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Cleavage of mixed tetrapnicogen trisulphide cage molecules by a cobalt(II)-ligand system. Crystal structure of the solid solution of [(tppme)Co(As_2S)]BF_4 and [(tppme)Co(PAsS)]BF_4

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Abstract

A solid solution of the mixed cage molecules PAs_3S_3 (50%) and $P_2As_2S_2$ (50%) reacts with $Co(BF_4)_2 \cdot 6H_2O$ in the presence of 1,1,1-tris(diphenylphosphinomethyl)ethane (tppme) yielding a crystalline material in good yield. The results of single crystal X-ray diffraction study and ^{31}P NMR and analytical data show that the product consists of a solid solution of the [(tppme)Co(As_2S)]BF_4 and [(tppme)Co(PAsS)]BF_4 compounds in ca. 2.3/1 ratio. The crystals are monoclinic, space group $P2_1/n$, with a 17.016(7), b 20.584(9), c 13.083(6) Å, β 104.86(6)°, $Z = 4$. The metal atom is in a six-coordinate environment formed by the tppme P atoms and the atoms of the heterocyclic As_2S or PAsS unit, which is η^3-bonded to the metal. The formation of these units from the solid solution of cage molecules provides insight into the process of cleavage of the latter molecules, assisted by the metal–ligand fragment.

Introduction

The tetrapnicogen trichalcogenides E_4X_3 (E = As, P; X = S, Se) react with various transition metal–ligand systems to give products that depend on the nature of the metal atom and its oxidation state. They may maintain their cage structure by coordination to the metal of one pnicogen atom [1], or undergo same modification of it, such as insertion into a basal bond [2] or replacement of a pnicogen atom by a metal moiety [3], ir even ultimately suffer drastic cleavage [4–7]. The last possibility is exemplified by the reactions of the E_4X_3 cage molecules with cobalt(II) tetrafluoroborate in the presence of the ligand tppme (tppme = 1,1,1-tris(diphenylphosphinomethyl)ethane) which afford the [(tppme)Co(E_2X)]BF_4 complexes [5–7] (E = As, P;

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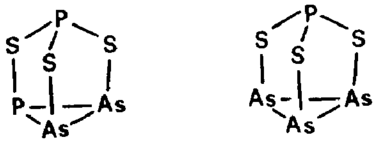
X = S, Se) containing the heterocyclic E_2X units η^3-bonded to the metal atom. The formation of such triatomic units suggests that all E_4X_3 molecules undergo similar cleavage processes promoted by the (tppme)Co^{II} system. With the aim of achieving some insight into the steps through which cleavage occurs we decided to investigate the reactivity of the (tppme)Co^{II} system toward "mixed" phosphorus-arsenic $P_xAs_{4-x}S_3$ ($x = 1$–3) sulfides with different P/As occupancies of the basal cage sites. Owing to difficulties in obtaining substantial samples of pure compounds corresponding to integral values of x in the above formula, the reaction of Co^{II} in the presence of tppme was finally carried out with a mixture of the compounds PAs_3S_3 and $P_2As_2S_3$ (Scheme 1).



Scheme 1

Experimental

All solvents were reagent grade, and were dried by distillation from suitable reagents. All reactions and manipulations were carried out under dry nitrogen. $^{31}P\{^1H\}$ NMR spectra were recorded (at 32.19 MHz) on a Varian CFT20 spectrometer; positive chemical shifts are downfield relative to 85% H_3PO_4. Mass spectra were recorded on a Kratos MS 80 mass spectrometer with an ionizing voltage of 70 eV. A direct insertion probe was employed, with source temperatures ranging from 100 to 180 °C. The ligand 1,1,1-tris(diphenylphosphinomethyl)ethane (tppme) was prepared by a published procedure [8]. P_4S_3 was purchased from Fluka (AG) and used after recrystallization from benzene; As_4S_3 was prepared by the method described in ref. 9.

