py$, $Cd\cdot py$, Hg)

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Abstract

Reactions of clusters $Mo_3S_4L_4$ (**2**) ($L=R_2P(S)S^-$; R = Et (**a**), Pr (**b**)) with MI_2 (M = Zn, Cd, Hg) in the presence of pyridine yielded ionic clusters $[Mo_3S_4L_3py_3]^+[MI_3py]^-$ (M = Zn (**9**), Cd (**10**); R = Et (**a**), Pr (**b**)) and $[Mo_3S_4L_3py_3]^+[HgI_3]^-$ (**11**) ($L=Pr_2P(S)S^-$), respectively. The cluster cations consist of a triangular array of Mo atoms which are bridged by three S atoms and capped by the fourth S atom. Each of the Mo atoms is chelated by one L and coordinated by one pyridine. **9a** crystallizes in the monoclinic space group $P2_1$ with $Z=2$ formula units in the unit cell of dimensions $a=1120.9(2)$, $b=1756.3(3)$, $c=1447.3(2)$ pm, $\beta=105.31(1)°$, $D_c=1.98$ mg/mm^3. The crystal structure was refined to $R=0.04$ using 5599 observed reflections and consists of $[Mo_3S_4(Et_2PS)_3py_3]^+[ZnI_3py]^-$. The coordination number of the Mo atoms is 8. The average distance Mo–Mo is 276.6(2) pm. The Zn atom is coordinated tetrahedrally with average distance Zn–I of 259.0(2) and Zn–N of 208.8(11) pm.

Key words: Molybdenum cluster metallates, Dithiophosphinate complexes, Crystal structures; ^{31}P NMR spectroscopy

Introduction

Previously we have reported convenient syntheses for complexes **1**–**8**: $[Mo_3S_7L_3]L$ (**1**), $Mo_3S_4L_4$ (**2**), $Mo_3MS_4L_6$ (**3**) (M = Mo, W, Sn), $Mo_2W_2S_4L_6$ (**4**), $Mo_2Co_2S_4L_2(CO)_2(CH_3CN)_2$ (**5**), $Mo_3XS_7L_3$ (**6**) (X = Cl, Br, I), $Mo_2S_4L_2$ (**7**), $Mo_3CuS_4L_4Ipy$ (**8**); $L=R_2P(S)S^-$, R = alkyl, py = pyridine.

Desulfurization of the ionic clusters **1** [1] with Ph_3P leads to **2** [2, 3]. Compounds **3**–**5** contain cubane-type cluster cores M_4S_4. We found that the 'incomplete' framework Mo_3S_4 in **2** can be systematically completed by appropriate reactions to give cubanes **3** [4–6] while cubanes **4** and **5** resulted from reactions of the dinuclear complexes **7** with $W(CO)_4L_2$ or $Co_2(CO)_8$ [7]. Even the halogen-containing clusters **6**, resulting from a reaction between **1** and alkylhalides, may be considered to belong to the class of cubane clusters according to Mo_3XS_4 as there are bonding interactions between S and X, though their nature is not clear as yet [8].

All these clusters have in common that they contain dialkyldithiophosphinato groups $R_2P(S)S^-$ which may be present as chelating or bridging ligands or as anions, e.g. in the ionic clusters **1**. According to these different functions they give rise to resonance signals in well separated regions of field strength in the ^{31}P NMR spectra. Resonances for chelating ligands will be found at 105–200 ppm and at 73–95 ppm for bridging ligands, while those for the anions appear at higher field strength (68–73 ppm).

Thus, ^{31}P NMR spectroscopy proved to be very helpful in the determination of the structure of cluster dithiophosphinates and revealed in combination with crystal structure analysis isomerism of many clusters, e.g. that of **4** according to Fig. 1 [7].

Recently we described the preparation of **8** from **2** and CuI in the presence of pyridine [9]. In **8** each Mo in the cubane-type core Mo_3CuS_4 is chelated by $R_2P(S)S^-$. Two of the Mo atoms are bridged by the fourth $R_2P(S)S^-$ while pyridine completes the coordination sphere of the third Mo and I is bonded to Cu.

