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Tribromohydroxyphosphonium Hexafluorometalate: Synthesis, Spectroscopic Characterization, and Crystal Structure of $Br_3POH^+AsF_6^-$

Rolf Minkwitz* and Markus Dzyk

Anorganische Chemie, Fachbereich Chemie der Universität Dortmund, 44221 Dortmund, Germany

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The reaction of tribromophosphine oxide in the superacidic systems XF/MF_5 ($X = H$, D; $M = As$, Sb) leads to tribromohydroxyphosphonium hexafluorometalates. The structure was successfully elucidated in the case of tribromohydroxyphosphonium hexafluoroarsenate. $Br_3POH^+AsF_6^-$ crystallizes in the orthorhombic space group *Pnma* (No. 53 with $a = 1292.5(1)$ pm, $b = 871.6(1)$ pm, and $c = 845.0(1)$ pm) with four formula units per cell. The Raman, IR, ^1H NMR, and ^{31}P NMR spectra of $Br_3POX^+MF_6^-$ ($X = H$, D; $M = As$, Sb) are reported.

Introduction

The reactions of halogen−phosphorus compounds in strongly acidic media have been studied since the 1960s.[1−7] In the case of tribromophosphine oxide, $POBr_3$, Paul et al. found, using cryoscopic and conductance techniques, that it has a predominantly basic oxygen atom, which is incompletely protonated in HSO_3F, but completely protonated by $H_2S_2O_7$ to form the Br_3POH^+ cation.[3] Dillon et al. and Hibbert et al., respectively, used ^{31}P NMR spectroscopy to investigate the behavior of $POBr_3$ in different acidic media.[5,6] The $\delta(^{31}P)$ value of $POBr_3$ has been shown to be markedly sensitive to acid strength. Dillon and co-workers found that in H_2SO_4 solutions a solvolysis of the P−Br bonds of the Br_3POH^+ cation to form $P(OH)_4^+$ takes place, while Br_3POH^+ in chloro- and fluorosulfuric acid is stable to solvolysis in these solvents.[6] Dillon et al. observed also the formation of the Br_3POH^+ cation as an intermediate in the reaction of PBr_3 or PBr_5 with acidic solvents such as H_2SO_4 (100%), oleum, or HSO_3Cl.[7] No attempts were yet made to isolate the Br_3POH^+ cation in the form of a phosphonium salt.

In recent years our research group was successful in isolation and characterization of such unstable onium salts by protonation of various precursors at low temperature in the superacidic system HF/MF_5 ($M = As$, Sb).[8−10] Within the scope of our investigations of the behavior of phosphorus compounds in the superacidic system HF/MF_5 ($M = As$, Sb) we isolated a series of $Br_3POX^+MF_6^-$ salts ($X = H$, D; $M = As$, Sb) and characterized them by X-ray diffraction and vibrational and NMR spectroscopy.[11−13]

Experimental Section

CAUTION. Avoid contact with these compounds, and note that the hydrolysis of AsF_6^- and SbF_6^- salts forms HF, which burns the skin and causes irreparable damage. Safety precautions should be taken when using and handling these materials!

Apparatus and Materials. All synthetic work and sample handling were performed by employing standard Schlenk techniques and a standard vacuum line (stainless steel or glass). Drying of HF and DF were carried out with fluorine (1.5 bar) in a stainless steel bomb. AsF_5 was synthesized from As and F_2. SbF_5 (Merck) was distilled repeatedly before use. The syntheses of Br_3PO and DF, using D_2SO_4 and CaF_2, were carried out by known literature methods.[14] Reactions in HF were carried out in a KEL-F reactor with a KEL-F valve. The Raman spectra were recorded on a Jobin Yvon T64000 spectrometer using an Ar^+ laser (514.5 nm) from Spectra Physics. The spectra were obtained in a glass cell cooled with solid CO_2.[15] Infrared spectra were recorded on a Bruker IFS 113v spectrophotometer. Spectra were obtained from a coated CsBr

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* Author to whom correspondence should be addressed. E-mail: minkwitz@citrin.chemie.uni-dortmund.de.