PAs_3S_3 and $P_2As_2S_3$ mixed crystals

P_4S_3 (1.1 g, 5 mmol) and As_4S_3 (5.9 g, 15 mmol) were allowed to react in 1/3 ratio as previously described [10,11], to give mixed crystals containing PAs_3S_3 (ca. 60%), $P_2As_2S_2$ (ca. 30%), and smaller amounts of P_4S_3, P_3AsS_3, and As_4S_3. The solid (7 g) was added to warm benzene (100 ml) and stirred for 30 min. The pale yellow solution was separated from the remaining solid by filtration. Yellow crystals (3 g) containing PAs_3S_3 and $P_2As_2S_3$ in ca. 1/1 ratio were obtained by evaporation of half of the solvent. The composition of the mixed crystals before and after crystallization from benzene was determined by ^{31}P NMR and mass spectroscopy by reference to published data [10].

Reaction of triphos-metal system with $PAs_3S_3/P_2As_2S_3$ mixed crystals

A solution of the stoichiometric amount of the 1/1 $PAs_3S_3/P_2As_2S_3$ mixture in warm benzene (40 cm^3) was added to a solution of $Co(BF_4)_2 \cdot 6\ H_2O$ (1 mmol) in ethanol (5 cm^3) and tppme (1 mmol) in benzene (30 cm^3). The solution was refluxed overnight and ethanol (10 cm^3) was then added. Concentration of the solution then gave orange crystals (yield 40% based on cobalt) which were filtered off on a glass frit in a closed system, washed with ethanol/benzene (1/1) and then light petroleum (b.p. 40–70 °C), and dried. The product was recrystallized from dichloromethane/benzene. Analytical data for samples obtained from three different reactions showed constant ratios between the elements [Co and S (1/1); Co and P (1/3.3); Co and As (1/1.7)]. As indicated below, the product so obtained is considered on the basis of analytical and ^{31}P NMR spectral data, as well as the results of the X-ray diffraction study, to consist of a solid solution of the compounds $[(tppme)Co(As_2S)]BF_4 \cdot C_6H_6$ (70%) and $[(tppme)Co(PAsS)]BF_4 \cdot C_6H_6$ (30%). The presence of one benzene molecule of solvation per metal atom was indicated by the mass spectral and analytical data and, in part, by the X-ray study.

X-ray structure determination

The product obtained by reaction of the $(tppme)Co^{II}$ moiety with the $PAs_3S_3/P_2As_2S_3$ 1/1 mixture crystallizes as orange prisms, which are isomorphous with those of the $[(tppme)Co(E_2X)]BF_4 \cdot$ solvent ($E_2X = P_2S$ [5], P_2Se [5], As_2S [6], As_2Se [7], As_2Te [7]; solvent = C_6H_6 [5–7] or C_2H_5OH [7]) compounds previously investigated. Lattice constants were determined from 24 reflections with $24 < 2\theta < 38°$, and X-ray data collection was performed using a Philips PW 1100 automated diffractometer and graphite-monochromated Mo-K_α radiation (λ 0.71069 Å). The crystal used had dimensions 0.28 × 0.24 × 0.20 mm.

Crystal data: $C_{47}H_{45}As_{1.7}BCoF_4P_{3.3}S$, $M = 1017.3$, monoclinic, space group $P2_1/n$, a 17.016(7), b 20.584(9), c 13.083(6) Å, β 104.86(6)°, V 4429(3) Å^3, $Z = 4$, D_c 1.525 g cm^{-3}, μ (Mo-K_α) 18.6 cm^{-1}.

The intensities of all reflections with $k \geqslant 0$ and $l \geqslant 0$ were measured in the range $5 < 2\theta < 46°$ in the ω–2θ scan mode with a scan width of $(1.00 + 0.30 \tan \theta)°$ and scan speed of 6° min^{-1}. No crystal decay was observed. Of the total 6675 reflections recorded, 2124 having $I > 3\sigma(I)$ were used for structure determination after correction for Lorentz, polarization, and absorption effects. Transmission factors were in the range 0.66–0.74. The principal computer programs used in the crystallographic calculations are listed in ref. 12.

