action may have alleviated some strain, for the corresponding angles in the PPh_3 complex are 116.3 (1), 114.7 (1), and 110.1 (1)° and 110.7 (1), 122.3 (1), and 111.3 (1)°. The two largest angles are associated with two phenyl rings in close proximity. The angles in the PCy_2Ph ligands are 122.7 (4), 111.1 (4), and 112.8 (4)°, and 122.9 (4), 112.0 (4), and 110.0 (4)°. These values are clearly normal and reflect the increasing steric interaction between the phosphine ligands.

Further studies will be reported on complexes of hexafluorobut-2-yne with ligands of varying basicity, in an attempt to determine the importance of this effect.

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Supplementary Material Available: Tables V and VIII, structure amplitudes for 1 and 2 (21 pages). Ordering information is given on any current masthead page.

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Preparation and Crystal Structure of Trisilver Undecaphosphide, Ag_3P_{11}, an Unusual Defect Tetrahedral Compound

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Single crystals of Ag_3P_{11} were prepared by heating the elemental components in evacuated silica tubes in the presence of iodine. They are monoclinic with the space group *Cm* and the lattice constants $a = 12.999$ (3) Å, $b = 7.555$ (2) Å, $c = 6.612$ (2) Å, $\beta = 118.84$ (2)°, and $Z = 2$. The crystal structure was determined from single-crystal diffractometer data and refined to a conventional *R* value of 0.059 for 44 variable parameters and 865 structure factors. The Ag atoms are approximately tetrahedrally coordinated by P atoms at distances varying between 2.47 and 2.61 Å. The AgP_4 tetrahedra are linked by shared P atoms, thus forming infinite chains along the *a* axis. Most P atoms have tetrahedral coordination of one Ag and three P or two Ag and two P atoms. One kind of P atoms has three P neighbors with a lone pair of electrons as a fourth "ligand". Bonding in Ag_3P_{11} is described with a simple covalent model where all near-neighbor interactions are rationalized as classical two-electron bonds in agreement with the diamagnetism and the semiconductivity of the compound. This also establishes the formal oxidation number +1 for the Ag atoms while the P atoms may be considered as forming a two-dimensionally infinite polyanion consisting of condensed 5-, 6-, and 14-membered rings. The structure of Ag_3P_{11} can be derived from that of cubic diamond by ordering of Ag atoms, P atoms, and vacancies on the positions of the carbon atoms. It is unusual in that there are four vacant sites but also only four lone pairs per cell. It nevertheless obeys Parthé's definition of a defect tetrahedral structure.

Introduction

According to Haraldsen and Biltz[1] the system Ag–P is characterized by only two binary phases to which they ascribed the compositions AgP_2 and "AgP_3". Both compounds were prepared by direct reaction of the elemental components and according to their tensiometric studies are in equilibrium with P vapor. Olofsson[2] showed from X-ray powder data that AgP_2 is isotypic with CuP_2 but found little evidence for a compound with higher P content. Our present reinvestigation of the phosphorus-rich part of the Ag–P system confirms the existence of AgP_2. For the other compound with higher P content our structure determination yields the composition Ag_3P_{11}.

Experimental Section

Starting materials were Ag powder (Alfa Ventron, <100 mesh, >99.99%) and red P (Merck, "rein") which was purified with diluted NaOH solution.[3] The powders were mixed in various ratios and annealed in evacuated silica tubes. The Ag content was around 60 mg and about 1–3 mg of iodine was added to most samples. After the heat treatment the iodine was identified as AgI in the X-ray powder patterns. The presence of iodine resulted in a better crystallized product but was not necessary to produce Ag_3P_{11}. No long-range transport of silver phosphides was observed. Iodine probably aids catalytically in the evaporation of phosphorus.[4]

With the starting compositions Ag:P = 1:2 the products were always AgP_2 (7 days of annealing; temperatures varied for different samples between 550 and 700 °C). Compositions Ag:P = 1:3 gave two-phase products of AgP_2 and Ag_3P_{11} (7 days; 400, 500, or 600 °C). Samples Ag:P = 1:4 and 1:5 resulted in Ag_3P_{11} and white P (7 days at temperatures between 400 and 600 °C). Two samples with the composition Ag:P = 1:5 and 1:10 were kept at 370 °C for 35 days. Their powder patterns correspond to Ag_3P_{11}; in addition several broad lines indicated a poorly crystallized product which was possibly red P.

Even with the addition of iodine to the samples the crystals of Ag_3P_{11} were small (typical size 6 × 10 × 60 μm). They had elongated lanceolate shape and a black shiny appearance. They are resistant to air and not soluble in nonoxidizing acids, but they dissolved in hot concentrated nitric acid. Magnetic measurements carried out with the Faraday technique showed Ag_3P_{11} to be diamagnetic.

Structure Determination

X-ray powder patterns were recorded with a Guinier camera and Cu $K\alpha_1$ radiation. They were indexed with the monoclinic cell found from the single-crystal diffraction photographs. Least-squares refinement with α-quartz as standard ($a = 4.9130$, $c = 5.4046$ Å) resulted in the following lattice constants: $a = 12.999$ (3) Å, $b = 7.555$ (2) Å, $c = 6.612$ (2) Å, $\beta = 118.84$ (2)°, $V = 568.8$ (3) $Å^3$ (here and in subsequent tables the estimated standard deviations of the least significant figures are shown in parentheses). With $Z = 2$ formula weights per cell, the calculated density is 3.879 g cm^{-3}. This agrees perfectly with the density of 3.881 g cm^{-3} found for the phase "AgP_3" by Haraldsen and Biltz.[1] A typical powder pattern with intensities calculated[5] from the refined structure is shown in Table I.

