the structure as consisting of layers parallel to the *b–c* plane that contain the Zn(1), P(1), and Ba polyhedra and are linked by the P(2) and Zn(2) polyhedra. Alternatively, there are 2-dimensional slabs running parallel to [101] that contain the Ba, Zn(2), P(1), and P(2) polyhedra, with the Zn(1) atoms in between. Finally, the Zn and P polyhedra join to form a layer of sorts parallel to the *a–b* plane with only the Ba^{2+} ions in between.

Conclusion

Some very simple aqueous reactions of zinc ions and phosphorous acid, together with an alkali or alkaline-earth metal in some cases, have yielded five new compounds with novel structures. This diversity is due, in part, to the Zn^{2+} ion's lack of a strong preference for octahedral versus tetrahedral coordination. The ability of the zinc ion to exist in a variety of coordination environments ($ZnO_4(H_2O)_2$, $ZnO_2(H_2O)_4$, etc.) allows structures to form with different packing arrangements of the tetrahedral HPO_3^{2-} ions, particularly in the presence of a second metal atom. In addition, the regularity of the Zn coordination polyhedra permits symmetrical connectivities with the phosphite groups that are conducive to the formation of infinite chains and sheets. Thus, while copper hydrogen phosphite, $Cu(H_2PO_3)_2$, contains dimers of edge-sharing Jahn–Teller distorted CuO_6 octahedra with four short (1.92–1.98 Å) and two long (2.33, 3.15 Å) Cu–O distances,[28] the analogous Zn compound, $Zn(H_2PO_3)_2 \cdot 3H_2O$, has a unique open framework containing infinite chains of edge-sharing ZnO_6 octahedra bridged by the phosphite groups (Figure 2).

Though the phosphate and phosphite ions both possess tetrahedral geometry, it is perhaps more apt to consider the phosphite as a pyramidal group in its structural chemistry since the H atom that occupies the fourth vertex of the HPO_3 tetrahedron does not bridge to other atoms. The results presented here suggest that, unlike the phosphates, the phosphite structures will tend to have open cavities lined by the phosphite hydrogen atoms, since these behave as "dead ends" in propagating the frameworks. In mixed-metal phosphites, the second metal atom (e.g., Na^+, K^+, etc.) plays a significant role in the framework due to the reduced bridging ability of the phosphite group compared to phosphate. The dependence of the observed framework on the identity of the second metal atom leads to a diversity of structures in the zinc–phosphite system. We are continuing to explore the preparation of new structure types in these phosphite systems.

Acknowledgment. We gratefully acknowledge the Robert A. Welch Foundation for financial support. The single crystal diffractometer was purchased under DOD Grant No. N-00014-86-G-0194.

Supplementary Material Available: Table SI, listing anisotropic thermal parameters and experimental crystallographic details (6 pages); Table SII, listing calculated and observed structure amplitudes (58 pages). Ordering information is given on any current masthead page.

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[28] *Structure Reports*; Calvert, L. D., Trotter, J., Eds.; Oosthoek, Scheltema, Holkema: Utrecht, The Netherlands, 1975; Vol. 39A, p 282.

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Mercury Complexes with One-Dimensional Chain Structures. Syntheses and Crystal Structures of $[Hg(C_5H_4NS)(CH_3CO_2)]_n$, $Hg(C_5H_4NS)_2$, and $Hg(CH_2P(S)Ph)_2$

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Reaction of $Hg(OAc)_2$, $OAc^- = CH_3CO_2^-$, with 1 equiv of mercaptopyridine, C_5H_5NS, in CH_2Cl_2 at 22 °C gives the compound $Hg(OAc)(C_5H_4NS)$ (**1**) in 82% yield. Hg atoms in **1** are bridged by the C_5H_4NS ligand to form a one-dimensional chain complex. Reaction of $Hg(OAc)_2$ with 2 equiv of C_5H_5NS in CH_2Cl_2 at 22 °C produces the complex $Hg(C_5H_4NS)_2$ (**2**) in 92% yield. **1** can be converted to **2** by the addition of 1 equiv of C_5H_5NS. Reaction of $HgCl_2$ with 2 equiv of Li(MTP), MTP = CH_2PPh_2S, in THF at −78 °C gives $Hg(MTP)_2$ (**3**) in 65% yield. The structures of **1**–**3** were determined by single-crystal X-ray diffraction. **2** and **3** form one-dimensional chain structures in the solid with weak Hg–S interactions. **1** crystallizes in the monoclinic space group $P2_1/c$ with $a = 8.693$ (5) Å, $b = 12.991$ (5) Å, $c = 8.110$ (4) Å, $\beta = 103.45$ (4)°, and $Z = 4$. **2** crystallizes in the monoclinic space group $P2_1/n$ with $a = 11.078$ (2) Å, $b = 4.0873$ (6) Å, $c = 12.533$ (2) Å, $\beta = 101.253$ (7)°, and $Z = 2$. **3** crystallizes in the monoclinic space group $C2/c$ with $a = 25.090$ (8) Å, $b = 10.886$ (5) Å, $c = 9.189$ (4) Å, $\beta = 91.83$ (3)°, and $Z = 4$.

