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Synthesis and Structural Study of a Cobalt Complex with the Diarsenic–Sulfur Cyclic Unit as a Trihapto Ligand

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The reaction of $Co(BF_4)_2 \cdot 6H_2O$ *with tetra-arsenic trisulfide in the presence of triphos (triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane), yields the compound* $[(triphos)Co(As_2S)]BF_4 \cdot C_6H_6$ *in which the diarsenic-sulfur cyclic unit acts as a trihapto ligand. The structure of the compound has been determined by single-crystal X-ray diffraction methods. The compound crystallizes in the monoclinic* $P2_1/n$ *space group with* $Z = 4$ *and unit cell dimensions:* $a = 16.987(7)$, $b = 20.608(7)$, $c = 13.098(5)$ Å, $\beta = 104.83(5)°$. *The metal atom is in a distorted six-coordinate environment formed by the triphos P atoms and by the atoms of the heterocyclic* As_2S *unit.*

Introduction

The reactivity of the phosphorus chalcogenide P_4X_3 (X = S, Se) cage molecules toward various metal–ligand systems has been recently investigated [1–6]. On reaction with the $(np_3)M$ (M = Ni, Pd) complexes formed by the tripod ligand tris(2-diphenylphosphinoethyl)amine, np_3, the P_4X_3 intact molecules are η^1-coordinated to the d^{10} metal site [1, 2]. In the reaction with the cycloocta-1,5-diene complex $[(cod)RhCl]_2$ in presence of the ligand 1,1,1-tris(diphenylphosphinomethyl)ethane, triphos, cleavage of the P_4X_3 molecules occurs with replacement of a basal P atom by the (triphos)Rh moiety [3]. More substantial cleavage of the P_4X_3 molecules occurs in the reactions with Co(II) or Ni(II) tetrafluoroborate in the presence of triphos, which yield the P_2X [4, 5] or P_3 [6] cyclic units η^3-coordinated to the metal atom.

We report here that the tetra-arsenic trisulfide (As_4S_3) molecule, having a similar structure [7, 8] to those of the above phosphorus chalcogenides [2, 9, 10], reacts with $Co(BF_4)_2 \cdot 6H_2O$ in the presence of triphos yielding the $[(triphos)Co(As_2S)]BF_4 \cdot C_6H_6$ compound which contains the unprecedented As_2S cyclic unit trihapto-bonded to the metal atom, as shown by X-ray diffraction.

Experimental

All solvents were reagent grade and were dried by distillation from suitable agents. All reactions and manipulations were carried out under dry nitrogen. Tetra-arsenic trisulfide [11] and triphos [12] were prepared according to published procedures.

Physical Measurements

Electronic spectra, conductivity and magnetic susceptibilities were measured by procedures already described [13]. ^{31}P n.m.r. spectra were collected on a Varian CFT 20 spectrometer, at 32.19 MHz. Phosphorus-31 positive chemical shifts were down-field, relative to H_3PO_4 at 0.0 ppm. Changes in chemical shifts on coordination are reported in ppm relative to the corresponding phosphorus in the free ligand.

Synthesis of the Complex $[(triphos)Co(As_2S)]BF_4 \cdot C_6H_6$

Finely powdered tetra-arsenic trisulfide (1 mmol) was added to a solution of $Co(BF_4)_2 \cdot 6H_2O$ (1 mmol) in ethanol (5 ml) and triphos (1 mmol) in benzene (50 ml). The resulting mixture was refluxed for two days under magnetic stirring. Ethanol (30 ml) was added and the resulting solid material was filtered, washed with benzene, dried, and extracted with methylene chloride (30 ml). Red-orange crystals of the compound were obtained by addition of ethanol (30 ml) to the methylene chloride solution and by slow evaporation of the resulting solution. The compound was collected on a sintered-glass frit in a closed system, washed with ethanol/benzene 1:1 and petroleum ether in turn, before being dried. The compound was crystallized from dichloromethane and benzene (Yield 60%). Calcd. for $C_{47}H_{45}As_2BCoF_4P_3S$: C, 54.8%; H, 4.4%; As, 14.5%;