In order to find out which other metals are capable of completing the framework of Mo_3S_4 in **2** with formation of cubanes Mo_3MS_4 we reacted MI_2 (M = Zn, Cd, Hg) with **2** in CH_2Cl_2. It soon turned out that the

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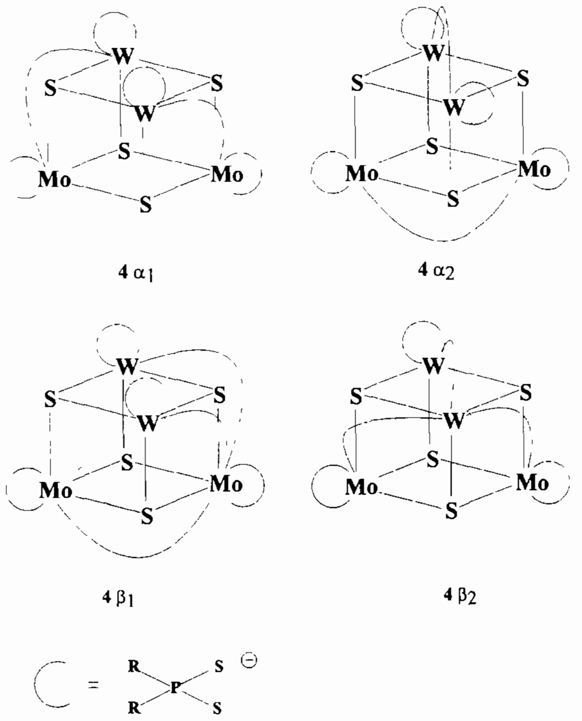


Fig. 1. Isomerism of $Mo_2W_2S_4(R_2PS_2)_6$ (**4**) (R = Et (**a**), Pr (**b**)) [7]

reactions only took place when some pyridine was present. However, in these cases no tetranuclear clusters of type **3** or **8** were obtained but ionic cluster compounds $[Mo_3S_4L_3py_3]^+[MI_3py]^-$ (M = Zn (**9**), Cd (**10**); L = $R_2P(S)S^-$, R = Et (**a**), Pr (**b**)) and $[Mo_3S_4L_3py_3]^+$-$[HgI_3]^-$ (**11**) (L = $Pr_2P(S)S^-$) containing metallate ions [10].

Like the starting complex **2** the complexes **9**–**11** belong to the group of trinuclear compounds with an Mo_3S_4 cluster core. This class has focussed the interests of other investigation groups and has been reviewed recently [11, 12].

There is only one example known of an ionic complex which is similar to **9**: $[Mo_3S_4([9]aneN_3)_3](ZnCl_4)$-$(ZnCl_3OH_2)_2 \cdot 3H_2O$ ($[9]aneN_3$ = 1,4,7-triazacyclononane) [13]. Analogous compounds containing Cd or Hg are unknown. However, the formation of a 'sandwich cubane-type cluster' containing the $Mo_3S_4HgS_4Mo_3$ core was recently described [14].

We now report the syntheses and properties of **9**–**11** as well as the results of an X-ray structure analysis in the case of **9a**.

Experimental

All syntheses were carried out under dinitrogen. Dinitrogen and solvents were purified and dried by standard methods. After preparation the substances could be safely handled in the presence of air. $^{31}P\{^1H\}$NMR, Bruker HX 90 R (CH_2Cl_2, 85% H_3PO_4 as external reference); ^1H NMR, Bruker AM 200 (CD_2Cl_2, TMS as internal reference); electronic spectra, Perkin-Elmer Lambda 5 (CH_2Cl_2), λ (nm), (ϵ (M^{-1} cm^{-1})); electric conductivities, Metrohm 518 conductimeter; IR, Perkin-Elmer 283, (KBr pellets); field desorption mass spectra, Varian MAT 311 A (activated tungsten emitters); molecular weights, Knauer osmometer (CH_2Br_2, 45 °C); magnetic measurements, Bruker magnet B-E 10 in combination with a microbalance Sartorius Type 4107 (Faraday-method), Pascal constants: [15]; melting points (uncorrected), Büchi 510 W; microanalyses (C, H, N), Institut fur Pharmazeutische Chemie der Universitat Dusseldorf; Mo, Zn and Cd, atomic absorption spectrometer Perkin-Elmer 3100; P, photometrically as molybdate-vanadate [16]; I, titration with silver nitrate and potentiometric indication [16]; S, gravimetrically as $BaSO_4$ [16].

The starting compounds **2** were prepared by published methods [2]. The products **9**–**11** were finally dried *in vacuo* at 50–60 °C.