The structure of the present solid was refined by assuming as initial values for the atomic coordinates those found for the isomorphous E_2X derivatives previously investigated [5–7]. However, in view of the analytical and NMR data (see below), which were indicative of a solid solution, as well as of the orientational disorder found for the triatomic ring in previous "pure" E_2X derivatives, mixed As/P/S occupancies of the ring sites were expected. This implied that some constraints had to be imposed on the model for refinement. Several sets of least-squares cycles were performed in which alternative sets of fractional As/S form factors (S being used both for S and P) were assigned to the ring sites, with the criteria that: (1) the R value should be as low as possible; (2) the distribution of equivalent isotropic U values for the ring sites should be uniform and consistent with those found for the isomorphous compounds [5–7]; (3) there should be consistency with the peak heights from the triatomic ring region of ΔF maps. The set of occupancy factors listed in Table 1 was obtained by this procedure. Since only the As_2S and PAsS derivatives appear to be present in the solid solution according to the NMR data, such occupancy factors are consistent with 0.70 and 0.30 fractions of the As_2S and PAsS compounds, respectively, in the solid solution. Although the composition is

Table 1

Fractional positional parameters ($\times 10^4$) for the structure of 0.70 [(tppme)Co(As_2S)]$BF_4 \cdot C_6H_6$ + 0.30 [(tppme)Co(PAsS)]$BF_4 \cdot C_6H_6$[a–c]

Atom	*x*	*y*	*z*
Co	6361(1)	5437(1)	3063(2)
P(1)	6683(3)	4580(2)	2249(3)
P(2)	7456(3)	5995(2)	2972(3)
P(3)	7017(3)	5092(2)	4662(3)
E(1)	5478(2)	6245(2)	3295(3)
E(2)	5277(1)	5825(1)	1663(2)
E(3)	4973(1)	5228(1)	3015(2)
C(1)	8268(8)	4797(7)	3605(10)
C(2)	7686(7)	4254(7)	3017(10)
C(3)	8241(8)	5422(7)	2888(10)
C(4)	8097(8)	4955(7)	4683(10)
C(5)	9138(7)	4506(7)	3832(10)
C(11)	5998(4)	3880(4)	2021(5)
C(12)	5244(4)	3970(4)	1304(5)
C(13)	4682(4)	3463(4)	1092(5)
C(14)	4874(4)	2865(4)	1598(5)
C(15)	5629(4)	2775(4)	2315(5)
C(16)	6191(4)	3283(4)	2527(5)
C(21)	6831(4)	4656(4)	902(6)
C(22)	6711(4)	5245(4)	358(6)
C(23)	6884(4)	5297(4)	−625(6)
C(24)	7178(4)	4761(4)	−1063(6)
C(25)	7298(4)	4171(4)	−519(6)
C(26)	7124(4)	4119(4)	464(6)
C(31)	7376(4)	6563(4)	1868(6)
C(32)	6782(4)	7045(4)	1726(6)
C(33)	6710(4)	7502(4)	919(6)
C(34)	7233(4)	7476(4)	254(6)
C(35)	7827(4)	6994(4)	396(6)
C(36)	7898(4)	6537(4)	1203(6)
C(41)	7937(5)	6553(4)	4080(6)
C(42)	7424(5)	6913(4)	4542(6)
C(43)	7751(5)	7370(4)	5324(6)
C(44)	8590(5)	7465(4)	5645(6)
C(45)	9102(5)	7105(4)	5183(6)
C(46)	8776(5)	6648(4)	4401(6)
C(51)	7058(5)	5622(4)	5811(6)
C(52)	7778(5)	5799(4)	6541(6)
C(53)	7761(5)	6245(4)	7337(6)
C(54)	7024(5)	6514(4)	7405(6)
C(55)	6303(5)	6337(4)	6676(6)
C(56)	6320(5)	5891(4)	5879(6)
C(61)	6726(4)	4331(4)	5225(6)
C(62)	7207(4)	4122(4)	6200(6)
C(63)	7015(4)	3548(4)	6648(6)
C(64)	6342(4)	3183(4)	6123(6)
C(65)	5861(4)	3392(4)	5148(6)
C(66)	6053(4)	3966(4)	4699(6)
B	4400(5)	1098(4)	2259(6)
F(1)	5172(4)	1191(5)	2726(8)
F(2)	4232(7)	475(4)	2247(10)
F(3)	3952(5)	1412(7)	2776(9)
F(4)	4239(7)	1315(5)	1284(6)