Single crystals were examined in Buerger precession and Weissenberg cameras. They have monoclinic diffraction symmetry and no other systematic extinctions besides those for a *C*-centered cell. Thus, space groups *C*2, *Cm*, and *C*2/*m* were possible of which *Cm* was found to be correct during the structure determination.

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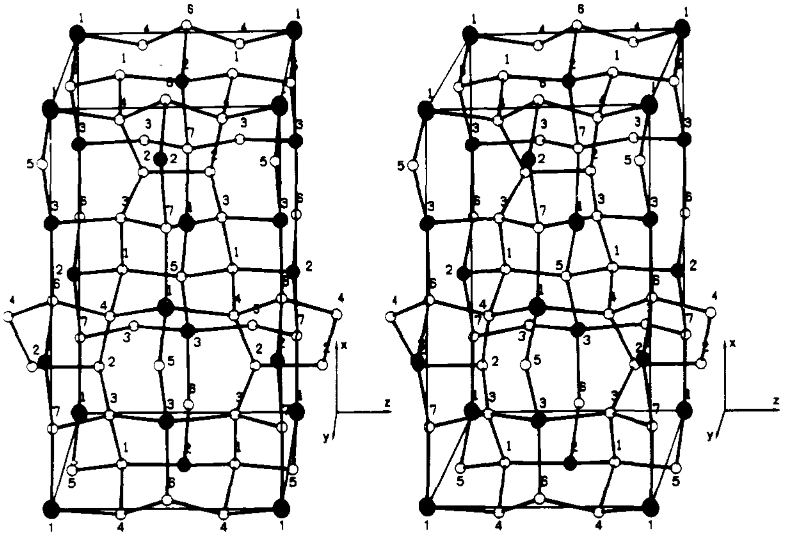

Figure 1. Stereoplot of the Ag_3P_{11} structure. The sizes of the atoms correspond to thermal parameters at the 75% probability limit. Ag atoms are black; P atoms are open circles. The numbers correspond to the atom designations.

Table I. X-ray Powder Pattern of Ag_3P_{11}[a]

hkl	Q_c	Q_o	I_c	I_o	hkl	Q_c	Q_o	I_c	I_o
110	252	-	10	-	003	2683	-	7	-
001	298	298	128	m	600	2777	-	13	-
200	309	309	107	w	222	2787	2787	72	s
-201	314	314	108	w	040	2803	2803	160	s
-111	404	404	85	w	-223	2815	2817	35	s
111	697	699	154	m	421	2818		336	
020	701	702	183	s	-603	2827	-	10	-
-311	729	729	360	s	-423	2863	2863	335	s
310	869	870	154	m	-621	2898	2898	104	w
201	699	900	132	m	-622	2914	2916	85	w
-202	916	917	89	w	312	2939	-	4	-
-401	947	947	26	vvw	331	3008	-	2	-
021	999	1000	1000	vs	-531	3072	3072	21	vvw
220	1009	-	15	-	-712	3099	-	7	-
-221	1015	-	18	-	041	3101	3101	81	w
-112	1152	1153	134	m	240	3112	3112	42	w
-312	1184	1183	163	m	-241	3117	-	40	
002	1192	-	44	-	511	3133	-	0	-
400	1234	1235	333	s	132	3139	3141	33	vvw
-402	1256	1257	327	s	-711	3228	-	25	w
221	1600	1602	133	m	-532	3235	3232	45	
311	1606	1605	90	w	113	3374	-	29	-
-222	1617	1616	92	w	023	3384	3383	121	m
-421	1648	-	10	-	620	3477	3476	33	vvw
130	1654	1656	42	vw	530	3505	-	5	-
-511	1670	1671	58	vw	-632	3527	3527	27	vvw
112	1737	1736	53	vw	-713	3566	-	30	-
-131	1806	1806	40	vw	402	3597	3594	78	vw
512	1833	1833	36	vw	-333	3637	-	20	-
022	1893	1896	71	w	-404	3664	3664	85	w
420	1935	1935	36	vw	241	3702	-	21	-
-422	1957	1957	44	vw	-242	3719	-	14	-
202	2086	-	36	-	-441	3750	3747	25	vvw
131	2098	-	10	-	-802	3788	3787	94	w
510	2103	-	21	-	203	3869	-	10	-
-203	2114	-	14	-	-314	3884	-	1	-
401	2117	-	13	-	-135	3989	3895	31	vvw
-331	2130	2131	84	w	-204	3908	-	2	-
-403	2162	-	12	-	-514	3948	-	3	-
-601	2198	2196	83	w	601	3952	-	6	-
-602	2214	2213	75	w	710	3954	3954	41	vw
-313	2236	-	13	-	-533	3994	-	1	-
330	2271	2270	100	w	042	3996	-	3	-
-113	2497	2497	112	w	-604	4036	-	3	-
-132	2554	2552	41	vvw	440	4037	4037	78	w
-332	2586	2588	39	vvw	-442	4059	4057	71	w
-513	2592	-	32	-					

[a] The Q values are defined by $Q = 10^4/d^2$ ($Å^{-2}$) (Guinier camera, Cu $K\alpha_1$ radiation).