Preparations

General procedure for the synthesis of ***9***

A dark red solution of 0.97 mmol of **2** in 10 ml of CH_2Cl_2 and 0.5 ml of pyridine was added to a solution of an excess (3.9 mmol) of ZnI_2 in 50 ml of CH_2Cl_2 and 5 ml of pyridine. The reaction mixture, the colour of which turned to dark green, was stirred at room temperature for 2 h and worked up as described below.

*Tris(diethyldithiophosphinato)-tri-μ-thio-μ₃-thio-tripyridine-triangulo-trimolybdenum(IV) triiodo(pyridine)zincate(II) (**9a**)*

When 100 ml of ether were added to the filtered reaction mixture a green solid separated from the solution. The precipitate was dissolved in CH_2Cl_2 and the dark green solution was allowed to stand at −35 °C overnight, filtered and layered with ether. After 12 h green crystals had been formed which were subsequently washed with hot isopropanol and boiling ether. The crystals were dissolved again in CH_2Cl_2 and the procedure described was repeated three times. Finally 0.62 g (42%) dark green crystals were obtained, decomp. 132 °C; δ_H (ppm) = 8.95 (broad), 7.74 (broad), 7.29 (broad), 2.30–1.50 (m), 1.40–0.20 (m); λ_{max} = 446 (sh) (6280), λ_{max} = 252 (62 500); molecular weight 832. *Anal.* Calc. for $C_{32}H_{50}I_3Mo_3N_4P_3S_{10}Zn$ (1638.3): C, 23.46; H, 3.08; N, 3.42; Mo, 17.57; I, 23.24; Zn, 3.99; S, 19.57. Found: C, 23.23; H, 3.12; N, 3.18; Mo, 18.13; I, 23.13; Zn, 4.06; S, 20.06%.

Tris(dipropyldithiophosphinato)-tri-μ-thio-μ_3-thio-tripyridine-triangulo-trimolybdenum(IV) triiodo(pyridine)zincate(II) (9b)

The solution was evaporated to dryness at room temperature. The dark green residue was dissolved in CH_2Cl_2 and worked up as described for **9a**. Further crystals of **9b** were obtained by cooling the filtrates and washing liquids to −35 °C. Yield 1.0 g (60%), green needles; decomp. 164 °C; δ_H (ppm) = 8.93 (broad), 7.72 (broad), 7.24 (broad), 2.35–0.50 (m); λ_{max} = 440 nm (sh) (4150), λ_{max} = 254 nm (49 000); molecular weight 857. *Anal.* Calc. for $C_{38}H_{62}I_3Mo_3N_4P_3S_{10}Zn$ (1722.4): C, 26.50; H, 3.63; N, 3.25; Mo, 16.71; I, 22.10; Zn, 3.80; S, 18.62. Found: C, 26.10; H, 3.47; N, 3.48; Mo, 16.25; I, 22.02; Zn, 3.53; S, 18.55%.

Synthesis of 10

Tris(diethyldithiophosphinato)-tri-μ-thio-μ_3-thio-tripyridine-triangulo-trimolybdenum(IV) triiodo(pyridine)cadmate(II) (10a)

A mixture of 0.97 mmol **2a** and 1.45 mmol of CdI_2 in 15 ml of CH_2Cl_2 and 2 ml of pyridine was stirred for 1 h at room temperature. After adding 50 ml of toluene to the dark green solution a black precipitate was formed. The solvent was decanted and the solid was washed three times with toluene and then with hot ether. The solid was dissolved in CH_2Cl_2 containing a few drops of pyridine and layered with ether. On standing overnight a precipitate had been formed that was filtered off and washed subsequently with methanol, isopropanol and ether. The solid was again dissolved in CH_2Cl_2 containing some drops of pyridine and filtered. After adding 100 ml of toluene and standing for 24 h at −35 °C bright green crystals were obtained. Yield 1.0 g (61%); decomp. 171 °C; δ_H (ppm) = 8.87 (broad), 7.67 (broad), 7.26 (broad), 2.32–0.30 (m); λ_{max} = 440 (sh) (7200), λ_{max} = 360 (sh) (9550), λ_{max} = 255 (78 400); molecular weight 830. *Anal.* Calc. for $C_{32}H_{50}CdI_3Mo_3N_4P_3S_{10}$ (1685.3): C, 22.81; H, 2.99; N, 2.32; Mo, 17.08; I, 22.59; S, 19.03; Cd, 6.67; P, 5.51. Found: C, 22.32; H, 2.84; N, 2.66; Mo, 17.09; I, 21.91; S, 19.55; Cd, 6.34; P, 5.40%.