Table 1 (continued)

Atom	x	y	z
C(71)	−401(12)	3035(12)	40(13)
C(72)	−652(11)	3213(12)	939(11)
C(73)	−253(12)	3253(12)	2013(11)
C(74)	−659(12)	4938(16)	55(16)
C(75)	69(12)	4914(14)	−259(16)
C(76)	648(15)	4445(13)	203(16)

[a] Estimated standard deviations on the least significant digits are in parentheses. [b] Sites labelled E(1)–E(3) have occupancies (in the order: As; S, or P): E(1) (0.25; 0.75), E(2) (0.70; 0.30), E(3) (0.75; 0.25). [c] Atoms Co–C(66) belong to the cation, B–F(4) to the anion, and C(71)–C(76) to the two fragments forming the model for the solvate benzene molecule.

only approximately known, we refer to these values for simplicity. We emphasize that only the nature of the components, not their precise ratio, is relevant to the discussion.

In the final refinement the Co, P, F atoms, and the ring sites were assigned anisotropic thermal parameters, and other atoms were refined isotropically. Phenyl groups of the tppme ligand were refined as rigid bodies with idealized geometry. Hydrogen atoms of the ligand were introduced in calculated positions (C–H 1.00 Å) with an overall temperature factor. A tetrahedral geometry was imposed on the BF_4^- anion, but the value of the B–F distance was refined (B–F 1.313(2) Å). The position of the benzene molecule of solvation could not be exactly identified because of the considerable disorder. On the basis of the ΔF maps, two C–C–C fragments were introduced in the model with an overall temperature factor and a single value for the C–C distance, which was refined (C–C 1.40(2) Å). The scattering factors for the neutral atoms and the anomalous dispersion corrections for Co and As were taken from ref. 13. The highest peaks (0.8 e Å^{-3}) in the final ΔF map could not be assigned any meaning. The least squares refinement, with the weighting scheme $w = [\sigma^2(F_0) + 0.0002 \mid F_0 \mid ^2]^{-1}$, led to $R = \Sigma(\| F_o \| - \| F_c \|)/\Sigma(\mid F_o \mid) = 0.067$ and $R' = [\Sigma w(\mid F_o \mid - \mid F_c \mid)^2/\Sigma w(F_c^2)]^{1/2} = 0.075$. The final positional atomic parameters are listed in Table 1.

Tables of thermal parameters, of bond lengths and angles, and hydrogen atom coordinates, and a list of observed and calculated structure amplitudes are available from the authors.

Results and discussion

The $P_xAs_{4-x}S_3 (x = 1–3)$ species have been obtained only in mixed crystals. In a recent study by Blachnik and Wickel [11] the compounds obtained from the reaction between P_4S_3 and As_4S_3, were separately detected and a plot of the concentration of the products vs. the P_4S_3/As_4S_3 ratio was presented. When the P_4S_3 and As_4S_3 reactants are mixed in a 1/3 stoichiometric ratio the equilibrium lies predominantly to the side of PAs_3S_3 and $P_2As_2S_3$ (Scheme 1) with significantly smaller amounts of P_3AsS_3 and unreacted P_4S_3 and As_4S_3. A careful recrystallization of the crude product from such a reaction removed the traces of P_4S_3, P_3AsS_3, and As_4S_3, and gave mixed crystals of PAs_3S_3 and $P_2As_2S_3$ in ca. 1/1 ratio. Such mixed crystals react with cobalt(II) tetrafluoroborate in the presence of tppme to yield an orange-red