The crystal used for the collection of the intensity data had the dimensions 15 × 50 × 30 μm and was mounted with the elongated axis approximately parallel to the ϕ axis of a four-circle diffractometer. Graphite-monochromatized Mo $K\alpha$ radiation was used with a scintillation counter and pulse-height discriminator. θ–2θ scans were taken with a speed of 0.04° (2θ) s^{-1}, a scan width of 1.1°, plus the angular separation of the α_1–α_2 doublet. Background was counted on each side of the scans for half the scan time. A total of 1768 reflections were measured within one-fourth of the reciprocal sphere up to $2\theta = 80°$. Because of the relatively low linear absorption coefficient ($\mu_{\mathrm{Mo}\,K\alpha} = 60.2$ cm^{-1}) and the small size of the crystal no absorption correction was made.

Table II. Atom Parameters of Ag_3P_{11}[a]

	Cm	*x*	*y*	*z*	*B*
Ag(1)	2a	0	0	0	1.49 (5)
Ag(2)	2a	4108 (2)	0	1956 (5)	0.80 (4)
Ag(3)	2a	7096 (3)	0	9773 (6)	1.44 (5)
P(1)	4b	4807 (5)	2529 (7)	4696 (10)	0.41 (8)
P(2)	4b	2363 (4)	1504 (7)	4926 (9)	0.68 (8)
P(3)	4b	1676 (5)	2230 (6)	7282 (9)	0.54 (7)
P(4)	4b	4193 (5)	2267 (7)	7327 (9)	0.59 (9)
P(5)	2a	9185 (7)	0	2767 (14)	0.66 (13)
P(6)	2a	5085 (7)	0	9490 (14)	0.52 (12)
P(7)	2a	1888 (7)	0	9548 (13)	0.75 (12)

[a] Positional parameters are multiplied by 10^4. Numbers in parentheses are esd's in the least significant digits. The last column contains B values ($Å^2$) as obtained in a least-squares refinement with isotropic thermal parameters.

The structure was solved and refined with a program system by Sheldrick.[6] The positions of the Ag atoms were deduced from a Patterson map, and the P atoms were located in difference Fourier syntheses. The structure was refined by full-matrix least-squares cycles. Scattering factors for neutral atoms[7] were used, corrected for anomalous dispersion.[8] Weights were assigned according to $w = 1/[\sigma^2(F_o) + kF_o^2]$, where k was a least-squares parameter which refined to $k = 0.00059$ during the final cycles. Because of a systematic error for weak reflections, all reflections with $F_o < 6\sigma$ were assigned zero weight in the final least-squares cycles. Similarly treated were the reflections $0k0$ which were somewhat more affected by absorption. An isotropic extinction correction was applied to the F_c values in the form $F_c = F(1 - xF^2/\sin\theta)$, where x refined to 0.00051. In the final cycles the Ag atoms were refined with ellipsoidal and the P atoms with isotropic thermal parameters. Because the Ag atoms have relatively large thermal amplitudes, we thought of the possibility of a partial occupancy of their positions. We therefore refined the occupancy factors of the Ag positions together with the thermal parameters. The resulting occupancy factors varied between 0.995 and 1.027 with standard derivations of 0.015, and thus the Ag positions can be considered as fully occupied. A similar result was also obtained for the positions of the P atoms. The final conventional R value is 0.0586 for the 865 reflections with nonzero weight and a total of 44 variable parameters. For a setting with the opposite absolute configuration R is 0.0591. The weighted R value is 0.0537. For the total of 1768 reflections R equals 0.122. A final difference Fourier synthesis showed no features lower than −3.3 or higher than 2.8 e $Å^{-3}$. A listing

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Table III. Interatomic Distances in Ag_3P_{11}[a]

Atom	Neighbors	Distance
Ag(1):	1 P(5)	2.517 (6)
	2 P(4)	2.588 (5)
	1 P(7)	2.612 (5)
Ag(2):	2 P(1)	2.484 (6)
	1 P(6)	2.504 (6)
	1 P(7)	2.536 (6)
Ag(3):	1 P(5)	2.471 (7)
	1 P(6)	2.528 (5)
	2 P(3)	2.554 (5)
P(1):	1 Ag(2)	2.484 (6)
	1 P(5)	2.184 (7)
	1 P(3)	2.203 (6)
	1 P(4)	2.245 (6)
P(2):	1 P(3)	2.205 (6)
	1 P(4)	2.207 (6)
	1 P(2)	2.273 (7)
P(3):	1 Ag(3)	2.554 (5)
	1 P(7)	2.182 (7)
	1 P(1)	2.203 (6)
	1 P(2)	2.205 (6)
P(4):	1 Ag(1)	2.588 (5)
	1 P(6)	2.173 (7)
	1 P(2)	2.207 (6)
	1 P(1)	2.245 (6)
P(5):	1 Ag(3)	2.471 (6)
	1 Ag(1)	2.517 (7)
	2 P(1)	2.184 (7)
P(6):	1 Ag(2)	2.504 (6)
	1 Ag(3)	2.528 (5)
	2 P(4)	2.173 (7)
P(7):	1 Ag(2)	2.536 (6)
	1 Ag(1)	2.612 (5)
	2 P(3)	2.182 (7)

[a] All distances shorter than 3.4 Å (for Ag) and 3.2 Å (for P atoms) are listed.

of the positional and isotropic thermal parameters is given in Table II. Observed and calculated structure factors and anisotropic thermal parameters of the Ag atoms are available as supplementary material.