Tris(dipropyldithiophosphinato)-tri-μ-thio-μ_3-thio-tripyridine-triangulo-trimolybdenum(IV) triiodo(pyridine)cadmate(II) (10b)

A mixture of 0.53 mmol of **2b**, 1.1 mmol of CdI_2, 10 ml of CH_2Cl_2 and 1 ml of pyridine was stirred at room temperature for 1 h. The dark green solution was layered with ether. After some time a dark green solid had separated that was washed repeatedly with boiling isopropanol and boiling ether. The solid was again dissolved in CH_2Cl_2, filtered and layered with ether. The procedure was repeated at least three times. Finally green needles were obtained. Yield 0.7 g (74%); decomp. 207 °C; δ_H (ppm) = 8.88 (broad), 7.72 (broad), 7.25 (broad), 2.20–0.50 (m); λ_{max} = 440 (sh) (5300), λ_{max} = 364 (sh) (8650), λ_{max} = 259 (57 100); molecular weight 900. *Anal.* Calc. for $C_{38}H_{62}CdI_3Mo_3N_4P_3S_{10}$ (1769.4): C, 25.79; H, 3.53; N, 3.17; Mo, 16.27; I, 21.52; P, 5.25; S, 18.12; Cd, 6.35. Found: C, 24.66; H, 3.50; N, 2.79; Mo, 16.32; I, 21.31; P, 5.11; S, 18.02; Cd, 6.37%.

Synthesis of 11

Tris(dipropyldithiophosphinato)-tri-μ-thio-μ_3-thio-tripyridine-triangulo-trimolybdenum(IV) triiodo-mercurate(II) (11)

0.79 mmol of **2b** was dissolved in 10 ml of CH_2Cl_2 and 0.1 ml of pyridine. A solution of 1.17 mmol of HgI_2 in 20 ml of CH_2Cl_2 and 0.5 ml of pyridine was added slowly with stirring at room temperature. After half an hour the solution was evaporated at 50 °C *in vacuo* to dryness. The residue was washed three times with 20 ml of boiling toluene and then subsequently with hot isopropanol and hot ether. The solid, together with crystals which had separated from the filtered washing liquids on standing overnight, was dissolved in CH_2Cl_2 and the solution layered with ether. In the course of a few hours dark green crystals had been formed. Yield 0.6 g (41%); decomp. 110 °C; δ_H (ppm) = 8.91 (broad), 7.73 (m), 7.25 (m), 2.50–0.60 (m); λ_{max} = 420 (sh) (6750), λ_{max} = 296 (sh) (27 400), λ_{max} = 252 (69 050), λ_{max} = 236 (68 550); molecular weight 902. *Anal.* Calc. for $C_{33}H_{57}HgI_3Mo_3N_3P_3S_{10}$ (1778.5): C, 22.29; H, 3.23; N, 2.36; Mo, 16.18; I, 21.41; S, 18.03. Found: C, 21.69; H, 3.29; N, 2.04; Mo, 15.89; I, 21.56; S, 17.73%.

Crystal structure determination of 9a

Suitable crystals of **9a** obtained by diffusion of ether into a solution of **9a** in CH_2Cl_2 were subjected to an X-ray crystal structure determination. A crystal of approximate size 0.4 × 0.4 × 0.6 mm showing several stairs has been used for the data collection and for the determination of the unit cell parameters of $a = 1120.9(2)$, $b = 1756.3(3)$, $c = 1447.3(2)$ pm and $\beta = 105.31(1)^\circ$ (36 reflections, $26 < 2\theta < 35^\circ$, Mo Kα, $\lambda = 71.073$ pm, four-circle diffractometer Siemens $P2_1$/P3, graphite monochromator). The monoclinic space group is $P2_1$ (No. 4 [17]) containing $Z = 2$ formula units, density $D_c = 1.98$ mg/mm^3. The intensities of 6529 reflections were measured at room temperature using a variable ω–2θ scan in the range of $4 < 2\theta < 54^\circ$ (Mo Kα). The indices ranged from 0 to $h = 14$, $k = 22$ and from $l = -18$ to $l = 17$. Of the 6226 independent reflections ($R_{int} = 0.06$) 5599 were classified observed ($F > 4\sigma_F$) and were used for the structure determination and refinement. No absorption correction was applied ($\mu = 3.3$ mm^{-1}). The intensities of three standard reflections did not show significant variations.