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TABLE I. Positional Parameters (×10^4) and Anisotropic Temperature Factors (×10^3) for [(triphos)Co(As_2S)] $BF_4 \cdot C_6H_6$.[a,b]

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	6363(1)	5435(1)	3061(1)	34(1)	35(1)	29(1)	−1(1)	8(1)	−1(1)
P(1)	6682(2)	4581(2)	2251(3)	39(2)	34(2)	29(2)	2(2)	6(2)	2(2)
P(2)	7462(2)	5995(2)	2972(3)	40(2)	37(2)	27(2)	−4(1)	9(2)	0(2)
P(3)	7021(2)	5088(2)	4662(3)	39(2)	40(2)	29(2)	−4(2)	8(1)	1(2)
As(1)	5278(1)	5829(1)	1655(1)	51(1)	65(1)	40(2)	13(1)	6(1)	5(1)
As(2)	4969(1)	5229(1)	3018(1)	41(1)	54(1)	67(1)	−5(1)	14(1)	8(1)
S	5483(2)	6253(1)	3297(2)	52(1)	48(1)	55(2)	4(1)	19(1)	−7(1)
F(1)	5183(6)	1193(5)	2804(10)	67(3)	132(4)	199(4)	−22(4)	−13(4)	−29(4)
F(2)	4233(8)	487(7)	2268(11)	166(4)	130(4)	204(4)	−61(4)	−73(4)	80(4)
F(3)	3962(8)	1392(8)	2733(11)	132(4)	256(4)	190(4)	14(4)	48(4)	−73(4)
F(4)	4177(8)	1341(6)	1276(10)	200(4)	131(4)	145(4)	−77(4)	10(4)	−13(4)

[a]Estimated standard deviations on the least significant digits are in parentheses. The form of the thermal ellipsoid is $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^* + \ldots)]$. [b]The As(1)–S sites have been assigned the following occupancy factors: As(1) (0.15 S, 0.85 As), As(2) (0.15 S, 0.85 As), S (0.70 S, 0.30 As).

Co, 5.7%; P, 9.0%; S, 3.1%. Found: C, 54.7%; H, 4.5%; As, 14.3%; Co, 5.6%; P, 9.0%; S, 3.0%. The molar conductance of the compound in *ca.* 10^{-3} *M* nitroethane solution at 20 °C is 87 Ω^{-1} mol^{-1} cm^2.

Crystal and Intensity Data

The crystal of [(triphos)Co(As_2S)] $BF_4 \cdot C_6H_6$ used for crystal data and intensity data collection was a prism with dimensions 0.25 × 0.30 × 0.40 mm. A Philips PW 1100 automated diffractometer and graphite monochromated Mo K_α radiation were used for all operations. Lattice constants were determined from refinement of the setting angles of 24 reflections, measured at 20 °C, having $13° < \theta < 19°$.

$C_{41}H_{39}As_2BCoF_4P_3S \cdot C_6H_6$, M = 1030.45, monoclinic, a = 16.987(7), b = 20.608(7), c = 13.098(5) Å, β = 104.83(5)°, V = 4432.4 Å^3, Z = 4, D_c = 1.544 g cm^{-3}, λ(Mo K_α) = 0.71069 Å, μ(Mo K_α) = 20.6 cm^{-1}, space group $P2_1/n$.

Intensities of two forms (±h, ±k, +l; 13550 reflections) were measured in the interval $5° < 2\theta < 48°$ by the $\theta-2\theta$ scan technique, with a symmetric scan range of $(1.10 + 0.30 \tan\theta)°$ and a scan speed of 6.0°/min in 2θ. Stationary background countings were taken at each end of the scan for a time equal to half the scan time. The intensities of three standard reflections monitored every 120 min. showed only small oscillations (<1%) about their mean values. Intensity data were merged to a unique set after correction for absorption (transmission coefficients ranging 0.53–0.64) and were subsequently corrected for Lorentz-polarization effects. A total of 3170 independent reflections having $I > 3\sigma(I)$ were used in the solution and refinement of the structure. The principal computer program used in the crystallographic calculations is listed in Ref. [14].