The crystal structure of Ag_3P_{11} is shown in Figures 1 and 2, and near-neighbor environments of the Ag atoms are shown in Figure 3. Interatomic distances and angles are listed in Tables III and IV.

Discussion

The architecture of the Ag_3P_{11} structure can be visualized in two ways depending on whether the emphasis is put on ionic or covalent bonding. When ionicity is stressed, the P atoms may be regarded as forming a two-dimensionally infinte polyanion consisting of condensed 5-, 6-, and 14-membered rings. The Ag atoms are tetrahedrally coordinated by P atoms. The AgP_4 tetrahedra are linked via corners, thus forming infinite chains along the *a* axis. When covalency is stressed on the other hand, the Ag–P and P–P bonds are considered equally important. The structure is then viewed as a tetrahedral compound. This is discussed at the end of the paper.

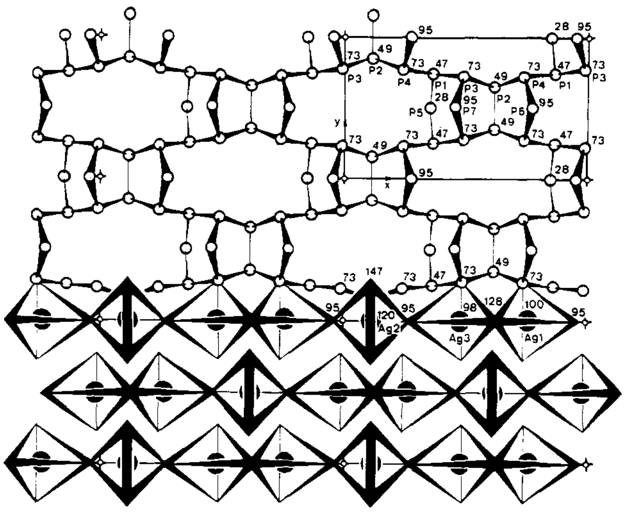

Figure 2. Projection of the Ag_3P_{11} structure perpendicular to the *C*-centered plane. The two-dimensionally infinite network of the P atoms is shown in the upper part, and the chains of the corner-shared AgP_4 tetrahedra are shown in the lower part of the drawing. The heights of the atoms above the projection plane are given in hundredths of the *z* coordinate.

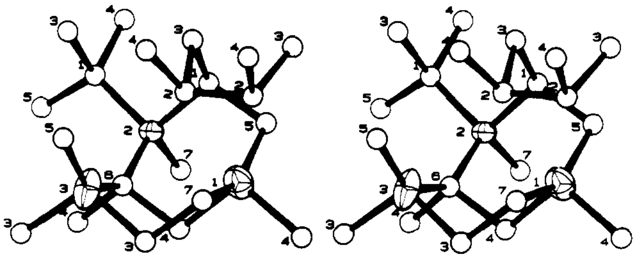

Figure 3. Stereoplot of the near-neighbor environments of the Ag atoms and the void in the structure of Ag_3P_{11}. The sizes of the atoms correspond to the 99% probability limit. The Ag atoms are drawn with their thermal ellipsoids; the P atoms with their isotropic thermal spheres. The numbers correspond to the atom designations.

Ag_3P_{11} is a polyphosphide where all near-neighbor interactions can be rationalized as classical two-electron bonds. So that formal oxidation numbers may be established, the electrons of the Ag–P bonds are counted as belonging to the P atoms and the P–P bonds are split homolytically. In this way the P(1), P(3), and P(4) atoms with one Ag and three P neighbors obtain oxidation number zero. This is also the oxidation number of P(2) which has three P neighbors and a lone pair of electrons as a fourth "ligand". The other P