The structure was solved by direct methods [18] and refined (504 parameters) by least-squares to $R = 0.041$ (0.045), $R_w = 0.050$ (0 051) for the observed (all) reflections. All H atoms were added in constructed positions (C–H 96 pm), the weighting scheme was $1/w = \sigma_F^2 + 0.0004F^2$, scattering factors including corrections for anomalous dispersion as implemented in the program system [18]. Residual electron densities ranged from 0.96 to -1.50×10^{-6} e/pm^3. Three of the terminal C atoms of the ethyl groups (C14, C24, C34) showed enlarged anisotropic displacement parameters and point to a certain positional disorder. However, a refinement using split positions did not improve the results. The final parameters of the non-H atoms are listed in Table 1, see also 'Supplementary material'.

Results and discussion

Syntheses and properties

Reaction of $Mo_3S_4(R_2PS_2)_4$ (**2**), the schematic structure of which is shown in Fig. 2, with MI_2 (M = Zn, Cd) in CH_2Cl_2 containing some pyridine for better solubility of the metal salts gave the ionic cluster compounds **9** and **10** according to eqn. (1). With HgI_2 compound **11**, the anion of which is free from pyridine, was formed under similar conditions (eqn. (2)).

$$\underset{\mathbf{2}}{2Mo_3S_4(R_2PS_2)_4} + 3MI_2 + 8py \longrightarrow$$

$$M(R_2PS_2)_2 + 2[Mo_3S_4(R_2PS_2)_3py_3]^+[MI_3py]^- \qquad (1)$$

9: M = Zn, **10**: M = Cd
a: R = Et, **b**: R = Pr

$$\underset{\mathbf{2b}}{2Mo_3S_4(Pr_2PS_2)_4} + 3HgI_2 + 6py \longrightarrow Hg(Pr_2PS_2)_2$$

$$+ \underset{\mathbf{11}}{2[Mo_3S_4(Pr_2PS_2)_3py_3]^+[HgI_3]^-} \qquad (2)$$

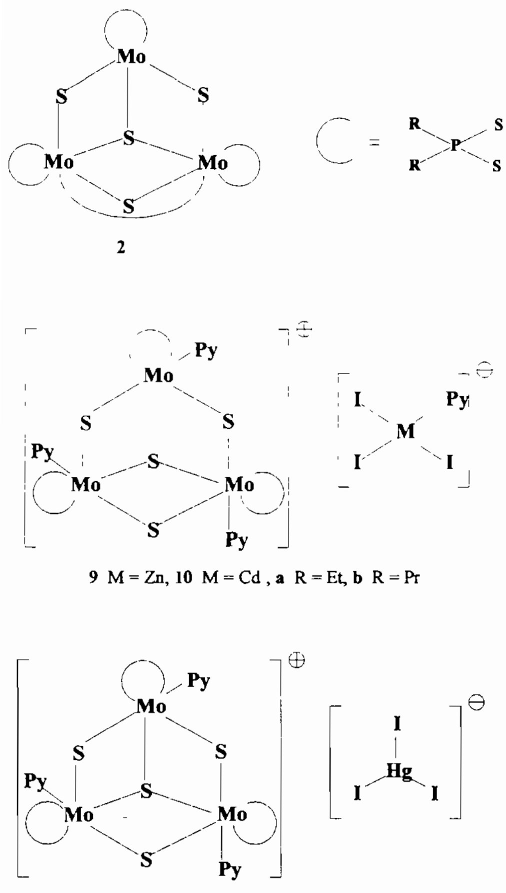
In both cases the corresponding neutral dithiophosphinates $M(R_2PS_2)_2$ [19] were observed as by-products which remained dissolved in the final mother liquors. They were identified by their $^{31}P\{^1H\}$ NMR [20] and EI mass spectra [21]. The diamagnetic compounds **9–11** form green to dark green crystals which are quite stable when exposed to the air and are soluble in CH_2Cl_2 and $CHCl_3$ giving deep green solutions. Figure 2 represents the schematic structures of **9–11** which are based on analytical, spectroscopic and conductivity data. In the case of **9a** the postulated structure has been confirmed by an X-ray structure analysis (see below).