Introduction

Syntheses and characterization of one-dimensional chain transition-metal compounds are of great current interest due to their unique and fascinating physical and chemical properties and their important application in catalysis, biological systems, and solid-state chemistry.[1] Extended one-dimensional chain complexes are especially interesting not only because of their possible anisotropic properties but also because of their value as a model for the study of bonding in the solid state.[1,2] Among the known one-dimensional inorganic compounds, square-planar one-dimensional platinum complexes are probably the best studied. Recently a new class of one-dimensional Au^I chain complexes with short metal–metal separations has also been reported.[3,4] Our interest in one-dimensional inorganic polymers and attempts to obtain a better understanding of the metal–metal interactions in such complexes have lead us to synthesize one-dimensional chain mercury compounds. A few one-dimensional chain Hg^{II} compounds are known. However, most of them contain conventional inorganic ligands such as halide, hydroxide, and pseudohalide.[5] Goodgame and co-workers recently reported a very interesting mercury complex, $Hg(C_4H_6NO)_2$, which readily binds to metal

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[1] *Extended Linear Chain Compounds*; Miller, J. S., Ed.; Plenum: New York and London, 1981–1983; Vol. 1–3.

[2] Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 846.

[3] (a) Mazany, A. A.; Fackler, J. P., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 801. (b) Mazany, A. A. Ph.D. Thesis, Case Western Reserve University, 1984. (c) Jones, P. G. *Gold Bull.* **1981**, *14*, 102.

[4] (a) Murray, H. H.; Briggs, D. A.; Garzon, G.; Raptis, R. G.; Porter, L. C.; Fackler, J. P., Jr. *Organometallics* **1987**, *6*, 1992. (b) Wang, S.; Fackler, J. P., Jr.; King, C.; Wang, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 3308.

[5] Wilkinson, G., Abel, E. W., Gillard, R. D., McCleverty, J. A., Eds.; *Comprehensive Coordination Chemistry*; Pergamon Press: Oxford, England, 1987; Vol. 5, Chapter 56.2, p 1047.

Table I. Crystallographic Data for **1**–**3**

	1	**2**	**3**
formula	$C_7H_7HgSO_2N$	$C_{10}H_8HgS_2N_2$	$C_{26}H_{24}HgS_2P_2$
fw	369.79	420.89	663.13
space group	$P2_1/c$	$P2_1/n$	$C2/c$
a, Å	8.693 (5)	11.078 (2)	25.090 (8)
b, Å	12.991 (5)	4.0873 (6)	10.886 (5)
c, Å	8.110 (4)	12.533 (2)	9.189 (4)
β, deg	103.45 (4)	101.253 (7)	91.83 (3)
V, Å^3	890.7 (7)	556.6 (1)	2508 (2)
Z	4	2	4
d_{calc}, g cm^{-3}	2.76	2.51	1.76
μ(Mo Kα), cm^{-1}	178.1	144.3	64.31
radiation (Mo Kα)	λ = 0.71069 Å	λ = 0.71069	λ = 0.71069
temp, °C	22	22	22
trans. coeff: max, min	0.966, 0.283	1.00, 0.671	1.00, 0.482
R^a	0.0499	0.0280	0.0538
R_w^b	0.0604	0.0391	0.0689

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum[w(|F_o| - |F_c|)]^{1/2}]/\sum(w|F_o|)^{1/2}$ $w^{-1} = [\sigma^2(|F_o|) + |g|F_o^2]$.