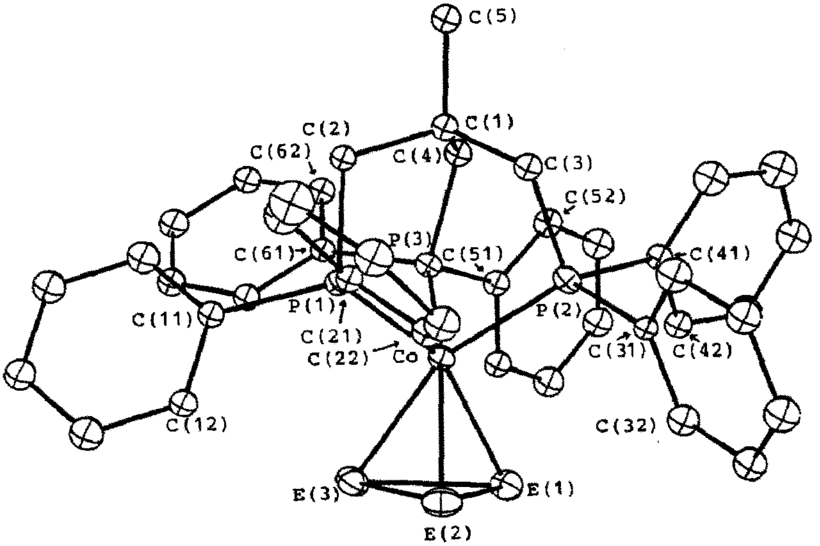
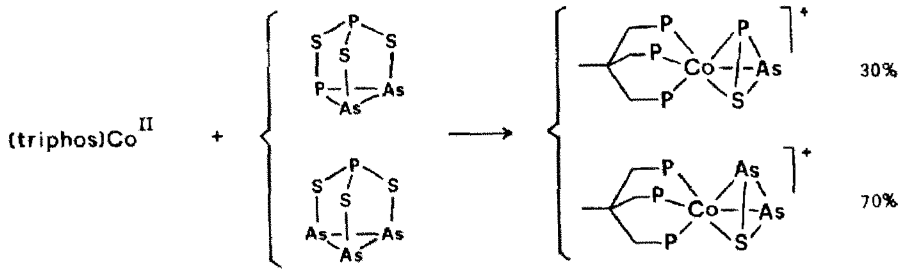


Fig. 1. Perspective view of the cation in the structure of 0.70 [(tppme)Co(As$_2$S)]BF$_4$·C$_6$H$_6$ + 0.30 [(tppme)Co(PAsS)]BF$_4$·C$_6$H$_6$, with 20% probability ellipsoids. Atomic sites of the E$_3$ ring have fractional occupancies as follows: E(1) (0.25 As, 0.75 S or P), E(2) (0.70 As, 0.30 S or P), E(3) (0.75 As, 0.25 S or P).

crystalline product which is air stable in the solid state. It dissolves in methylene chloride, tetrahydrofuran, and acetone, but the solutions slowly decompose in the air. The product consists of a solid solution of the compounds [(tppme)Co(As$_2$S)] BF$_4$ · C$_6$H$_6$ (70%) and [(tppme)Co(PAsS)]BF$_4$ · C$_6$H$_6$ (30%) (Scheme 2), as indicated



Scheme 2

mainly by the results of the X-ray diffraction study and by the NMR data. A view of the structure of the cation is shown in Fig. 1. Although detailed comparisons between the present structure, which is averaged over those of the two species forming the solid solution, and the structures of the individual As$_2$S [6] and P$_2$Se [5] derivatives (the latter being regarded as a reasonable model for the unknown PAsS one) are not possible, it appears from the selected values of bond distances listed in Table 2 that the Co–P(tppme) distances in the structure in this study are much the same as those found in the other two compounds, whereas distances involving the Co atom and the ring sites are generally intermediate between those in the other two compounds, but closer to the As$_2$S values. We note that this represents the first isolation of a complex with the cyclic thiaphospharsirene unit, containing three different atoms, which acts as a ligand on a transition metal; with the Co atom it forms a pseudotetrahedral arrangement of four different atoms.