Table IV. Interatomic Angles (Deg) in Ag_3P_{11}

Angle	Deg	Angle	Deg
P(5)–Ag(1)–P(4)	108.8 (1) (2×)	P(7)–P(3)–P(1)	108.9 (3)
P(5)–Ag(1)–P(7)	146.2 (2)	P(7)–P(3)–P(2)	109.4 (3)
P(4)–Ag(1)–P(4)	105.8 (2)	P(7)–P(3)–Ag(3)	105.8 (3)
P(4)–Ag(1)–P(7)	90.9 (1) (2×)	P(1)–P(3)–P(2)	98.2 (3)
P(1)–Ag(2)–P(1)	100.6 (2)	P(1)–P(3)–Ag(3)	104.2 (2)
P(1)–Ag(2)–P(6)	110.7 (1) (2×)	P(2)–P(3)–Ag(3)	128.8 (2)
P(1)–Ag(2)–P(7)	111.3 (1) (2×)	P(6)–P(4)–P(2)	108.4 (3)
P(6)–Ag(2)–P(7)	111.9 (2)	P(6)–P(4)–P(1)	107.7 (3)
P(5)–Ag(3)–P(6)	139.2 (3)	P(6)–P(4)–Ag(1)	105.5 (3)
P(5)–Ag(3)–P(3)	109.1 (1) (2×)	P(2)–P(4)–P(1)	97.4 (3)
P(6)–Ag(3)–P(3)	93.5 (1) (2×)	P(2)–P(4)–Ag(1)	129.8 (2)
P(3)–Ag(3)–P(3)	110.0 (1)	P(1)–P(4)–Ag(1)	106.3 (2)
P(5)–P(1)–P(3)	110.0 (3)	P(1)–P(5)–P(1)	117.5 (4)
P(5)–P(1)–P(4)	111.0 (3)	P(1)–P(5)–Ag(3)	114.9 (2) (2×)
P(5)–P(1)–Ag(2)	109.2 (3)	P(1)–P(5)–Ag(1)	104.9 (2) (2×)
P(3)–P(1)–P(4)	94.4 (3)	Ag(3)–P(5)–Ag(1)	95.9 (3)
P(3)–P(1)–Ag(2)	120.5 (2)	P(4)–P(6)–P(4)	104.0 (4)
P(4)–P(1)–Ag(2)	110.8 (2)	P(4)–P(6)–Ag(2)	98.7 (2) (2×)
P(3)–P(2)–P(4)	95.2 (3)	P(4)–P(6)–Ag(3)	104.7 (2) (2×)
P(3)–P(2)–P(2)	104.4 (2)	Ag(2)–P(6)–Ag(3)	141.5 (3)
P(4)–P(2)–P(2)	105.1 (2)	P(3)–P(7)–P(3)	101.1 (4)
		P(3)–P(7)–Ag(2)	99.2 (2) (2×)
		P(3)–P(7)–Ag(1)	105.3 (2) (2×)
		Ag(2)–P(7)–Ag(1)	140.9 (3)

Table V. Silver–Phosphorus Distances in Various Compounds[a]

compd	other Ag neighbors	$\bar{\chi}$	range, Å	av, Å	ref
$(C_{12}H_6O_4)_2(Ph_3PAg)_4 \cdot 2C_6H_6$	3 O (3×), 4 O (1×)	3.5	2.342 (4)–2.378 (5)	2.357	16
$Ph_3P \cdot AgNO_3$	4 O	3.5	2.369 (6)	2.369	17
$(Ph_3PAgCl)_4$	3 Cl	3.0	2.376 (3)–2.388 (3)	2.382	18
$[MeN(PPh_2)_2Ag_2Br_2]_2$	3 Br	2.8	2.380 (5)–2.391 (6)	2.385	49
$RhAg_2(C{\equiv}CC_6F_5)_5(PPh_3)_3$	3 $\pi(C{\equiv}C)$		2.388 (2)–2.390 (2)	2.389	19
$(Et_3PAgCl)_4$	3 Cl	3.0	2.389 (2)	2.389	20
$(Et_3PAgBr)_4$	3 Br	2.8	2.402 (5)	2.402	20
$[Ag(P(OMe)_3)_2NO_3]_2$	1 P + 2 O	3.0	2.411 (3)–2.412 (3)	2.411	21
$(Ph_3PAgBr)_4$	3 Br	2.8	2.415 (5)–2.429 (2)	2.422	22
$(Mo_2S_3Ag_4)(PPh_3)_4$	3 S	2.5	2.406 (2)–2.438 (3)	2.422	23
$C_{18}H_{10}(CH_2PPh_2)_2AgCl$	1 P + 1 Cl	2.5	2.411 (3)–2.458 (3)	2.434	24
$(Et_3PAgI)_4$	3 I	2.5	2.438 (2)	2.438	25
$[(CH_2(PPh_2)_2)_3Ag_3Br_2]Br$	1 P + 2 Br	2.6	2.413 (8)–2.459 (8)	2.441	49
$(Ph_3PAgI)_4 \cdot 1.5CH_2Cl_2$	2 I, 3 I	2.5	2.430 (3)–2.454 (3)	2.442	26
$[Ag(PPh_2Et)_2]_2Ni(S_2C_2(CN)_2)_2$	1 P + 2 S	2.4	2.439 (2)–2.459 (2)	2.449	27
$(Ph_3PAgI)_4$	3 I	2.5	2.455 (4)–2.462 (5)	2.458	26
$[S(EtPPh_2)_2AgI]_2$	1 P + 2 I	2.4	2.461 (2)	2.461	28
$[Ag(PPh_3)_2]_3Fe(O_2C_2S_2)_3$	1 P + 2 S	2.4	2.455 (2)–2.480 (2)	2.467	29
$[Ag(C_{36}H_{30}P_2)Cl]_2$	1 P + 2 Cl	2.7	2.467 (2)–2.472 (2)	2.469	30
$[S(EtPPh_2)_2AgCl]_2$	1 P + 2 Cl	2.7	2.461 (4)–2.481 (4)	2.471	31
$[(Ph_3P)_2Ag]_3Al(O_2C_2S_2)_3$	1 P + 2 S	2.4	2.465 (4)–2.492 (3)	2.478	28
$[(Ph_3P)_2AgNCS]_2$	1 P + 1 N + 1 S	2.5	2.455 (3)–2.503 (5)	2.479	32
$(n\text{-}C_3H_7)_3PAgSCN$	1 P + 1 N + 1 S	2.5	2.48 (3)	2.48	33
$[Ag(PPh_3)_2]_2Ni(S_2C_2(CN)_2)_2$	1 P + 2 S	2.4	2.465 (3)–2.504 (4)	2.484	34
$[C_5H_{10}(PPh_2)_2AgCl]_2$	1 P + 2 Cl	2.7	2.472 (3)–2.499 (4)	2.489	35
$PhC{\equiv}CAgPMe_3$	1 P + 1 $\pi(C{\equiv}C)$		2.490 (4)	2.490	36
$[Ag(PPh_3)_2]_2Ni(S_2C{=}C(CN)_2)_2$	1 P + 2 S	2.4	2.463 (5)–2.519 (5)	2.491	34
$(Ph_3P)_4Ag_2Br_2$	1 P + 2 Br	2.6	2.479 (6)–2.513 (7)	2.496	22
Ag_3P_{11}	3 P	2.1	2.471 (7)–2.612 (4)	2.535	b