TABLE 1 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients U_{eq} (pm $\times 10^{-1}$) of the non-H atoms of $[Mo_3S_4(Et_2PS_2)_3py_3]^+[ZnI_3py]^-$ (**9a**) with e s d.s in parentheses

	x	y	z	U_{eq} [a]
Zn	3682(1)	7500	3960(1)	61(1)
I(1)	1615(1)	7300(1)	2688(1)	65(1)
I(2)	5550(1)	7745(1)	3252(1)	88(1)
I(3)	4247(1)	6517(1)	5348(1)	90(1)
Mo(1)	829(1)	2822(1)	1976(1)	29(1)
Mo(2)	278(1)	1334(1)	1382(1)	30(1)
Mo(3)	1996(1)	2147(1)	723(1)	29(1)
S(1)	346(2)	1486(2)	−175(2)	35(1)
S(2)	1020(2)	3310(2)	556(2)	36(1)
S(3)	−1095(2)	2303(2)	1351(2)	37(1)
S(4)	2185(2)	1788(2)	2310(2)	31(1)
S(11)	2551(2)	3618(2)	3014(2)	40(1)
S(12)	−322(2)	4057(2)	2176(2)	43(1)
S(21)	−76(3)	716(2)	2882(2)	43(1)
S(22)	−1607(2)	479(2)	670(2)	43(1)
S(31)	2506(2)	2422(2)	−882(2)	42(1)
S(32)	3585(2)	1131(2)	701(2)	41(1)
P(1)	1364(2)	4511(2)	2744(2)	39(1)
P(2)	−1454(2)	109(2)	2011(2)	40(1)
P(3)	3432(2)	1433(2)	−673(2)	40(1)
N(1)	518(7)	2550(5)	3491(6)	39(3)
N(2)	1374(7)	192(5)	1366(6)	39(3)
N(3)	3839(7)	2859(5)	1340(6)	37(2)
N(4)	3503(9)	8538(6)	4614(7)	55(3)
C(11)	1761(11)	5156(7)	1899(8)	53(4)
C(12)	3079(12)	5412(8)	2160(11)	64(5)
C(13)	1392(12)	5077(8)	3788(9)	56(4)
C(14)	1098(19)	4625(12)	4588(10)	92(7)
C(15)	1463(11)	2300(7)	4238(8)	54(4)
C(16)	1297(13)	2076(8)	5079(9)	62(5)
C(17)	118(14)	2092(10)	5216(9)	74(6)
C(18)	−836(13)	2326(10)	4478(10)	71(5)
C(19)	−609(10)	2548(8)	3636(9)	55(4)
C(21)	−1119(12)	−890(7)	2096(9)	55(4)
C(22)	−1063(12)	−1261(9)	3024(11)	70(5)
C(23)	−2902(10)	244(10)	2345(11)	70(5)
C(24)	−3926(16)	−183(15)	1825(22)	165(16)
C(25)	1202(9)	−240(6)	594(8)	43(3)
C(26)	1910(11)	−865(7)	537(10)	56(4)
C(27)	2861(12)	−1073(7)	1347(9)	58(4)
C(28)	3035(12)	−652(7)	2154(10)	57(4)
C(29)	2285(10)	−19(6)	2159(8)	48(4)
C(31)	4926(10)	1476(8)	−908(9)	56(4)
C(32)	5782(11)	2078(10)	−335(10)	71(5)
C(33)	2589(11)	699(7)	−1466(8)	54(4)
C(34)	2288(18)	906(13)	−2503(10)	103(8)
C(35)	4747(9)	2603(7)	2084(8)	51(4)
C(36)	5840(11)	3002(9)	2439(11)	69(5)
C(37)	6076(14)	3639(11)	2000(14)	90(7)
C(38)	5142(13)	3897(9)	1209(13)	83(7)
C(39)	4050(12)	3498(7)	903(10)	62(5)
C(41)	2467(12)	8935(9)	4453(10)	70(5)
C(42)	2365(16)	9632(10)	4829(11)	82(6)
C(43)	3475(17)	9961(9)	5381(12)	81(7)
C(44)	4493(16)	9565(11)	5545(13)	94(7)
C(45)	4535(13)	8861(10)	5162(12)	85(6)

[a] U_{eq} is defined by $U_{eq} = \frac{1}{3}(U_{11}a^{*2}a^2 + 2U_{12}a^*b^*ab \cos \gamma + \quad)$

In accordance with the suggested structures the $^{31}P\{^1H\}$ NMR spectra show only one singlet. This is found in the range of chelating dialkyldithiophosphinato ligands (**9a**, **10a**: $\delta_P = 118.4$ ppm; **9b**, **10b**, **11**: $\delta_P = 113.4$ ppm).