(1) Gillespie, R. J.; Kapoor, R.; Robinson, A. *Can. J. Chem.* **1966**, *44*, 1203.
(2) Paul, R. C.; Kapila, V. P.; Malhotra, K. C. *J. Chem. Soc. A* **1970**, 2267.
(3) Paul, R. C.; Kapila, V. P.; Puri, j. K.; Malhotra, K. C. *J. Chem. Soc. A* **1971**, 2132.
(4) Paul, R. C.; Paul, K. K.; Malhotra, K. C. *J. Inorg. Nucl. Chem.* **1972**, *34*, 2523.
(5) Dillon, K. B.; Nisbet, M. P.; Waddimgton, T. C. *J. Chem. Soc., Dalton Trans.* **1978**, 1455.
(6) Hibbert, R. C.; Logan, N. *J. Chem. Soc., Dalton Trans.* **1985**, 865.
(7) Dillon, K. B.; Nisbet, M. P.; Waddington, T. C. *J. Chem. Soc., Dalton Trans.* **1979**, 883.
(8) Minkwitz, R.; Schneider, S. *Angew. Chem., Int. Ed.* **1999**, *38*, 714.
(9) Minkwitz, R.; Hirsch, C.; Hartl, H. *Angew. Chem., Int. Ed.* **1998**, *37*, 1681.
(10) Minkwitz, R.; Schneider, S.; Preut, H. *Angew. Chem., Int. Ed.* **1998**, *37*, 494.
(11) Minkwitz, R.; Schneider, S. *Angew. Chem., Int. Ed.* **1999**, *38*, 210.
(12) Minkwitz, R.; Schneider, S.; Kornath, A. *Inorg. Chem.* **1998**, *37*, 1345.
(13) Minkwitz, R.; Bäck, B. *Z. Naturforsch.* **1994**, *49b*, 221.
(14) Klement, R. In *Handbuch der präparativen anorganischen Chemie*, 2nd ed.; Enke, F., Brauer, G., Ed.; Stuttgart, 1975.
(15) Werner, A. Dissertation, University of Dortmund, 1988.

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plate in a low-temperature cuvette.[16] NMR spectra were recorded with a Bruker DPX spectrometer. Single crystals were placed in Lindemann capilllaries in a cooled stream of dry nitrogen, and an X-ray diffraction study was carried out at −100 °C using a Nonius Kappa CCD-(1152 × 1242 pixel) diffractometer.

Synthesis of $Br_3POX^+MF_6^-$ (X = H, D; M = As, Sb). In a typical reaction, 5 mL of XF (X = H, D) was distilled into a Kel-F reactor at −196 °C, followed by 0.2 mmol of MF_5 (M = As, Sb). The mixture was warmed to 20 °C to form the superacid. The reactor was cooled to −196 °C, and $POBr_3$ (0.2 mmol) was added. The mixture was warmed to −78 °C. After removal of volatile compounds at −78 °C under dynamic vacuum (during 7 days) colorless solids, stable up to −30 °C (arsenate) and −25 °C (antimonate), respectively, were obtained. NMR spectra were recorded in SO_2 at −60 °C; standards are TMS for ^1H and 85% H_3PO_4 for ^{31}P. The obtained data are as follows. **$Br_3POH^+AsF_6^-$:** ^1H, 10.5 (s); ^{31}P, −52.7(s). **$Br_3POH^+SbF_6^-$:** ^1H, 10.3(s); ^{31}P, −52.2(s).

Results and Discussion

Synthesis and Properties. Tribromohydroxyphosphonium hexafluorometalates can be isolated at −78 °C by protonation of tribromophosphine oxide in the superacidic systems XF/MF_5 (X = H, D; As, Sb) with stoichiometric amounts of pentafluorometalates (eq 1). The resulting colorless salts are

$$Br_3PO + XF + MF_5 \xrightarrow{XF/-78\ °C} Br_3POX^+MF_6^- \qquad (1)$$

$$(X + H, D; M + As, Sb)$$

sensitive toward moisture and have low solubility in sulfur dioxide at −60 °C and HF at −78 °C. The solids are stable for several months at −70 °C under a nitrogen atmosphere, decomposing at −30 °C in the case of the hexafluoroarsenates and at −25 °C in the case of hexafluoroantimonates back to the precursors.

