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Silver(I) Complexes with Heterocyclic Thiones and Triphenylphosphine as Ligands. The Crystal Structure of Silver(I) Pyridine-2-thione Bis(triphenylphosphine) Chloride [$Ag(PPh_3)_2(py2SH)Cl$]

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Abstract

The complex formation between [$Ag(PPh_3)Cl]_4$ and heterocyclic thiones (L) [L = pyridine-2-thione (py2SH), pyridine-4-thione (py4SH), pyrimidine-2-thione (pymtH), 1,3-thiazolidine-2-thione (tzdtH), 1-methyl-1,3-imidazoline-2-thione (meimtH), benz-1,3-thiazoline-2-thione (bztzH), benz-1,3-imidazoline-2-thione (bzimtH_2), 5-nitro-2-benz-1,3-imidazoline-2-thione (nbzimtH_2) and quinazolinone-2-thione (qnotH_2)] has been investigated. The infrared spectral data suggest the formation of mononuclear complexes of the general formula [$Ag(PPh_3)_2(L)Cl$] in which the thione ligands behave as monodentate, coordination occurring through the S atom. The crystal structure of the pyridine-2-thione complex has been determined by single-crystal X-ray diffraction methods. The yellow crystals are monoclinic, space group $P2_1/c$ with $a = 14.362(2)$, $b = 10.302(1)$, $c = 25.054(3)$ Å, $\beta = 93.38(1)°$, $D_{calc} = 1.398$ Mg m^{-3}, $V = 3700.3$ Å^3 and $Z = 4$.

Introduction

The knowledge of the coordination behaviour of heterocyclic thione ligands is useful for the study of the coordination of heavy metals to nucleotides and related compounds of nucleic acids which may have an antitumour activity [1]. For this reason we recently studied the structural properties of a number of mononuclear [2, 3] or binuclear [4, 5] Cu(I) complexes which show a distorted trigonal or tetrahedral configuration about the copper atom. In order to find out the influence of bulky ligands on the molecular geometry of such compounds we studied also mixed complexes of Cu(I) with heterocyclic thiones and triphenylphosphine as ligands [6–8]. In this work our study is continued with the synthesis and characterization of novel Ag(I) complexes of the general formula [$Ag(PPh_3)_2(L)X$] for an additional reason. This is of considerable interest in the chemistry of silver complexes due to their industrial applications [9] as in organic catalysis, photographic processes, photocells and in studies of electrode and surface processes.

Experimental

Reagents

[$Ag(PPh_3)Cl]_4$ was prepared from AgCl and PPh_3 as described in the literature [10]. $C_4H_8N_2S$ (meimtH) and $C_7H_5N_3O_2S$ (nbzimtH_2) were supplied by Aldrich; PPh_3, $C_7H_6N_2S$ (bzimtH_2), $C_3H_5NS_2$ (tzdtH) and $C_8H_6N_2OS$ (qnotH_2) were supplied by EGA; AgCl and C_5H_5NS (py2SH, py4SH), $C_4H_4N_2S$ (pymtH) were supplied by Merck. All thiones were used after recrystallization from ethanol.

Physical Measurements

IR spectra, conductivities, magnetic susceptibility measurements and elemental analyses of carbon, nitrogen and hydrogen were performed as described previously [8].

Preparation of the Complexes

0.5 mmol of [$Ag(PPh_3)Cl]_4$ and 2 mmol of the appropriate thione were added to 60 ml acetone, and refluxed for 30 min. The reaction mixture was stirred for an additional 2 h at 40 °C, filtered and allowed to evaporate slowly at room temperature. The microcrystalline solid thus formed was collected by filtration, washed with small amounts of ethanol and ether and dried in vacuum. Single crystals

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suitable for X-ray diffraction studies were obtained by slow evaporation of [Ag(PPh_3)$_2$(py2SH)Cl] in THF.