[a] The second column lists the other (besides the one P) neighbors of the Ag atoms, and the third column their average Pauling electronegativity $\bar{\chi}$. [b] This work.

atoms with two Ag and two P neighbors obtain oxidation number −1. The resulting oxidation numer of the Ag atoms is +1. All bonds are saturated, and the compound should be diamagnetic and semiconducting. Indeed Haraldsen[9] found "AgP_3" to be diamagnetic which is confirmed by our measurements. There remains little doubt that his "AgP_3" actually corresponds to the compound described in the present work. Not only is there excellent agreement in the densities, the tensiometric studies[1] actually indicated a somewhat higher P content, and the formula AgP_3 was apparently only adopted to obtain a simple atom ratio.

Bond Lengths. The Ag–P bond lengths vary between 2.47 and 2.61 Å with average lengths of 2.576, 2.502, and 2.527 Å for Ag(1), Ag(2), and Ag(3), respectively. The shortest Ag–Ag interaction with 3.70 Å for Ag(1)–Ag(3) is negligible. The relatively high variation in the average Ag–P distances is surprising. It may possibly be rationalized by strains in the structure and by the high polarizability of Ag atoms. The thermal parameters of the Ag atoms are high, and although their absolute values may be affected by systematic errors of the data, they are higher than those of the P atoms. This is opposite of what is usually observed for transition metal polyphophides, e.g., CrP_4,[10] MnP_4,[11] ReP_4,[12] FeP_4,[13] or RuP_4.[14] The relatively large thermal amplitudes of the Ag atoms give an indication of the weak directional character of the Ag–P bonds. In this context one is reminded of the large number of Ag solid electrolytes with exceptionally high mobility of the Ag atoms which also is attributed[15] to the high polarizability of Ag(I).

The overall average Ag–P bond length of 2.535 Å in Ag_3P_{11} is greater than that of any Ag–P bond known so far. It can be seen from Table V that in general the shortest Ag–P bonds are found when the other ligands of Ag are atoms like O or Cl with high electronegativity. With decreasing electronegativity of the other ligands the bond lengths of the Ag–P bonds increase and become greatest in Ag_3P_{11} where Ag atoms are surrounded solely by P atoms, the ligands with the lowest electronegativity of Table V (occasionally disregarding weakly bonded second nearest metal neighbors). This correlation was already noted[18,20] for the series $(Et_3PAgX)_4$ and $(Ph_3PAgX)_4$.

The P–P bond lengths vary between 2.173 and 2.273 Å. The weighted average P–P bond length is 2.209 Å which corre-

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sponds to the usual average bond lengths of 2.22 ± 0.02 Å for P–P single bonds found in elementary P modifications[37] and other polyphosphides.[10–14,38]

Relation to Other Transition Metal Polyphosphides. It is illuminating to discuss the structure and bonding characteristics of Ag_3P_{11} together with the structures of the transition metal polyphosphides of the highest P content. In all these compounds optimal use is made of the transition-metal d orbitals which are either fully occupied with nonbonding electrons or utilized for metal–phosphorus and metal–metal bonding.

In CrP_4 and MoP_4,[10] the three modifications of MnP_4,[11,39] ReP_4,[12] the two modifications of FeP_4,[13,40] RuP_4, and OsP_4[14] the transition-metal atoms are approximately octahedrally surrounded by P atoms, and the P atoms are tetrahedrally bound to metal and P atoms. Simple conventional covalent bonding models rationalize the near-neighbor environments in these compounds.[10–14] The transition-metal atoms all have formal oxidation number +2 and use two d orbitals ($d_{x^2-y^2}$ and d_{z^2}) for the six bonds to the P ligands ("d^2sp^3 hybrid"). The other three d orbitals either are fully occupied with nonbonding electrons or are involved in metal–metal bonding. Thus Cr in CrP_4 with a d^4 system is using one d (e.g., the d_{xy}) orbital to hold two nonbonding electrons. The two remaining electrons use the two remaining (d_{xz} and d_{yz}) orbitals which overlap with the corresponding ones of neighboring Cr atoms, thus forming a continuous chain of Cr–Cr bonds via edges of the edge-sharing CrP_6 octahedra. Mn and Re in their tetra(poly)-phosphides obtain a d^5 system and form pairs. Fe, Ru, and Os with d^6 systems have the three $\sim t_{2g}$ orbitals fully occupied with nonbonding electrons, and metal–metal bonding is no longer possible.