X-ray Crystal Structure of $Br_3POH^+AsF_6^-$. Tribromohydroxyphosphonium hexafluoroarsenate crystallizes in the orthorhombic space group *Pnma* (No. 53 with a = 1292.5(1) pm, b = 871.6(1) pm, c = 845.0(1) pm) with four formula units per unit cell. The crystal structure was solved via the Patterson method and successive difference Fourier syntheses. For refinement, full-matrix least-squares methods were applied. The hydrogen atom was taken from Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement parameters. The coordinates of the hydrogen atom were held on and an isotropic displacement parameter was fixed for the hydrogen atom. For the data reduction, structure solution, and refinement, programs in the SHELXTL package, PLATON, MISSYM, and PARST were used.[17−20] The crystal data are summarized in Table 1.[21] Bond lengths and selected angles are shown in Table 2. Figure 1 shows the tribromohydroxyphosphonium cation with a hydrogen bond [O···F(2): 249.5(9) pm] and weak interionic contacts to the nearest fluorine atoms of the anions, and the arrangement of $Br_3POH^+AsF_6^-$ in the unit cell is depicted in Figure 2.

Table 1. Crystal Data and Structure Refinement for $Br_3POH^+AsF^-_6$

	$Br_3POH^+AsF_6^-$
space group (No.)	*Pnma* (53)
cryst syst	orthorhombic
a [Å]	12.925(1)
b [Å]	8.716(1)
c [Å]	8.485(1)
vol [Å^3]	955.9(2)
density (calcd) [g cm^{-3}]	2.562
Z	4
formula mass [g mol^{-1}]	476.63
abs coeff [cm^{-1}]	163.09
temp [°C]	−100(2)
wavelength [Å]	0.71073
R^a [$I > 2\sigma(I)$]	R1 = 0.0322; wR2 = 0.0646
R^a (all data)	R1 = 0.0509; wR2 = 0.0799

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. Refinement method: full matrix, least-squares calculations based on F^2.

Table 2. Bond Lengths [pm], Selected Angles [deg], and Interionic Distances [pm] for $Br_3POH^+AsF_6^-$ [a]

P−O	153.2(6)	O−P−Br(1)	111.7(3)
P−Br(1)	211.5(3)	O−P−Br(2)	108.5(2)
P−Br(2)	211.2(2)	Br(2)−P-Br(1)	109.6(7)
As−F(1)	174.8(4)		
As−F(2)	169.0(5)	F(5)−As−F(5a)	176.4(3)
As−F(3)	172.3(5)	F(1)−As−F(2)	89.5(2)
As−F(4)	168.7(5)	F(2)−As−F(4)	92.6(2)
As−F(5)	168.7(4)	F(4)−As−F(3)	90.6(2)
F(1)···O	249.5(9)	F(3)−As−F(1)	87.3(2)
Br(1)···F(3)	303.8(4)		
Br(2)···F(3)	305.8(3)		

[a] Symmetry operation: a = x, 0.5 − y, z.

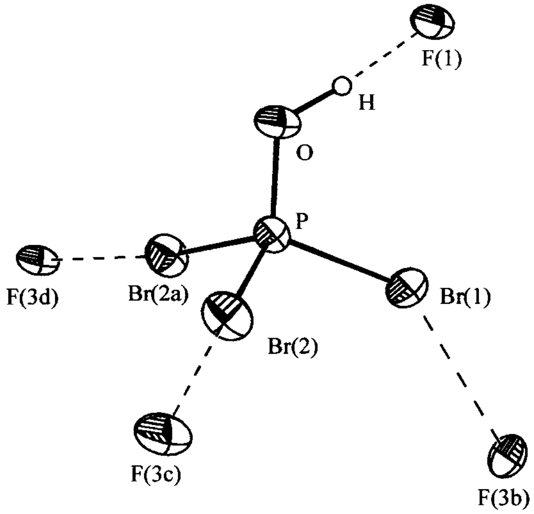

Figure 1. Fragment of the structure of $Br_3POH^+AsF_6^-$, showing the Br_3POH^+ cation with interionic contacts (50% probability ellipsoids for the non-hydrogen atoms); symmetry operations: a = x + 0.5, −y + 1, z; b = x, y + 1, z; c = −x + 1.5, −y + 0.5, z; d = −x + 0.5, −y + 0.5, z.