Collection and Reduction of X-ray Data

Intensity data were measured at room temperature with a Syntex P3 autodiffractometer with graphite-monochromated Mo Kα radiation. Crystal and intensity data are given in Table 1. Unit cell parameters were derived by least-squares refinement based on diffractometer angles of 25 automatically centered general reflections between 24–26° 2θ. The intensities of six references monitored every 138 reflections showed no significant variation. Intensities were corrected for Lorentz and polarization effects but no absorption correction was applied.

Solution and Refinement of the Structure

The structure was partially solved using direct methods with SHELX76 [11a] and completed with all non-H atoms by difference Fourier with the X-RAY 76 programme package [11b].

The positional and anisotropic thermal parameters of all non-H atoms were refined by blocked full matrix least-squares using F with SHELX76. Atomic scattering factors for neutral Ag were taken from International Tables for X-Ray Crystallography [12] and those for the remaining atoms were incorporated in the programme.

TABLE 1. Summary of crystal and intensity collection data

Formula	$C_{41}H_{35}ClAgNP_2S$
M_r	779.03
Space group	$P2_1/c$
Z	4
a (Å)	14.362(2)
b (Å)	10.302(1)
c (Å)	25.054(3)
β (°)	93.38(1)
V (Å^3)	3700.4
D_c (Mg m^{-3})	1.398
D_m (Mg m^{-3})	1.375
F(000)	1592
μ(Mo Kα) (cm^{-1})	7.10
Radiation (Å)	Mo Kα (λ = 0.71069)
Crystal dimensions (mm)	0.35 × 0.27 × 0.20
Scan mode	$\theta/2\theta$
Scan speed (°/min)	3–30
2θ range (°)	4–55
hkl range	$0 \rightarrow 19, 0 \rightarrow 14, -33 \rightarrow 33$
Reflections measured/unique/ R_{int}	10662/9574/0.032
Observed reflections ($F_o \geqslant 2.5\sigma(F_o)$)	7307
No. refined parameters	466
Weighting scheme	$1/(\sigma^2(F_o) + 0.0008{F_o}^2)$
$\lvert\Delta\sigma\rvert_{max}$	0.256
$\lvert\Delta\sigma\rvert_{max}/\lvert\Delta\rho\rvert_{min}$ (e Å^{-3})	0.882/–0.698
R	0.0457
R_w	0.0477

H atoms were included at calculated positions very close to those from a difference Fourier map, with anisotropic temperature factors assumed equal to those of the bonded C or N atoms. Their positional and thermal parameters were also refined. The quantity minimized was $\Sigma w \Delta F^2$ where the weights w were initially unity and in the final cycles given by $1/w = \sigma^2(F_o) + 0.0008{F_o}^2$ so that the mean values of $w\Delta F^2$ for ranges of increasing F_o were almost constant.

Results and Discussion

In a preceding paper [6] we examined the reaction of [Cu(PPh_3)X]$_4$ ('cubane' for X = Cl and 'step like' for X = Br, I) with pyridine-2-thione (py2SH), pyridine-4-thione (py4SH) and pyrimidine-2-thione (pymtH) in toluene. This reaction results in the formation of binuclear complexes of general formula [Cu(PPh_3)(L)X]$_2$, in which thione molecules are monodentate with sulfur atoms as bridging coordinating groups. In this work we observe the corresponding reaction between the cubane [Ag(PPh_3)Cl]$_4$ and several heterocyclic thiones. Unexpectedly, the result in this case is solely mononuclear complexes of the type [Ag(PPh_3)$_2$(L)X] which were found to be stable against air oxidation. Yields, colours, melting points and analytical data are presented in Table 2.

The compounds are insoluble in water and very slightly soluble in some organic solvents. As would be expected for d^{10} species, all isolated complexes are diamagnetic. Their resultant electrolytic conductivities are consistent with non-electrolytic behaviour.