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3)^a for **1**

atom	x	y	z	U_{iso}
Hg	1490 (1)	7340 (1)	6200 (1)	39 (1)^b
S	−204 (8)	6615 (5)	2408 (10)	46 (3)^b
O(1)	2784 (22)	8531 (12)	4272 (25)	51 (5)
O(2)	4153 (25)	7758 (14)	6511 (27)	63 (5)
N(1)	1878 (22)	5852 (12)	5048 (26)	30 (4)
C(1)	2939 (31)	5139 (19)	5919 (27)	47 (7)
C(2)	3180 (30)	4225 (17)	5198 (35)	40 (6)
C(3)	1394 (32)	4743 (18)	2671 (38)	48 (7)
C(4)	1144 (29)	5672 (17)	3507 (33)	39 (6)
C(5)	2423 (33)	4014 (19)	3580 (38)	50 (7)
C(6)	4084 (29)	8317 (16)	5228 (34)	36 (6)
C(7)	5655 (34)	8643 (21)	4869 (43)	62 (8)

^{a}Estimated standard deviations in the least significant digits are given in parentheses. ^{b}Equivalent isotropic U defined as one-third of the trace of the U_{ij} tensor.

ions through the bidentate 2-pyrrolidone ligand to form a new class of fascinating polymeric macrocyclic bimetallic complexes.[6] This promoted us to explore the synthesis of Hg complexes which contain the deprotonated 2-mercaptopyridine (MPY) or the CH_2PPh_2S (MTP) ligand because both ligands are known to function not only as a monodentate ligand but also as a bidentate ligand.[4,7] We report here the syntheses and crystal structures of three new compounds with the formulas Hg(MPY)(OAc) (OAc = CH_3CO_2), $Hg(MPY)_2$, and $Hg(MTP)_2$. These compounds have one-dimensional chain structures in the solid.

Results and Discussion

Synthesis and Structure of Hg(MPY)(OAc) (1). The acetate ligand in the compound $Hg(OAc)_2$ can be readily protonated and replaced by mercaptopyridine to form free acid. This is apparently driven by the great affinity of the Hg center for the sulfur atom on the MPY ligand. The reaction of $Hg(OAc)_2$ with 1 equiv of mercaptopyridine ligand, C_5H_5NS, in CH_2Cl_2 solution generates the new compound Hg(MPY)(OAc) (**1**) quantitatively. **1** is a colorless compound. The presence of the acetate ligand in **1** was ascertained by the characteristic stretching frequency of the carboxylate group at 1578 cm^{-1} in the IR spectrum and the chemical shift of the CH_3 group at 2.14 ppm in the ^1H NMR spectrum. The structure of **1** was determined by single-crystal X-ray diffraction analysis.

Atomic coordinates and thermal parameters for **1** are given in Table II. Bond lengths and angles are given in Table III. The

Table III. Bond Lengths (Å) and Angles (deg)^a for **1**

Hg–O(1)	2.631 (20)	Hg–O(2)	2.334 (21)
Hg–N(1)	2.207 (18)	Hg–S′	2.375 (8)
S–C(4)	1.784 (23)	O(2)–C(6)	1.259 (33)
O(1)–C(6)	1.244 (29)	N(1)–C(4)	1.286 (31)
N(1)–C(1)	1.379 (29)	C(2)–C(5)	1.352 (38)
C(1)–C(2)	1.362 (36)	C(3)–C(5)	1.391 (35)
C(3)–C(4)	1.426 (36)		
C(6)–C(7)	1.521 (42)		
O(1)–Hg–O(2)	51.5 (6)	O(1)–Hg–N(1)	97.8 (7)
O(2)–Hg–N(1)	90.2 (7)	O(1)–Hg–S′	107.5 (4)
O(2)–Hg–S′	121.1 (5)	N(1)–Hg–S′	147.7 (5)
C(4)–S–Hg′	101.6 (9)	Hg–O(1)–C(6)	87.1 (16)
Hg–O(2)–C(6)	100.9 (15)	Hg–N(1)–C(1)	121.4 (16)
Hg–N(1)–C(4)	118.7 (14)	C(1)–N(1)–C(4)	119.8 (20)
N(1)–C(1)–C(2)	121.1 (23)	C(1)–C(2)–C(5)	120.3 (23)
C(4)–C(3)–C(5)	118.3 (25)	S–C(4)–N(1)	118.8 (18)
S–C(4)–C(3)	119.9 (19)	N(1)–C(4)–C(3)	121.3 (21)
C(2)–C(5)–C(3)	119.0 (25)	O(1)–C(6)–O(2)	120.4 (25)
O(1)–C(6)–C(7)	123.0 (25)	O(2)–C(6)–C(7)	116.5 (22)

^{a}Estimated standard deviations in the least significant digits are given in parentheses.

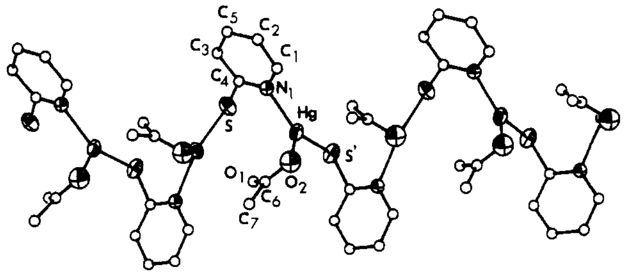

Figure 1. Chain structure of **1** showing 50% thermal ellipsoids and the labeling scheme.