A compound "CoP_4" with octahedral and tetrahedral coordination of the Co and P atoms does not form, apparently because the additional electron per formula unit would now need to be accommodated in an antibonding state which is, of course, a destabilizing factor.[41] The actual compositions found so far for the Co, Rh, and Ir compounds with the highest P content are CoP_3, RhP_3, and IrP_3.[42] In these isostructural compounds the transition-metal atoms are again six-coordinate to P, and the P atoms are approximately tetrahedrally coordinated. The metal atoms have formal oxidation number +3 and obtain a d^6 system. Again all d orbitals are fully employed in the same way as in FeP_4 and RuP_4, but the composition is now changed. In agreement with the bonding model the compounds are diamagnetic and semiconducting or semimetallic.[42,43]

In going further to the right in the periodic table, one arrives at NiP_3 which has the same structure as CoP_3 but has metallic conductivity, thus accommodating the additional electron in a delocalized state.[42,44] In PdP_2[45] the Pd atoms are in square-planar coordination and have a d^8 system. The remaining d orbital is involved in Pd–P bonding ("dsp^2 hybrid"). Thus again all d orbitals are utilized.

The bonding characteristics of the polyphosphides of the coinage metals can also be rationalized nicely to a first approximation with such simple considerations. In Ag_3P_{11} the Ag atoms obtain a d^{10} system. Thus all d states are used to hold 10 nonbonding electrons, and only the 5s and 5p orbitals are available for bonding to the P atoms. The coordination is now tetrahedral ("sp^3 hybrid"). Similarly the tetrahedral bonds of the P atoms in Ag_3P_{11} can be rationalized with a sp^3 hybrid of the 3s and 3p states.

For saturation of tetrahedral bonds of four-coordinated Ag and P atoms only three P atoms per Ag atom are required (composition "AgP_3" = "Ag_3P_9"). The additional P(2) atoms in Ag_3P_{11} with three P neighbors and a lone pair have near-neighbor environments like the P atoms in elemental P modifications. They may thus be considered as "elemental" P which dilutes the saturated composition "AgP_3". Apparently the additional "elemental" P in Ag_3P_{11} is needed to obtain a three-dimensional network without too much strain.

In Au_2P_3 the Au atoms are linearly coordinated to two P atoms (again a d^{10} system, "sp hybridization"), two-thirds of the P atoms have four near neighbors, but in the remaining one-third the P atoms have only three neighbors and a lone pair.[46] These P atoms may again be considered as "elemental" P diluting the saturated composition "Au_2P_2". Thus with Ag_3P_{11} and Au_2P_3 we observe the first transition metal polyphosphides which have a higher P content than needed to satisfy the near-neighbor bonding requirements of the metal atoms. Such higher P contents, however, are observed in many polyphosphides of the main-group and rare-earth elements.[38] It remains to be demonstrated whether such "higher" polyphosphides of other transition metals could not be prepared with special techniques.

Defect Tetrahedral Structure. The Ag_3P_{11} structure may be derived from the diamond structure by ordering of Ag atoms, P atoms, and vacancies on the positions of the carbon atoms in the diamond. The transformation matrix from the face-centered cubic diamond cell to the monoclinic cell of Ag_3P_{11} is $2,2,0//-1,1,0//-^1/_2,-^1/_2,0$, and the lattice constants of the monoclinic cell in terms of the diamond cell are $a \approx 2(2^{1/2})a_d$, $b \approx 2^{1/2}a_d$, $c \approx (3/2)^{1/2}a_d$, and $\beta \approx 90° + \sin^{-1}(1/3^{1/2})$, ideally 125.26°. The cell volume of the monoclinic cell of Ag_3P_{11} corresponds to that of four face-centered diamond cells. Ag_3P_{11} may be considered as a defect tetrahedral compound[47,48] in that four atomic sites which are occupied in the diamond are vacant in Ag_3P_{11}. These four positions are approximately at 0.16, 0, 0.3; 0.66, 0.5, 0.3; 0.16, 0.5, 0.3; 0.66, 0, 0.3 of the monoclinic cell and one could denote the formula with $Ag_6\square_4P_{22}$; i.e., of the 32 diamond-like positions in Ag_3P_{11} four are unoccupied. Nevertheless there are not $4 \times 4 = 16$ lone pairs pointing at these positions because some of the atoms adjacent to the voids have their "lone pairs" overlapping (and only half-filled), thus forming normal two-electron bonds. In this way the compound obtains five-membered rings formed by P(2), P(2), P(3), P(7), P(3), and P(2), P(2), P(4), P(6), P(4). The six-membered rings are all in chair configuration as is appropriate for a structure derived from the diamond structure. Since there are only four lone pairs per cell—at the P(2) atoms—the Parthé formula for this defect tetrahedral structure is $1_6 0 5_{22}$. Here one zero stands for four lone pairs and the Ag and P atoms are symbolized by the number of valence electrons they contribute.

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Supplementary Material Available: Listings of structure factor amplitudes and anisotropic thermal parameters of the Ag atoms (11 pages). Ordering formation is given on any current masthead page.