Description of the Structure

Fractional atomic coordinates and selected bond distances and angles are given in Tables 3 and 4, respectively. See also 'Supplementary Material'. An ORTEP [13a] view of the molecule is given in Fig. 1 and a MOLDRAW [13b] view of the molecular packing in the unit cell in Fig. 2. The silver atom is surrounded by four donor, two P, one S and one Cl atoms in a distorted tetrahedral coordination. The largest deviation from the ideal geometry, P–Ag–P = 123.0(0)°, may be attributed to steric interaction between the two PPh_3 ligands. The Ag–P bond distances, (Ag–P1 = 2.482(1) and Ag–P2 = 2.476(1) Å), somewhat longer than the single covalent bond length, fall in the middle of the range of values 2.375(2)–2.630(3) Å found for a number of various similar compounds in which the silver atoms are coordinated to two (or three) phosphorous atoms [10, 14–19].

The Ag–S and Ag–Cl bond distances are within the expected ranges. So the Ag–S = 2.625(1) Å bond

TABLE 2. Elemental analyses and some physical properties of the complexes

Compound	Yield	Color	Melting point (°C)	Analysis: found (calc.) (%)		
				C	H	N
$[Ag(PPh_3)_2(py2SH)Cl]$ (I)	85	yellow	173	62.23(63.21)	4.07(4.52)	1.65(1.79)
$[Ag(PPh_3)_2(py4SH)Cl]$ (II)	68	yellow	197[a]	62.80(63.21)	4.39(4.52)	1.62(1.79)
$[Ag(PPh_3)_2(pymtH)Cl]$ (III)	90	yellow	178	62.78(61.59)	4.45(4.39)	3.84(3.59)
$[Ag(PPh_3)_2(tztdtH)Cl]$ (IV)	74	grey	183	60.12(59.51)	4.60(4.48)	1.85(1.78)
$[Ag(PPh_3)_2(meimtH)Cl]$ (V)	70	grey	174	61.05(61.27)	4.80(4.88)	3.62(3.57)
$[Ag(PPh_3)_2(bztzH)Cl]$ (VI)	80	pale yellow	172	62.00(61.84)	3.93(4.22)	1.57(1.67)
$[Ag(PPh_3)_2(bzimtH_2)Cl]$ (VII)	75	grey	240	62.96(61.13)	4.48(4.43)	3.24(3.42)
$[Ag(PPh_3)_2(quotH_2)Cl]$ (VIII)	82	white	246	64.69(64.92)	4.28(4.45)	3.48(3.44)
$[Ag(PPh_3)_2(nbzimtH_2)Cl]$ (IX)	85	yellow	244	60.20(59.83)	3.92(4.08)	4.66(4.86)

[a]Decomposition.

TABLE 3. Fractional atomic coordinates (×10^4, for Ag and P1 × 10^5) and B_{eq} values (×10^2) of the non-hydrogen atoms

Atom	x	y	z	B_{eq} [a]
Ag	23814(2)	19594(2)	14326(1)	305
P1	24219(5)	26297(7)	23859(3)	249
P2	3452(1)	2859(1)	783(0)	268
Cl	2592(1)	−533(1)	1523(0)	435
S	725(1)	2229(1)	944(0)	462
C1	1738(2)	1622(3)	2820(1)	302
C2	938(2)	1053(4)	2595(2)	460
C3	406(3)	238(4)	2904(2)	631
C4	669(3)	−13(4)	3424(2)	594
C5	1472(3)	529(4)	3649(2)	550
C6	2009(3)	1356(3)	3349(1)	425
C7	2078(2)	4288(3)	2496(1)	289
C8	1774(3)	4765(3)	2980(1)	420
C9	1576(3)	6071(4)	3033(2)	544
C10	1677(3)	6913(3)	2615(2)	530
C11	1986(3)	6470(3)	2143(2)	484
C12	2177(2)	5161(3)	2076(1)	377
C13	3594(2)	2543(3)	2703(1)	256
C14	4112(2)	3655(3)	2834(1)	296
C15	5035(2)	3549(3)	3033(1)	357
C16	5436(2)	2347(3)	3105(1)	379
C17	4926(2)	1234(3)	2980(1)	365
C18	4013(2)	1325(3)	2777(1)	317
C19	4677(2)	3047(2)	1001(1)	285
C20	4990(2)	2637(3)	1506(1)	351
C21	5921(3)	2725(4)	1676(1)	450
C22	6551(3)	3255(4)	1342(2)	455
C23	6255(3)	3663(3)	837(1)	443
C24	5333(2)	3552(3)	663(1)	394
C25	3539(2)	1947(3)	170(1)	300
C26	3664(3)	2520(3)	−323(1)	427
C27	3824(3)	1766(4)	−766(1)	521
C28	3845(3)	442(4)	−720(2)	557
C29	3713(3)	−145(3)	−237(2)	555
C30	3554(3)	604(3)	210(1)	416
C31	3063(2)	4476(3)	577(1)	317
C32	2190(3)	4606(3)	321(1)	433
C33	1806(3)	5832(4)	208(2)	532
C34	2306(4)	6923(4)	372(2)	552
C35	3166(3)	6815(3)	621(2)	516
C36	3560(3)	5603(3)	726(1)	410
C37	201(2)	771(3)	840(1)	389
C38	−683(3)	638(5)	562(2)	590
C39	−1065(3)	−562(6)	483(2)	750
C40	−617(4)	−1670(6)	681(2)	790
C41	217(3)	−1536(5)	952(2)	641
N	599(2)	−344(3)	1022(1)	434