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(16) Bayersdorfer, L.; Minkwitz, R.; Jander, J. *Z. Anorg. Allg. Chem.* **1972**, *392*, 137.

(17) Sheldrick, G. M. *SHELXTL PLUS, An Integrated System for Solving, Refining and Displaying Structures from Diffraction Data*; Universität of Göttingen: Göttingen, Germany, 1987.

(18) Spek, A. L. The EUCLID Package. In *Computional Crystallography*; Sayre, D., Ed.; Clarendon Press: Oxford, 1982; p 528.

(19) Le Page, Y. *J. Appl. Crystallogr.* **1987**, *20*, 264.

(20) Nardelli, M. *Comput. Chem.* **1983**, *7*, 95.

(21) Crystallographic data for the structure reported in this paper have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissentschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldhafen, under the number CSD-412033.

Table 3. Raman and IR Frequencies and Their Possible Assignment for $Br_3POX^+MF_6^-$ (X = H, D; M = As, Sb)[a]

$Br_3POD^+AsF_6^-$		$Br_3POD^+SbF_6^-$		$Br_3POH^+AsF_6^-$		$Br_3POH^+SbF_6^-$		
IR −50 °C	Raman −78 °C	IR −50 °C	Raman −78 °C	IR −50 °C	Raman −78 °C	IR −50 °C	Raman −78 °C	possible assignment
2052 w	n.o.	2030 w	n.o.	2556 m	n.o.	2713 m	n.o.	ν(OX)
1213 w		1206 w				1302 w		δ(POX)
1039 m	1039 (6)	1037 m	n.o.	1118 m	n.o.	1157 w	n.o.	δ(POX)
						1063 w		δ(POX)
1002 m								δ(POX)
						1012 m		δ(POX)
809 s	n.o.	818 m	n.o.	863 m	n.o.	880 m	n.o.	ν(PO)
592 m	589 (8)	591 m	572(10)	597 w	591 (12)	595 w	580 (5)	δ(POX)
553 m								ν_{as}(PBr)
524 s	520 (7)	525 vs	529 (15)	524 vs	523 (10)	528 vs	510 (5)	ν_{as}(PBr)
			512 (18)					ν(PBr)
445 m	405 (8)	446 m	484 (11)	452 w	445 (45)	n.o.	475 (3)	ν(PBr)
				390 vs	382 (48)			ν(PBr)
345 s	342 (100)	353 s	332 (16)	353 vs	346 (100)	355 s	349 (100)	ν_s(PBr)
295 m	294 (13)	280 vs	289 (15)	312 w	n.o.	280 vs	281 (25)	δ(OPBr)
247 m	249 (19)	265 m	280 (16)	n.o.	251 (71)	249 m	262 (18)	$\rho(PBr_3)$
	226 (21)		215 (15)		223 (76)		199 (95)	$\rho(PBr_3)$
	187 (81)		202 (31)		189 (96)		186 (12)	$\delta_s(PBr_3)$
	168 (16)		n.o.		162 (22)		144 (40)	$\delta_{as}(PBr_3)$
					150 (18)			$\delta(PBr_3)$
	139 (43)		146 (8)		137 (75)		136 (15)	$\delta_{as}(PBr_3)$
	125 (62)		110 (9)		125 (69)		125 (50)	$\delta(PBr_3)$
	720 (9)			729 s				MF_6^-
717 vs								MF_6^-
702 vs					701 (75)			MF_6^-
	698 (22)	680 vs		699 s				MF_6^-
668 s	671 (21)	660 vs		661 m	673 (89)	678 s	672 (10)	MF_6^-
		636 s	646 (100)			661 s	648 (31)	MF_6^-
						636 s	641 (12)	MF_6^-
538 s	540 (7)	555 m		547 s		553 m		MF_6^-
392 s	405 (8)			406 s	410 (43)	394 w		MF_6^-
372 m	377 (14)	385 w		379 s	378 (50)			MF_6^-
			300 (11)			321 m	310 (3)	MF_6^-
		246 w						MF_6^-

[a] vs = very strong; s = strong; w = weak; n.o. = not observed; X = H, D.