2

9 M = Zn, 10 M = Cd, a R = Et, b R = Pr

11 (R = Pr)

Fig 2 Schematic structures of the starting complex **2** and the ionic clusters **9–11**

The ^1H NMR spectra show that the resonances of the protons of pyridine (7.24–8.95 ppm) are significantly shifted when compared with those of the free base [22]. The α protons are stronger shifted to low field (0.28–0.36 ppm) than the γ protons (0.10–0.17 ppm) whereas the β protons are shifted to higher field strength (0.09–0.14 ppm). This can be interpreted as a consequence of the coordination of the nitrogen base to the metal [23–25].

Moreover, shifts of characteristic IR absorption bands [(ν (cm^{-1})) ν (C=C- and C=N-): 1598(s), 1481(w); ν (C-H-in-plane deformation): 1249(w), 1220(s), 1150(w); ν (totally symmetric in-plane breathing): 1065(m), 1005(m); ν (out-of-plane ring deformations): 688(s), 623(w)] show that the pyridine molecules are coordinated as ligands [26, 27].

No signals for molecular ions could be detected in the FD mass spectra of **9–11**. In the case of **9b** a group of signals in the range $m/z = 950–972$ corresponds to the fragment $[Mo_3S_4(Pr_2PS_2)_3]^+$.

The intense bands in their electronic spectra most probably result from CT transitions.

In accordance with the ionic structure of **9–11** solutions of these compounds in CH_2Br_2 exhibit high electric conductivities which even exceed that of the 1:1 electrolyte $[Bu_4N]ClO_4$ (Table 2). The low molecular weights which have been found osmometrically in CH_2Br_2 also indicate a considerable dissociation of the compounds into the cluster cations and metallates.

Magnetic susceptibilities show compounds **9–11** to be diamagnetic. The experimental values are close to those calculated from Pascal constants [15] and indicate spin-pairing of the d electrons of Mo^{4+} by Mo–Mo bonds [(χ_M ($\times 10^{-6}$ cm^3 mol^{-1})) **9a**: $\chi_M = -955.0$, calc. $\chi_M = -973.9$; **9b**: $\chi_M = -975.1$, calc. $\chi_M = -1045.1$; **10a**: $\chi_M = -939.4$, calc. $\chi_M = -985.9$; **10b**: $\chi_M = -994.7$, calc. $\chi_M = -1057.1$; **11**: $\chi_M = -1070.0$, calc. $\chi_M = -1021.6$].

According to the analytical data **11** contains only three pyridines in contrast to **9** and **10**, in which four molecules of this ligand are coordinated. From this finding and from the $^{31}P\{^1H\}$ NMR spectra which show as mentioned above in all cases only one singlet, it can be concluded that the anion in **11** is free from pyridine and is probably $[HgI_3]^-$. Anions $[HgI_3]^-$ [28–32] and $[MI_3py]^-$ (M = Zn, Cd) [33, 34] have been reported in the literature whereas nothing is known about $[HgI_3py]^-$.

Crystal structure of $[Mo_3S_4(Et_2PS_2)_3py_3]^+[ZnI_3py]^-$ (9a)

Figure 3 shows the crystal structure of $[Mo_3S_4(Et_2PS_2)_3py_3]^+[ZnI_3py]^-$ (**9a**); main bond distances and bond angles are given in Table 3. The cation contains an Mo_3S_4 core which is close to symmetry C_{3v}. The Mo triangle is bridged by one μ_3-S and three μ-S atoms in the arrangement of an incomplete cubane missing one corner. This core has been reported earlier, e.g. for $Mo_3S_4(Et_2PS_2)_4$ (**2a**) [35]. The coordination number of the Mo atoms is increased to eight by the pyridine rings. Excluding the Mo–Mo distances the remaining six neighbours are arranged in a distorted octahedron with deviations from idealized geometry of up to 20°. The three pyridine rings are perpendicular to the Mo triangle the angles between the corresponding planes are 90.7, 91.2 and 91.0°, respectively. The pyridine

TABLE 2 Molar conductivities λ_M of **9–11** and $[Bu_4N]ClO_4$ (CH_2Br_2, 25 °C, 10^{-3} M)