[a]$B_{eq} = 8/3\pi^2 \text{ trace } \tilde{U}$.

length is close to 2.635(7) Å in $[Ag_2(PPh_3)_4(S_2C_2(CN)_2]$ [14] and to 2.566(3) and 2.612(2) Å in $[Ag(PPh_3)_2]_3Al(O_2C_2S_2)_3$ [19], but it is longer than the value of 2.40 Å for two coordinated silver atoms in $[AgSC_6H_{11}]$ [20]. All three distances Ag–P, Ag–S, Ag–Cl in this complex are slightly longer than the sum 2.44, 2.56, 2.51 Å respectively, of the corresponding tetrahedral radii [21]. In contrast, the Cu–P = 2.301(2), Cu–S = 2.374(2), Cu–Cl = 2.361(2) Å bond lengths in the analogous Cu complex, $[Cu(PPh_3)_2(C_5H_5NS)Cl]$ [22] are somewhat shorter than the sum of the corresponding tetrahedral radii [21].

In the essentially planar C_5H_5NS ligand the S–C37 = 1.693(4) Å distance is comparable to that of 1.692(2) Å in other compounds with the same ligand [6, 8]. As in the case of the Cu complex the coordination of the C_5H_5NS ligand to the AgP_2Cl core is completed via an intramolecular N–H···Cl hydrogen bond since the H(N42) atom is only 2.009(3) Å apart from Cl and the N–H···Cl angle is 165.9° [(N···Cl = 3.067(3) Å].

TABLE 4. Selected interatomic distances (Å) and angles (°)[a]

Ag–P1	2.482(1)	P2–C31	1.825(3)
Ag–P2	2.476(1)	S–C37	1.693(4)
Ag–Cl	2.595(1)	C37–C38	1.417(5)
Ag–S	2.625(1)	C37–N	1.352(4)
P1–C1	1.827(3)	C38–C39	1.362(8)
P1–C7	1.810(3)	C39–C40	1.388(9)
P1–C13	1.821(3)	C40–C41	1.349(8)
P2–C19	1.819(3)	C41–N	1.351(6)
P2–C25	1.820(3)		
Cl–Ag–S	104.2(0)	P1–C1–C2	117.1(2)
P2–Ag–S	103.7(0)	P1–C7–C12	117.1(2)
P2–Ag–Cl	111.0(0)	P1–C7–C8	124.4(2)
P1–Ag–S	112.9(0)	P1–C13–C18	118.5(2)
P1–Ag–Cl	100.8(0)	P1–C13–C14	122.2(2)
P1–Ag–P2	123.0(0)	P2–C19–C24	122.3(3)
Ag–P1–C13	112.1(1)	P2–C19–C20	119.5(3)
Ag–P1–C7	114.6(1)	P2–C25–C30	117.1(2)
Ag–P1–C1	115.8(1)	P2–C25–C26	123.7(2)
C7–P1–C13	103.3(1)	P2–C31–C36	122.4(2)
C1–P1–C13	103.3(1)	P2–C31–C32	118.5(2)
C1–P1–C7	106.4(1)	S–C37–N	121.7(3)
Ag–P2–C31	109.8(1)	S–C37–C38	122.6(3)
Ag–P2–C25	116.0(1)	C38–C37–N	115.6(3)
Ag–P2–C19	118.4(1)	C37–C38–C39	120.1(4)
C25–P2–C31	105.1(1)	C38–C39–C40	121.3(5)
C19–P2–C31	105.2(1)	C39–C40–C41	118.3(5)
C19–P2–C25	101.0(1)	C40–C41–N	120.0(5)
Ag–S–C37	111.2(1)	C37–N–C41	124.6(3)
P1–C1–C6	123.4(2)		