Solution and Refinement of the Structure

The compound is isomorphous with the [(triphos)-Co(P_2X)] $BF_4 \cdot C_6H_6$ (X = S, Se) compounds previously investigated [4, 5]. Therefore coordinates of non-hydrogen atoms from the structures of the latter compounds provided the first model for the As_2S derivative. The triatomic As_2S ring was found to be affected by orientational disorder about the pseudo-threefold axis of the cation, as already found for the P_2X units in the structures of the isomorphous compounds [4, 5]. The occupancies of sites in the As_2S ring were estimated by examination of the residual electron density in ΔF maps calculated without contributions from the atoms of such ring, as well as from the results of least squares refinements in which either the occupancy factors or the temperature factors of the atomic sites of the ring were refined.

The R factor was quite sensitive to variations in the As/S occupancies of those sites: it was lowest in correspondence of the narrow distribution of population parameters which led to comparable values of the equivalent isotropic temperature factors for the three sites. The final values of population parameters were extracted from this range. Anisotropic temperature factors were assigned to the Co, P and F atoms and to the As/S sites, whereas C and B atoms were refined isotropically. The benzene solvate molecule was refined as a rigid group with idealized geometry (C–C = 1.395 Å). Hydrogen atoms were introduced in calculated positions (C–H = 1.00 Å) with overall isotropic temperature factors which were refined separately for hydrogen atoms in the cation or in the benzene molecule (respective final values: 0.085 and

TABLE II. Positional Parameters ($\times 10^4$) and Isotropic Temperature Factors ($\times 10^3$) for [(triphos)Co(As$_2$S)]BF$_4$·C$_6$H$_6$.[a]

Atom	x/a	y/b	z/c	U (Å^2)
C(1)	8277(7)	4788(6)	3592(9)	40(3)
C(2)	7679(7)	4266(6)	3021(9)	41(3)
C(3)	8261(7)	5403(6)	2915(9)	39(3)
C(4)	8096(7)	4955(6)	4677(9)	38(3)
C(5)	9119(6)	4486(6)	3803(10)	48(3)
C(11)	5985(6)	3892(5)	2018(8)	30(3)
C(12)	5244(6)	3972(6)	1317(9)	41(3)
C(13)	4690(7)	3469(6)	1090(10)	49(3)
C(14)	4852(7)	2871(6)	1592(9)	52(3)
C(15)	5603(7)	2784(6)	2303(10)	52(3)
C(16)	6183(7)	3294(6)	2505(9)	50(3)
C(21)	6843(6)	4651(6)	926(9)	34(3)
C(22)	6738(7)	5228(6)	368(9)	44(3)
C(23)	6886(8)	5288(7)	−632(9)	49(3)
C(24)	7182(8)	4760(7)	−1048(12)	60(3)
C(25)	7292(9)	4154(8)	−531(11)	72(3)
C(26)	7111(8)	4118(7)	470(11)	58(3)
C(31)	7387(7)	6568(6)	1873(9)	32(3)
C(32)	6821(8)	7042(6)	1716(9)	48(3)
C(33)	6736(7)	7509(6)	905(9)	48(3)
C(34)	7255(8)	7458(7)	256(9)	54(3)
C(35)	7843(8)	6998(7)	396(10)	47(3)
C(36)	7911(8)	6547(6)	1214(9)	46(3)
C(41)	7925(6)	6548(6)	4073(10)	41(3)
C(42)	7434(7)	6916(6)	4517(10)	50(3)
C(43)	7769(9)	7367(6)	5332(11)	65(3)
C(44)	8622(9)	7444(7)	5669(11)	67(3)
C(45)	9105(9)	7065(8)	5192(12)	82(3)
C(46)	8774(9)	6636(7)	4395(11)	59(3)
C(51)	7055(7)	5625(6)	5767(9)	39(3)
C(52)	7783(7)	5779(6)	6538(9)	52(3)
C(53)	7766(9)	6228(7)	7351(11)	61(3)
C(54)	7050(8)	6499(7)	7419(11)	61(3)
C(55)	6315(8)	6326(7)	6693(10)	56(3)
C(56)	6348(7)	5882(6)	5888(9)	46(3)
C(61)	6729(7)	4328(6)	5201(9)	35(3)
C(62)	7208(7)	4115(6)	6183(9)	42(3)
C(63)	7008(8)	3536(6)	6627(9)	50(3)
C(64)	6317(8)	3175(7)	6092(10)	51(3)
C(65)	5854(8)	3385(6)	5151(9)	48(3)
C(66)	6048(7)	3970(6)	4682(9)	39(3)
C(71)	9575(7)	3207(7)	1533(13)	175(4)
C(72)	9462(7)	2989(7)	497(13)	197(4)
C(73)	9743(7)	3360(7)	−228(13)	272(4)
C(74)	10137(7)	3949(7)	83(13)	292(4)
C(75)	10251(7)	4167(7)	1118(13)	281(4)
C(76)	9970(7)	3796(7)	1844(13)	276(4)
B	4480(16)	1086(13)	2259(19)	105(4)