Table 2

Selected bond lengths (Å) in the structure of 0.70 $[(\text{tppme})\text{Co}(\text{As}_2\text{S})]\text{BF}_4 \cdot \text{C}_6\text{H}_6$ + 0.30 $[(\text{tppme})\text{Co}(\text{PAsS})]\text{BF}_4 \cdot \text{C}_6\text{H}_6$ (**1**) compared with the corresponding distances in the structures of $[(\text{tppme})\text{Co}(\text{As}_2\text{S})]\text{BF}_4 \cdot \text{C}_6\text{H}_6$ (**2**) and $[(\text{tppme})\text{Co}(\text{P}_2\text{Se})]\text{BF}_4 \cdot \text{C}_6\text{H}_6$ (**3**)

	1	**2**	**3**
Co–P(1)	2.200(5)	2.193(4)	2.238(6)
Co–P(2)	2.218(5)	2.223(4)	2.195(6)
Co–P(3)	2.220(5)	2.227(4)	2.218(6)
Co–E(1)	2.313(4)	2.325(2)	2.272(6)
Co–E(2)	2.380(3)	2.389(2)	2.327(6)
Co–E(3)	2.386(3)	2.393(3)	2.403(4)
E(1)–E(2)	2.246(4)	2.264(2)	2.144(8)
E(1)–E(3)	2.256(4)	2.278(3)	2.228(6)
E(2)–E(3)	2.318(3)	2.339(3)	2.247(6)

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of our product in CD_2Cl_2 at room temperature exhibits two broad bands centred at 33.40 and −106.40 ppm respectively, in a 10/1 integration ratio. Both signals, which are affected by the cobalt quadrupole moment, become sharper on cooling but are not resolved into their fine structures even at −80 ° C. The shift of the larger signal essentially matches those for the P(tppme) atoms of the $[(\text{tppme})\text{Co}(\text{E}_2\text{X})]\text{BF}_4$ complexes (E = As, P; X = S, Se), which are practically independent of the nature of the atoms in the E_2X ring [5,6]. The smaller signal may be assigned by assuming that the free P_4S_3 molecule and the "mixed" P_3AsS_3 and $\text{P}_2\text{As}_2\text{S}_3$ ones exhibit a high field resonance for the basal phosphorus atoms. Such shift (−121 ppm for P_4S_3, −103 ppm for P_3AsS_3, and −90 ppm for $\text{P}_2\text{As}_2\text{S}_3$ [14]), moves downfield as the number of heteroatoms in the basal triatomic ring increases. A similar trend is found on going from the P_3 triatomic unit in the compound $[(\text{tppme})\text{Co}(\text{P}_3)]$ (−276 ppm [4]) to the P_2S heterocyclic unit in $[(\text{tppme})\text{Co}(\text{P}_2\text{S})]\text{BF}_4$ (−211 ppm [5]). The signal at −106.40 ppm in the present spectrum, which is in the low field region for unsubstituted P atoms in three-membered rings, suggests that only one P atom can now be present in a ring of that type. In the light of the analytical and structural data, this also suggests that the present material is a solid solution of the $[(\text{tppme})\text{Co}(\text{PAsS})]\text{BF}_4$ and $[(\text{tppme})\text{Co}(\text{As}_2\text{S})]\text{BF}_4$ derivatives. The relative intensities of the tppme and PAsS signals are consistent with the presence of ca. 23% of $[(\text{tppme})\text{Co}(\text{PAsS})]\text{BF}_4$ in the mixed crystals.

Both "mixed" $\text{P}_2\text{As}_2\text{S}_3$ and PAs_3S_3 cage molecules, Scheme 1, which are the sources of the cyclic units formed in our product, have a phosphorus atom in the apical position. However, the former has one P and two As atoms in the base whereas the latter has three As atoms. On the assumption that cleavage of the cage, under the influence of the (tppme)Co system follows a definite path, the possibility that the apical atom enters the final E_2X fragment can be ruled out, since the As_2S unit could not be formed in this way. This view is consisted with the results of previous work, showing that disruption of the cage by the (tppme)Co system starts at the base sites [3]. Moreover, if the simplifying, but apparently reasonable, assumption is made that either atom pair, P–As or As–As, has essentially the same probability of being extruded from the base of either reacting cage molecule during the formation of the PAsS or As_2S ring, then such rings, in the above order, would be expected to form from the present 1/1 mixture of $\text{P}_2\text{As}_2\text{S}_3$ and PAs_3S_3 in a 1/2 ratio. It is gratifying that this is rather close to the 1/2.3 ratio found for the amounts of components in the final solid solution.

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