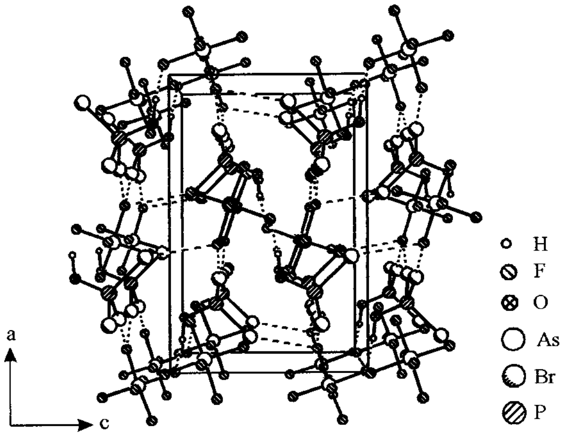

Figure 2. Structure of $Br_3POH^+AsF_6^-$, showing the arrangement in the crystal lattice.

The cation has C_s symmetry and the anion a distorted octahedral structure. The PO bond length of 153.2(6) pm lies in the range between typical PO single bonds and double bonds and is lengthened compared to the precursor [$POBr_3$: PO, 147.0(3)].[22,23] The phosphorus−bromine bond lengths are equal (211.5(3) and 211.2(2) pm, respectively) and by comparison to the precursor are shortened [$POBr_3$: PBr, 213.1(6)−214.7(1) pm].[22,23] With angles between 108.5(2)° and 111.7(3)° the phosphorus has a distorted trigonal pyramidal environment and the distortion from ideal trigonal pyramidal shape is less than it was measured for $POBr_3$ in the solid state.[22,23]

There are interionic bromine−fluorine contacts of 303.8(4)−305.8(3) pm. Together with the hydrogen bond [O···F(1): 249.5(9) pm], the bromine−fluorine contacts result in the formation of a three-dimensional linkage of anions and cations. The As−F bond lengths of the anion which are involved in the hydrogen bond and the Br···F contacts are lengthened compared to the other As−F lengths, and with maximum deviations from ideal octahedron angles up to 3.6°, a distorted octahedral structure results for the AsF_6^- anions in the $Br_3POH^+AsF_6^-$ salt.

Vibrational Spectra. The infrared and Raman spectra of the $Br_3POD^+AsF_6^-$ are shown in Figure 3. The observed frequencies of the $Br_3POX^+SbF_6^-$ salts (X = H, D; M = As, Sb) are summarized in Table 3. The assignments for the Br_3POX^+ cation were made by comparison to the precursor and the $Cl_3POX^+MF_6^-$ salts.[24,25]

Assuming that the Br_3POX^+ cation has C_s point symmetry, then $8\ A_1 + 4\ A_2 = 12$ fundamental vibrations are expected. All modes were active in both Raman and IR spectra. On

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(22) Templeton, L.; Templeton, D. *Acta Crystallogr.* **1971**, *B27*, 1678.
(23) Olie, K.; Mijlhoff, F. C. *Acta Crystallogr.* **1969**, *B25*, 974.
(24) Nyquist, R. A. *Appl. Spectrosc.* **1987**, *41*, 272.
(25) Minkwitz, R.; Dzyk, M. *Eur. J. Inorg. Chem.*, submitted for publication.