[a] Estimated standard deviations on the least significant digits are in parentheses. The isotropic temperature factors are of the form $\exp[-8\pi^2 U(\sin^2\theta)/\lambda^2]$.

0.21 Å^2). The function $\Sigma w(|F_o| - |F_c|)$ was minimized in the least squares, with weights $w = 1/\sigma^2(F_o)$. The final values of the discrepancy indices were: $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.058$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.059$. The final difference Fourier map showed few peaks lower than 0.8 eÅ^{-3} in the region occupied by the solvent molecule.

The scattering factors for the neutral atoms and the anomalous dispersion terms for As and Co were taken from Ref. [15]. Fractional coordinates and temperature factors for the non-hydrogen atoms are listed in Tables I and II. Selected values of bond distances and angles appear in Table III. Listings of hydrogen atom coordinates and of the observed and calculated structure factors are available from the authors on request.

Results and Discussion

The reaction of cobalt(II) tetrafluoroborate hydrate in the presence of triphos with tetra-arsenic trisulfide affords the complex of formula [(triphos)Co(As$_2$S)]BF$_4$, which crystallizes with one molecule of benzene. The diamagnetic compound is moderately air-stable in the solid state. It is soluble in acetone, dichloromethane and nitroethane, where it undergoes decomposition in a few hours in air. The complex behaves as a 1:1 electrolyte in nitroethane solution.

The structure of the compound consists of [(triphos)Co(As$_2$S)]$^+$ cations, BF$_4^-$ anions and solvate benzene molecules. Figure 1 shows a perspective view of the cation. The metal atom is in a distorted six-coordinate environment formed by the triphos P atoms and by the atoms of the heterocyclic As$_2$S unit in a staggered arrangement similar to that previously found for the P$_2$X (X = S, Se) derivatives [4, 5]. The site occupancies in the As$_2$S ring, which are affected by orientational disorder about the pseudo-threefold axis of the cation (see Experimental), are specified in Table I. The sulfur atom resides with highest probability in the site forming the shortest contact distances with the other atoms in the cation.