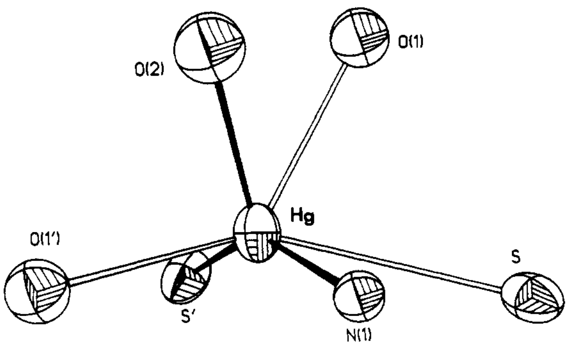

Figure 2. Diagram showing the coordination geometry around the Hg atom in **1** and the labeling scheme.

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(6) (a) Goodgame, D. M. L.; William, D. J.; Winpenny, E. P. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 261. (b) Goodgame, D. M. L.; William, D. J.; Winpenny, E. P. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1044. (c) Goodgame, D. M. L.; Williams, D. J.; Winpenny, E. P. *J. Chem. Soc., Chem. Commun.* **1988**, 437.

(7) Deeming, A. J.; Karim, M.; Bates, P. A.; Hursthouse, M. B. *Polyhedron* **1988**, *7*, 1401 and references therein.

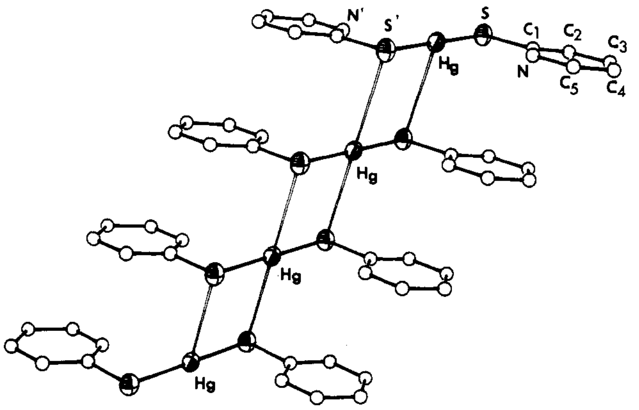

Figure 3. Chain structure of **2** showing 50% thermal ellipsoids and the labeling scheme.

Table IV. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$)[a] for **2**

atom	x	y	z	U_{iso}[b]
Hg	5000	0	0	34 (1)
S	3543 (2)	-3237 (6)	657 (2)	36 (1)
N	5685 (6)	-3369 (24)	2082 (5)	38 (2)
C(1)	4507 (8)	-4328 (18)	1915 (7)	28 (3)
C(2)	4004 (8)	-6120 (26)	2659 (8)	38 (3)
C(3)	4759 (8)	-7011 (23)	3641 (7)	40 (3)
C(4)	5998 (11)	-6056 (31)	3832 (8)	51 (4)
C(5)	6409 (9)	-4216 (26)	3031 (8)	45 (4)

[a] Estimated standard deviations in the least significant digits are given in parentheses. [b] Equivalent isotropic U defined as one-third of the trace of the U_{ij} tensor.

Table V. Bond Lengths (Å) and Angles (deg)[a] for **2**

Hg-S	2.356 (2)	S-C(1)	1.779 (8)
N-C(1)	1.339 (11)	N-C(5)	1.343 (11)
C(1)-C(2)	1.385 (14)	C(2)-C(3)	1.395 (12)
C(3)-C(4)	1.402 (15)	C(4)-C(5)	1.399 (16)
S-Hg-S'	180.0 (1)	Hg-S-C(1)	96.7 (3)
C(1)-N-C(5)	117.3 (8)	S-C(1)-N	117.6 (7)
S-C(1)-C(2)	118.6 (6)	N-C(1)-C(2)	123.8 (8)
C(1)-C(2)-C(3)	118.8 (8)	C(2)-C(3)-C(4)	118.4 (9)
C(3)-C(4)-C(5)	118.2 (9)	N-C(5)-C(4)	123.5 (9)

[a] Estimated standard deviations in the least significant digits are given in parentheses.