[a] e.s.d.s given in parentheses.

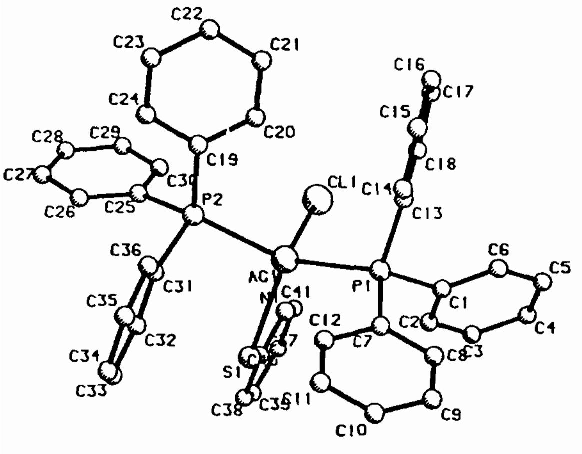

Fig. 1. A view of the [Ag(PPh$_3$)$_2$(py2SH)Cl] molecule.

Infrared Spectra

Infrared spectra of the reported complexes when compared with those of the free ligands, provide informations concerning the mode of coordination.

The IR spectra of the silver complexes are completely analogous to those of the corresponding

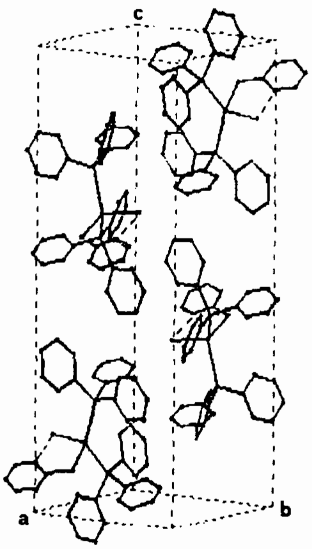

Fig. 2. A view of the molecular packing in the unit cell.

copper complexes, except for the 600–250 cm^{-1} region. They show the absence of ν(SH) at 2500 cm^{-1} and the presence of ν(NH), as well as the characteristic four thioamide bands [23, 24], suggesting that the ligands exist in the thione form in the solid state.

The ν(NH) absorption in the complexes appears as a broad band at 3110–3180 cm^{-1}, about 10–20 cm^{-1} lower than in the free ligands solid state spectra. Such shifts are usually regarded as signifying that the ligands are not N-bonded to the metal [25]. Analysis of the thioamide bands has been used successfully to differentiate between M–N and M–S contacts for various thione ligands. In this instance, however, the thioamide bands which show the most significant changes upon coordination, namely thioamide I and thioamide IV, are in many cases masked by strong triphenylphosphine bands. However, negative shifts in the order of 20–60 cm^{-1}, characteristic of thione–S coordination [26], are observed for the thioamide II and thioamide III bands. Since the shifts are all in the same direction the bonding pattern is deduced to be the same for all the thiones investigated.

Supplementary Material

Tables of coefficients of the anisotropic temperature factors, interatomic distances and angles, coordinates of the non-H atoms and observed and calculated structure factors with standard deviations are available from the authors on request.

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