The bond length between the two sites with predominant As character in the heterocyclic ring (As(1)–As(2) = 2.339(2) Å, Table III) is appreciably longer than the other two distances in the ring, of 2.264(3) and 2.278(3) Å, both of which involve the predominantly S position. The above 'As–As' distance is however quite shorter than the As–As bond lengths in the two forms of As$_4$S$_3$, in the range 2.44–2.48 Å [7, 8]. It is also shorter than the interatomic distance, 2.43 Å, detected both for the free As$_4$ molecule [16] and for the homocyclic As$_3$ unit existing in the dinuclear [(triphos)Co-μ-(η^3-As$_3$)Co(triphos)](BPh$_4$)$_2$ complex [17]. It is however only slightly shorter than the 2.372(5) Å bond length in As$_3$Co(CO)$_3$ [18]. Presumably the present short dis-

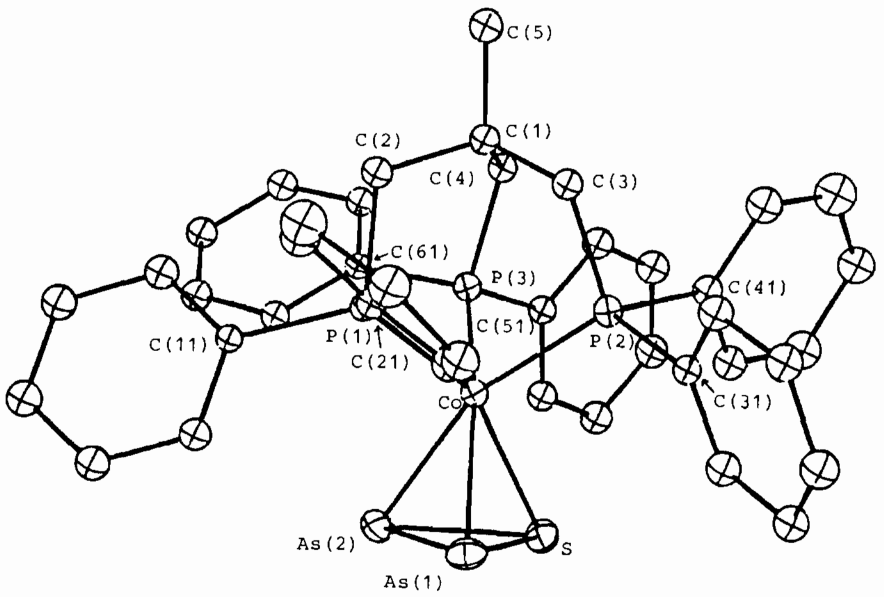

Fig. 1. Perspective view of the [(triphos)Co(As$_2$S)]$^+$ cation with 20% probability ellipsoids. The first carbon atom of each phenyl group is labelled. The occupancy factors of the As(1), As(2) and S sites are specified in footnote b to Table I.

TABLE III. Selected Bond Distances (Å) and Angles (°) for [(triphos)Co(As$_2$S)]BF$_4$·C$_6$H$_6$.[a]

Co–P(1)	2.193(4)	P(1)–C(21)	1.83(1)
Co–P(2)	2.223(4)	P(2)–C(3)	1.84(1)
Co–P(3)	2.227(4)	P(2)–C(31)	1.84(1)
Co–As(1)	2.389(2)	P(2)–C(41)	1.85(1)
Co–As(2)	2.393(2)	P(3)–C(4)	1.84(1)
Co–S	2.325(3)	P(3)–C(51)	1.81(1)
As(1)–As(2)	2.339(2)	P(3)–C(61)	1.84(1)
As(1)–S	2.264(3)	C(1)–C(2)	1.54(2)
As(2)–S	2.278(3)	C(1)–C(3)	1.54(2)
P(1)–C(2)	1.85(1)	C(1)–C(4)	1.57(2)
P(1)–C(11)	1.83(1)	C(1)–C(5)	1.52(2)
P(1)–Co–P(2)	94.4(1)	C(3)–P(2)–C(31)	107.4(5)
P(1)–Co–P(3)	94.1(1)	C(3)–P(2)–C(41)	105.7(6)
P(2)–Co–P(3)	89.5(1)	C(31)–P(2)–C(41)	98.4(5)
As(1)–Co–As(2)	58.6(1)	Co–P(3)–C(4)	108.3(4)
As(1)–Co–S	57.4(1)	Co–P(3)–C(51)	117.5(4)
As(2)–Co–S	57.7(1)	Co–P(3)–C(61)	121.1(4)
As(2)–As(1)–S	59.3(1)	C(4)–P(3)–C(51)	104.7(5)
As(1)–As(2)–S	58.7(1)	C(4)–P(3)–C(61)	103.5(5)
As(1)–S–As(2)	62.0(1)	C(51)–P(3)–C(61)	99.8(5)
Co–P(1)–C(2)	108.8(4)	P(1)–C(2)–C(1)	114.8(8)
Co–P(1)–C(11)	118.4(4)	P(2)–C(3)–C(1)	115.3(8)
Co–P(1)–C(21)	120.7(4)	P(3)–C(4)–C(1)	116.6(8)
C(2)–P(1)–C(11)	106.4(5)	C(2)–C(1)–C(3)	112(1)
C(2)–P(1)–C(21)	101.9(5)	C(2)–C(1)–C(4)	110(1)
C(11)–P(1)–C(21)	98.6(5)	C(2)–C(1)–C(5)	106(1)
Co–P(2)–C(3)	107.2(4)	C(3)–C(1)–C(4)	111(1)
Co–P(2)–C(31)	118.9(4)	C(3)–C(1)–C(5)	109(1)
Co–P(2)–C(41)	118.3(4)	C(4)–C(1)–C(5)	109(1)