structure is shown in Figure 1. Hg atoms are bridged by the mercaptopyridine ligand through S and N atoms to form a infinite helical chain with a Hg-Hg separation of 4.076 (2) Å. The Hg-S distance of 2.375 (8) Å and Hg-N(1) distance of 2.210 (2) Å are normal bonding distances. The O(2) atom on the carboxylate is coordinated to the Hg atom with a typical Hg-O bond length of 2.33 (2) Å. The O(2), N(1), S', and Hg atoms are nearly coplanar: O(2)-Hg-N(1) = 90.2 (7)°, O(2)-Hg-S' = 121.1 (5)°, and N(1)-Hg-S' = 147.7 (5)°. The Hg atom is 0.1146 (8) Å from the N(1)-S'-O(2) plane. The O(1) atom on the carboxylate group weakly bridges two Hg atoms: Hg-O(1) = 2.63 (2) Å, and Hg'-O(1) = 2.73 (1) Å. The S atom has also weak interactions with the Hg atom: Hg-S = 3.23(1)Å. The geometry of the Hg^{II} center is, therefore, a distorted octahedron as illustrated in Figure 2. Hg^{II} ion is usually linearly two-coordinate although a few three- or four-coordinate Hg^{II} complexes are known.[5] To our knowledge compound **1** is the first example of a Hg^{II} complex having a helical chain structure with organic ligands. The chain structure and the labile acetate ligand make this compound of interest. Conceivably a positively charged polymer may be obtained by protonating the acetate ligand. We have attempted unsuccessfully to protonate the acetate ligand using HBF_4. However, the acetate can be readily protonated and replaced by another mole of C_5H_5NS ligand. As a result the polymer dissociates and a new compound, $Hg(MPY)_2$ (**2**), is obtained.

Table VI. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$)[a] for **3**

atom	x	y	z	U_{iso}[b]
Hg	5000	39 (1)	7500	32 (1)
P	4086 (2)	1523 (4)	5631 (5)	33 (1)
S	4594 (2)	2247 (5)	4310 (5)	46 (2)
C	4259 (6)	51 (20)	6318 (19)	40 (5)
C(11)	3257 (5)	2167 (10)	3652 (12)	50 (8)
C(12)	2747 (5)	2055 (10)	3015 (12)	63 (9)
C(13)	2400 (5)	1156 (10)	3505 (12)	61 (9)
C(14)	2562 (5)	369 (10)	4632 (12)	66 (10)
C(15)	3072 (5)	480 (10)	5269 (12)	51 (7)
C(16)	3419 (5)	1379 (10)	4780 (12)	33 (6)
C(21)	4253 (5)	3597 (11)	7372 (13)	53 (8)
C(22)	4188 (5)	4316 (11)	8610 (13)	74 (10)
C(23)	3861 (5)	3907 (11)	9711 (13)	69 (10)
C(24)	3599 (5)	2781 (11)	9573 (13)	64 (9)
C(25)	3665 (5)	2062 (11)	8335 (13)	44 (7)
C(26)	3991 (5)	2470 (11)	7234 (13)	32 (6)

[a] Estimated standard deviations in the least significant digits are given in parentheses. [b] Equivalent isotropic U defined as one-third of the trace of the U_{ij} tensor.

Table VII. Bond Lengths (Å) and Angles (deg)[a] for **3**

Hg-C	2.124 (16)	P-C	1.771 (22)
P-S	1.954 (7)	P-C(26)	1.820 (13)
P-C(16)	1.830 (12)		
C-Hg-C'	179.3 (2)	S-P-C	115.4 (6)
S-P-C(16)	112.0 (4)	C-P-C(16)	106.6 (7)
S-P-C(26)	112.2 (5)	C-P-C(26)	105.1 (7)
C(16)-P-C(26)	104.7 (6)	Hg-C-P	112.8 (10)
P-C(16)-C(11)	120.4 (4)	P-C(16)-C(15)	119.6 (4)
P-C(26)-C(21)	119.9 (4)	P-C(26)-C(25)	120.1 (4)

[a] Estimated standard deviations in the least significant digits are given in parentheses.

Synthesis and Structure of $Hg(MPY)_2$ (2). $Hg(MPY)_2$ can be obtained quantitatively either by the reaction of $Hg(OAc)_2$ with 2 mol of mercaptopyridine ligands or by the reaction of Hg(MPY)(OAc) with 1 equiv of mercaptopyridine ligand. The compound forms long fiberlike crystals, suggesting a possible one-dimensional chain structure. This was confirmed by a single-crystal X-ray diffraction analysis.