Compound	λ_M (Ω^{-1} cm^2 mol^{-1})
$[Mo_3S_4(Et_2PS_2)_3py_3]^+[ZnI_3py]^-$ (**9a**)	8.58
$[Mo_3S_4(Pr_2PS_2)_3py_3]^+[ZnI_3py]^-$ (**9b**)	9.34
$[Mo_3S_4(Et_2PS_2)_3py_3]^+[CdI_3py]^-$ (**10a**)	12.27
$[Mo_3S_4(Pr_2PS_2)_3py_3]^+[CdI_3py]^-$ (**10b**)	12.46
$[Mo_3S_4(Pr_2PS_2)_3py_3]^+[HgI_3]^-$ (**11**)	12.80
$[Bu_4N]ClO_4$	3.41

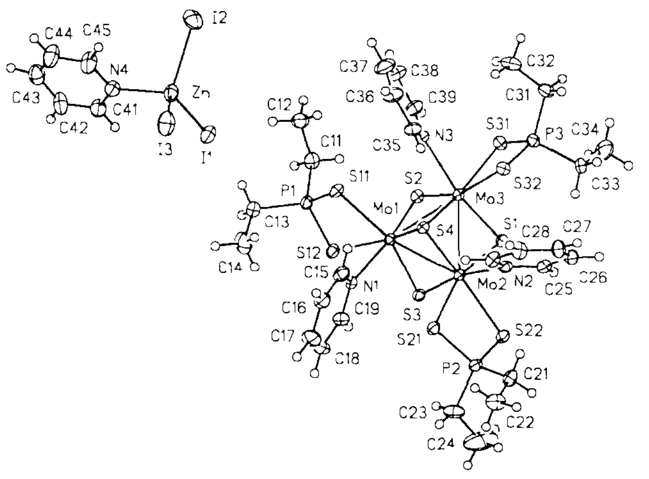


Fig. 3. Molecular structure of $[Mo_3S_4(Et_2PS_2)_3py_3]^+[ZnI_3py]^-$ (**9a**) with displacement ellipsoids of 25% probability The radius of the H atoms was set to 15 pm

TABLE 3 Main distances (pm) and bond angles (°) of **9a** with e.s.d s in parentheses

Zn–I1	257.5(2)	I1–Zn–I2	114.0(1)
Zn–I2	259.9(2)	I1–Zn–I3	116.9(1)
Zn–I3	259.7(2)	I2–Zn–I3	111.0(1)
Zn–N4	208.8(11)	N4–Zn–I1	105.5(2)
		N4–Zn–I2	102.6(3)
		N4–Zn–I3	105.3(3)
Mo1–Mo2	276.9(2)	Mo1–Mo2–Mo3	60.0(1)
Mo1–Mo3	276.8(2)	Mo2–Mo3–Mo1	60.1(1)
Mo2–Mo3	276.2(2)	Mo3–Mo1–Mo2	59.8(1)
Mo1–S4	233.5(3)	Mo1–S4–Mo2	72.6(1)
Mo2–S4	234.4(2)	Mo2–S4–Mo3	72.3(1)
Mo3–S4	233.7(3)	Mo3–S4–Mo1	72.7(1)
Mo1–S2	228.8(3)	Mo1–S3–Mo2	74.4(1)
Mo1–S3	229.6(2)	Mo1–S2–Mo3	74.2(1)
Mo2–S1	229.1(3)	Mo2–S1–Mo3	74.4(1)
Mo2–S3	228.6(3)		
Mo3–S1	227.8(3)		
Mo3–S2	230.0(3)		

rings reduce the maximal possible symmetry to C_3, however this symmetry is not fulfilled in the crystal structure. The Zn atom does not complete the Mo_3S_4 core to a distorted cubane as in similar W, Sn or Cu compounds [4, 5, 9] but is incorporated into the anion $[ZnI_3py]^-$ with average bond distances Zn–I of 259.0(2) and Zn–N4 of 208.8(11) pm. The coordination of the metal atom is distorted tetrahedrally with angles between 102.6(3) and 116.9(1)°. The geometry of the bidentate ligands is in the range known by earlier structure determinations of related compounds, e.g. $[Mo_3S_7(R_2PS_2)_3]^+[Et_2PS_2]^-$ [36].

Supplementary material

Lists of crystallographic data, anisotropic displacement parameters, H atom coordinates, bond distances, bond angles, and structure factors have been deposited as Supplementary Publication No. CSD 400400. Copies can be obtained through the Fachinformationszentrum Karlsruhe, Gesellschaft fur wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, by citation of the CSD No, the authors, and the reference.

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