[a] The occupancies of sites As(1), As(2) and S are as specified in footnote b to Table I.

tance is largely determined by the partial S substitution in the As sites. The Co–S bond length, 2.325(3) Å, is smaller than the Co–As ones, of 2.389(2) and 2.393(2) Å, as would be expected from the predominant occupations of the sites in the triatomic unit. The Co–P(1) distance, 2.193(4) Å, formed by the triphos P atom lying opposite the S site, is significantly shorter than the other two Co–P distances of 2.223(4) and 2.227(4) Å. A similar asymmetry in the mode of bonding of the triphos ligand was detected for the P_2Se derivative, where the Co–P (triphos) bond lying in a *trans* position to the bond having predominant Co–Se character is shorter than the other two Co–P(triphos) linkages [5]. Although a detailed rationalization of such asymmetry in the coordination by the phosphine ligand seems difficult, it certainly originates from dissimilarities produced by the presence of the heteroatom in the triatomic ring between the pairs of orbitals in π sets which the Co(As_2S) or Co(P_2Se) conical fragment makes available for bonding to the phoshine ligand. The removal of degeneracies in such sets of orbitals going from a trigonal fragment, *e.g.* Co(P_3), to the previous less-symmetrical ones is proved by simple computational procedures [19].

The $^{31}P\{^1H\}$ n.m.r. spectrum in CD_2Cl_2 of the compound exhibits at room temperature a broad resonance at 33.70 ppm due to the triphos P atoms. The coordination chemical shift of the ligand (58.95 ppm) is practically identical to that found for the analogous cobalt complexes having triphos as a co-ligand and the P_2S or P_2Se cyclic unit trihapto bonded to the metal [5]. The sensitivity of the triphos chemical shift to replacement of the chalcogen or pnicogen atoms in the triatomic ring might be due to involvement of the phosphine ligand in lower-energy molecular orbitals than the cyclic unit [6]. The triphos resonance, strongly affected by the cobalt quadrupole moment, becomes sharper on cooling but it is not resolved into a fine structure even at −70 °C.

The absorption spectrum of the compound in nitroethane solution is similar to the reflectance spectrum and shows a shoulder at *ca.* 450 nm and a band at 380 nm, with respective ϵ_M values of 730 and 1450. These frequencies are practically identical to those found for the isoelectronic P_2S and P_2Se derivatives [5].

The reactions of the P_4S_3, P_4Se_3, or As_4S_3 cage molecules with Co(II) in the presence of triphos lead in every case to a chelating triatomic ring formed by one chalcogen and two pnicogen atoms. This suggests that the differences in atomic orbital energies and sizes between P and As or S and Se are overridden by other factors, probably related to orbital symmetry requirements.

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