The structure of **2** is shown in Figure 3. Atomic positional and thermal parameters are given in Table IV. Bond angles and lengths are listed in Table V. The molecule is essentially planar with the sulfur atoms at the maximum deviation from the molecular plane (±0.087 (2) Å). The Hg atom lies on a center of symmetry and is linearly coordinated by two sulfur atoms with bond lengths similar to those found in **1**. The N and C(2) atoms are indistinguishable based on electron density differences. The assignment of atom positions are based on the fact that the N atom is only 2.92 Å away from the Hg atom. Therefore, it is unlikely that there is a hydrogen atom bonded to this atom. Photographs of X-ray diffraction by the crystal showed that the fiber axis of the crystal coincides with the unique crystallographic 2_1 axis on which the Hg atoms lie. The complex has an one-dimensional chain structure with a intermolecular Hg-Hg separation of 4.0873 (6) Å, similar to the distance found in **1** (Figure 3). Short intermolecular Hg-Hg separations have also been observed in the structure[8a] of $Hg(SCH_3)_2$, Hg-Hg = 3.90 (2) Å, and the compound[8b] $[Hg(S(t\text{-}C_4H_9))_2]_n$, Hg-Hg = 3.76 (1) Å. The one-dimensional chain structure of **2** resembles the well-known square-planar Pt^{II} complexes that have one-dimensional columnar structures in the solid. The molecule of **2** is linked together by the weak intermolecular Hg-S bonds: Hg-S(intermolecular) = 3.383 (2) Å, and S-Hg-S = 180.0 (1)°. The coordination geometry of the Hg^{II} atom is square planar. Similar weak intermolecular Hg-S bridges were also found in the structure[8a] of

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(8) (a) Bradley, D. C.; Kunchur, N. R. *J. Chem. Phys.* **1964**, *8*, 2258. (b) Kunchur, N. R. *Nature* **1964**, *204*, 468.

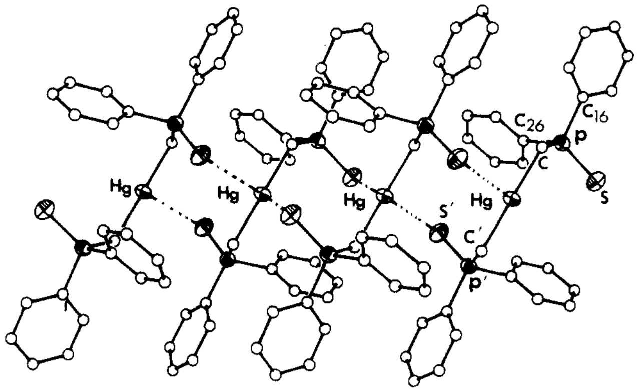

Figure 4. Chain structure of **3** showing 50% thermal ellipsoids and the labeling scheme.

$Hg(SCH_3)_2$: Hg-S = 3.25 (5) Å.

Compound **2** is capable of binding to metal ions through the N atom to form bimetallic complexes. Reactions of **2** with metal ions such as Pd^{II}, Cu^{I}, and Au^{I} yielded colored new compounds that are currently under investigation in our laboratory.

Synthesis and Structure of $Hg(MTP)_2$ (3). The reaction of $HgCl_2$ with[9] Li(MTP) in 1:2 ratio in THF solution yields the new compound $Hg(MTP)_2$ (**3**) in 65% yield. Compound **3** is a air-stable white solid. The molecular structure of this compound has been briefly described in a preliminary communication.[10]

Atomic positional and thermal parameters are given in Table VI. Bond distances and angles are listed in Table VII. As shown in Figure 4, the Hg atom is linearly coordinated to two carbon atoms. The preference of binding to C atoms in the MTP ligand by the Hg atom can be attributed to the strong covalent Hg-C bond. Compound **3** is the first example of a structurally characterized Hg^{II}-ylide complex. Again as found in compound **2**, Hg atoms in **3** lie on the unique crystallographic 2-fold axis with a Hg-Hg separation of 4.595 (2) Å. In the lattice, weak intermolecular Hg-S interactions are believed to exist. The Hg atom is weakly bonded to two sulfur atoms with a long Hg-S bond length, 3.17 Å, and a S-Hg-S angle of 76.9°. These weak intermolecular interactions as shown in Figure 4 could be responsible for the one-dimensional structure of **3**. The study of the ^1H NMR and ^{31}P NMR of **3** in solution shows that the molecular structure of **3** in solution is consistent with the solid structure.

The three structures of Hg^{II} complexes described here are unique in that they all have one-dimensional chain structures and contain organic ligands. The coordination versatility displayed by these compounds in the solid also has been observed in certain inorganic mercury compounds such as HgS more than 20 years ago.[11] HgS crystallizes in the cubic form (metacinnabarite) and the hexagonal form (cinnabar). In the cubic form the Hg atom forms tetrahedral Hg-S bonds (Hg-S = 2.52 Å). However, in the hexagonal form, the crystal has a helical-chain structure with two linearly coordinated short Hg-S bonds (Hg-S = 2.36 Å) and four long Hg-S bonds (3.10, 3.30 Å). These interesting observations in the solid-state structures of mercury compounds have not been well understood.