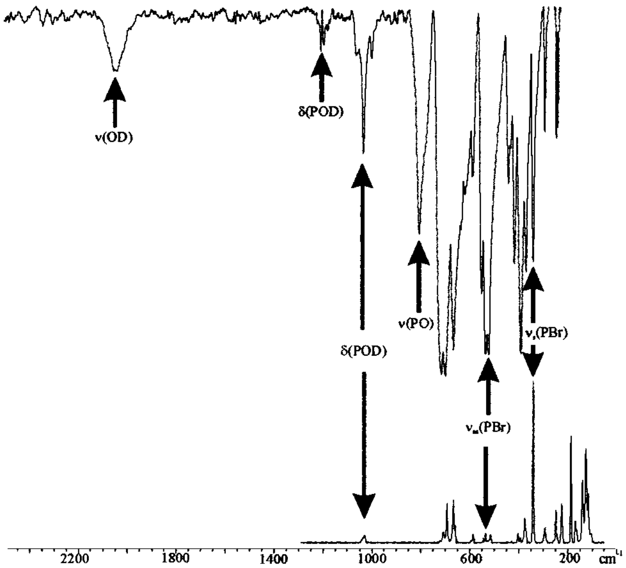

Figure 3. IR and Raman spectra of $Br_3POD^+AsF_6^-$.

account of the window material (CsBr) in the low-temperature cuvette for IR measurements, vibrational modes below 220 cm^{-1} were not detectable.

The OH and OD stretching modes are detected in the range 2720−2030 cm^{-1}, respectively. The corresponding POX (X = H, D) deformation modes are observed in the region 1002−1160 cm^{-1} (A_1) and at 580 cm^{-1} (A_2). Important for the spectroscopic evidence of the Br_3POX^+ cation is the position of the PO stretching mode. Compared to the precursor the PO stretching mode is shifted 400 cm^{-1} to lower wavenumbers, which is corresponding to protonation of Br_3PO at the O atom.[24] The PBr stretching modes are observed in the range 332−530 cm^{-1}. The symmetric stretching modes are at the same position as by the precursor.[24] In contrast to that the asymmetric stretching modes are shifted up to 60 cm^{-1} to higher wavenumbers in comparison to the analogous vibrations in phosphoroxybromide.[24] In the range 110−312 cm^{-1} the PBr_3 deformation modes are detected. According to the interactions between the bromine and fluorine atoms (see above) there were more vibrational modes of the PBr_3 group detected than would be expected. Because of cation−anion interactions, the MF_6^- ions (M = As, Sb) do not show ideal O_h symmetry. This lowered symmetry can be seen in the spectra, where splitting of the anion vibrational modes is observed.[26]

Table 4. ^1H and ^{31}P NMR Spectroscopy Data for $Br_3POH^+MF_6^-$ (M = As, Sb) and Literature Data for Br_3PO in Acidic Media

	$\delta(^{31}P)$	$\delta(^1H)$
$Br_3POH^+AsF_6^-$ [a]	−52.7 (s)[b]	10.5 (s)
$Br_3POH^+SbF_6^-$ [a]	−55.2 (s)	10.3 (s)
Br_3PO in H_2SO_4 + 65% SO_3[c]	−57. 9 (s)	
Br_3PO in H_2SO_4 + 25% SO_3[c]	−76.1 (s)	
Br_3PO in H_2SO_4[c]	−80.4 (s)	
Br_3PO[c]	−103.4 (s)	

[a] Measured in SO_2 at −60 °C. [b] (s) = singlet. [c] References 5−7.

^1H and ^{31}P NMR Spectra of $Br_3POH^+MF_6^-$ (M = As, Sb). The ^1H NMR spectra of freshly prepared $Br_3POH^+MF_6^-$ (M = As, Sb) dissolved in SO_2 with TMS as external standard at −60 °C shows a singlet at $\delta = 10.5$ ppm (AsF_6^-) and $\delta = 10.3$ ppm (SbF_6^-) for the hydroxyl group. In the ^{31}P NMR spectra a singlet at $\delta = -52.7$ ppm for the arsenate and $\delta = -52.2$ ppm for the antimonate was observed. The signal when compared to its precursor is more than 51 ppm shifted to lower fields. This result is comparable to the results of Dillon et al. and Hibbert et al., respectively, for the Br_3POH^+ cation formed by protonation of $POBr_3$ in H_2SO_4 or other high acidic solvents (Table 4).[5−7]

Supporting Information Available: Tables listing detailed crystallographic data, atomic positional parameters, and bond lengths and one X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(26) Emara, A. A. A.; Schrobilgen, G. J. *Inorg. Chem.* **1992**, *31*, 1323.