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Comparison between d^1–d^1 and d^9–d^9 Magnetic Exchange in Binuclear Vanadyl and Copper(II) 1,3,5-Triketonates. Crystal and Molecular Structure of $Cu_2(DANA)_2(py)_2$

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The binuclear complex bis(1,5-bis(*p*-methoxyphenyl)-1,3,5-pentanetrionato)bis(pyridine)dicopper(II), $Cu_2(DANA)_2(py)_2$, has been crystallized and examined by X-ray diffraction techniques. The structure consists of binuclear monomers in which each copper atom is bound to four ketonic oxygen atoms and an axial pyridine. Crystal data is as follows: $P2_1/c$, $a = 8.413$ (2) Å, $b = 22.791$ (5) Å, $c = 11.109$ (2) Å, $\beta = 91.60$ (2)°, $Z = 2$, $R_1 = 0.035$, $R_2 = 0.050$. The d^9–d^9 system, $Cu_2(DANA)_2(py)_2$, exhibits strong intramolecular antiferromagnetism ($-2J = 825$ cm^{-1}) resulting in nearly diamagnetic behavior at room temperature. These results are contrasted to the structurally related d^1–d^1 system, $(VO)_2(DANA)_2$, in which the value of $-2J$ is 160 cm^{-1}. The magnetic differences are discussed in terms of the orbital symmetry of the exchanging electrons.

Introduction

An intriguing feature of the 1,3,5-triketones as a class of ligands is their ability to bind two metal ions in a relatively constant ligand environment.[1-8] In addition, in all cases studied to date in which the individual metal ions are paramagnetic, the binuclear molecules exhibit a net antiferromagnetism due to superexchange interactions. The nature of the superexchange interactions is presumably determined by the bonding interactions taking place between the metal ions and the two triketonate moieties which invariably exist in a very nearly coplanar arrangement in these complexes. Since bond lengths and angles in the parts of the molecules associated with the metal ions are found to be very similar for a variety of metal ions, differences in magnetic properties should be largely attributable to differences in the symmetry of the metal orbitals containing unpaired electrons. Hence, by investigating the magnetic properties and structures of a series of binuclear 1,3,5-triketonates, it should be possible to make definitive statements about how magnetic exchange is influenced by the orbital symmetry of exchanging electrons. Perhaps the simplest comparison to be made is this regard is a d^1–d^1 system to a d^9–d^9 system since both contain the same number of unpaired electrons and there are no significant complications due to spin–orbit contributions. This study was undertaken to compare the magnetic properties of structurally similar binuclear VO^{2+} and Cu(II) complexes containing the same 1,3,5-triketonate ligand.

Experimental Section

Ligand Synthesis. The ligand 1,5-bis(*p*-methoxyphenyl)-1,3,5-pentanetrione, H_2DANA,[9] was prepared by the method of Miles, Harris, and Hauser.[10]

Bis(1,5-bis(*p*-methoxyphenyl)-1,3,5-pentanetrionato)dioxovanadium(IV), $(VO)_2(DANA)_2$. A solution of 0.79 g (0.005 mol) of VCl_3 to 100 mL of absolute ethanol was prepared by refluxing and stirring. To this was added a solution of 1.6 g (0.005 mol) of H_2DANA dissolved in 100 mL of absolute ethanol followed by 0.23 g (0.01 mol) of Na metal dissolved in 50 mL of absolute ethanol. The solution was refluxed for 18 h and filtered to separate NaCl. The filtrate was concentrated under reduced pressure to 50 mL and cooled at −10 °C for 24 h. The resulting red powder melts with decomposition at 330–335 °C. Anal. Calcd for $C_{38}H_{32}O_{12}V_2$: C, 58.31; H, 4.09; V, 13.04. Found: C, 58.49; H, 4.59; V, 12.40.

Bis(1,5-bis(*p*-methoxyphenyl)-1,3,5-pentanetrionato)dicopper(II), $Cu_2(DANA)_2$. A solution of 1.0 g (0.005 mol) of $Cu(C_2H_3O_2)_2{\cdot}H_2O$ in 50 mL of methanol was heated, and a solution of 1.6 g (0.005 mol of H_2DANA in 25 mL of $CHCl_3$ was added dropwise. A green precipitate formed immediately. It does not melt to 300 °C. Anal. Calcd for $C_{38}H_{32}O_{10}Cu_2$: C, 58.76; H, 4.12. Found: C, 58.65; H, 4.25.

$Cu_2(DANA)_2(py)_2$. The green $Cu_2(DANA)_2$ was dissolved in a small amount of pyridine. The solution was exaporated to dryness in an efficient hood to yield dark blue-green crystals of $Cu_2(DANA)_2(py)_2$. This product was redissolved in a minimum of pyridine which was concentrated at room temperature to about 50% of the original volume. Large dark blue crystals, suitable for single-crystal X-ray structure determination resulted. Anal. Calcd for $C_{38}H_{32}O_{10}Cu_2(C_5H_5N)_2$: C, 61.67; H, 4.50; N, 3.00. Found: C, 61.75; H, 4.61; N, 2.96.

Magnetic Susceptibility. Magnetic susceptibility as a function of temperature was measured with use of the standard Faraday technique

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