Compound **3** has been found to react readily with transition-metal ions such as[10] Au^{I}, Pt^{II}, and Pd^{II} to produce new bimetallic and trimetallic complexes. The details of these study will be published in subsequent papers.

Conclusion

Three new mercury complexes with one-dimensional chain structures have been synthesized. The chain structures of **2** and **3** are attributed to the weak intermolecular Hg-S interactions in the solid. Compounds **2** and **3** are potential precursors for the synthesis of heterobimetallic complexes.

Experimental Section

General Procedures. All reactions were performed by using standard Schlenk techniques under an atmosphere of dry N_2. All solvents were freshly distilled over appropriate drying agents prior to use. ^1H NMR spectra were taken on a Varian XL-200 spectrometer at 200 MHz. The ^{31}P NMR spectrum was recorded on a Varian XL-200 instrument at 81 MHz. Elemental analyses were done by Desert Analytics Co., Tucson, AZ.

$HgCl_2$ and $Hg(OAc)_2$ were purchased commercially and used without further purification. Li(MTP) was prepared according to the literature methods.[9]

Preparation of Hg(MPY)(OAc) (1). First, 300 mg of $Hg(OAc)_2$ (0.94 mmol) was dissolved in 10 mL of CH_2Cl_2 at room temperature. Then, 100 mg of mercaptopyridine (0.90 mmol), C_5H_5NS, was added to the solution. The yellow color of C_5H_5NS disappeared rapidly. A clear colorless solution was obtained within a few minutes. After 1 h, the solution was concentrated to 5 mL. Excess diethyl ether was added. Colorless crystals of **1** precipitated (290 mg, 0.78 mmol, 82% yield). ^1H NMR spectrum in $CDCl_3$ (δ, ppm): 2.14, singlet, 3 H; 7.05, mult, 1 H; 7.31, mult, 1 H; 7.46, mult, 1 H; 8.14, mult, 1 H. Anal. Calcd for $C_7H_7HgSO_2N$: C, 22.73; H, 1.89; N, 3.79. Found: C, 22.86; H, 1.89; N, 3.71. IR spectrum in CH_2Cl_2: 1578 cm^{-1}, weak, br. Mp: 175 °C.

Preparation of $Hg(MPY)_2$ (2). (a) First, 500 mg of $Hg(OAc)_2$ (1.57 mmol) was dissolved in 20 mL of CH_2Cl_2. Then, 348 mg of C_5H_5NS (3.14 mmol) was added to this solution. After the mixture was stirred for 1 h at room temperature, a colorless solution was obtained. The solution was concentrated then to 10 mL. Excess diethyl ether was added. Colorless fiberlike crystals of **2** were obtained (600 mg, 1.43 mmol, 91% yield). (b) First, 55 mg of **1** (0.149 mmol) was dissolved in 5 mL of CH_2Cl_2. Then, 16 mg of C_5H_5NS (0.144 mmol) was added to this solution. The mixture was stirred for 1 h. The solution was then concentrated to 1 mL. Diethyl ether was added. The colorless crystals of **2** were obtained in 56% yield (35 mg, 0.083 mmol). ^1H NMR spectrum in $CDCl_3$ (δ, ppm): 6.97, mult, 1 H; 7.29, mult, 1 H; 7.45, mult, 1 H; 8.13, mult, 1 H. Anal. Calcd for $C_{10}H_8HgS_2N_2$: C, 28.54; H, 1.92. Found: C, 27.70; H, 1.71. Mp: 191 °C.

Preparation of $Hg(MTP)_2$ (3). A solution of Li(MTP) (960 mg, 4.0 mmol) in 20 mL of THF was cooled to -78 °C. Then, 500 mg of $HgCl_2$ (1.8 mmol) was added to this solution. After the mixture was slowly warmed up to 0 °C, the white solid of **3** formed and precipitated from the solution. The solution was stirred for 1 h at 0 °C. After filtration, the white solid was washed with cold THF, then ethyl alcohol, and finally diethyl ether. A yield of 780 mg(1.2 mmol, 65%) of **3** was obtained. ^1H NMR spectrum in $CDCl_3$ (δ, ppm): 2.32, doublet, 2 H, $^2J_{Hg-H}$ = 135 Hz, $^2J_{P-H}$ = 12 Hz; 7.40, mult, 6 H; 7.80, mult, 4 H. ^{31}P NMR spectrum in $CDCl_3$ (δ, ppm): 44.78, singlet, $^2J_{Hg-P}$ = 148 Hz. Anal. Calcd for $C_{26}H_{24}HgS_2P_2$: C, 47.09; H, 3.65. Found: C, 46.37; H, 3.43. Mp: >230 °C.

Crystallographic Studies. Colorless single crystals of **1** were grown from CH_2Cl_2/diethyl ether solution by slow diffusion of the solvent at 22 °C. The fiberlike crystals of **2** and **3** were obtained by the same manner.

Crystals were mounted on glass fibers with epoxy. Unit cells were determined from 25 machine-centered reflections. Data were collected on a Nicolet R 3m/E diffractometer controlled by a Data General Nova 4 minicomputer by using graphite-monochromated Mo Kα radiation at ambient temperature over the range $2 \leq 2\theta \leq 45°$ ($|h| \leq 9$, $k \leq 14$, $l \leq 9$ for **1**; $|h| \leq 17$, $-k \leq 5$, $-l \leq 14$ for **2**; $|h| \leq 28$, $k \leq 12$, $-l \leq 10$ for **3**). Crystals of the three compounds belong to the monoclinic crystal system. All three crystals did not show any significant decay. All data were corrected for absorption by empirical methods. Corrections for secondary extinction were applied for **3** by multiplying[12] F_c by $[1 + 0.0002xF_c^2(\sin 2\theta)]^{-1/4}$; refinements gave $x = 0.00059$. Data were processed on a Data General Eclipse S 140 minicomputer using the SHELXTL crystallographic software (version 5.1). Scattering factors including terms for anomalous dispersion were taken from ref 13.

The space group $P2_1/c$ for **1**, $P2_1/n$ for **2**, and $C2/c$ for **3** were established uniquely from the systematic absences. The position of the Hg atom in **1** was determined by heavy-atom methods while the positions of Hg atoms in **2** and **3** were determined by direct methods. All non-hydrogen atoms were located by subsequent difference Fourier syntheses.

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(9) (a) Seyferth, D.; Welch, D. E. *J. Organomet. Chem.* **1964**, *2*, 1. (b) Seyferth, D.; Welch, D. E.; Ferren, J. K. *J. Am. Chem. Soc.* **1963**, *85*, 642.

(10) Wang, S.; Fackler, J. P., Jr. *Organometallics* **1988**, *7*, 2415.

(11) Wells, A. F. *Structural Inorganic Chem*, 5th ed.; Clarendon Press: Oxford, England, Oxford University Press: New York, 1984.

(12) Sheldrick, G. M. "SHELXTL. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data"; Nicolet XRD Corp.: Madison, WI, 1986.

(13) *International Tables for X-ray Crystallography*; Vol. IV, 1974, Kynoch Press: Birmingham: England, 1974; Vol. IV (present distributor D. Reidel, Dordrecht, The Netherlands).

All non-hydrogen atoms in **2** and **3** were refined anistropically. Only Hg and S atoms in **1** were refined anisotropically. The phenyl groups in **3** were refined as rigid bodies with fixed C–C distance of 1.395 Å and C–C–C angle of 120°. The positions of hydrogen atoms on the methyl group in **1** and on the phenyl group in **3** were calculated by using fixed C–H bond length, 0.96 Å. Their contributions were included in the structure factor calculations. The largest peaks, 1.68 and 0.98 e/Å^3 in the final difference Fourier maps of **1** and **2**, are at 1.23 and 1.18 Å from the Hg atom, respectively. The largest peak in the final difference Fourier map of **3**, 2.4 e/Å^3 is at 1.02 Å from the Hg atom. The data for crystallographic analyses are given in Table I.

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Supplementary Material Available: Tables S1–S6, listing crystallographic data, H atom parameters, and anisotropic temperature factors for **1–3** (4 pages); Tables S7 and S8, listing observed and calculated structure factors for **1** and **2** (12 pages). Ordering information is given on any current masthead page.

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Structure and Magnetic Properties of Bis[(2,6-diacetylpyridine dioxime)chlorocopper(II)] Tetrachlorocuprate

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The synthesis, structure, and low-temperature magnetic susceptibility of a novel trinuclear copper(II) compound are described. The complex is a sandwich made of two Cu(DAPDH$_2$)Cl$^+$ cations (the bread) and a CuCl$_4^{2-}$ anion (the filling) where DAPDH$_2$ is the ligand 2,6-diacetylpyridine dioxime. The two Cu(DAPDH$_2$)Cl$^+$ ions, related by a crystallographic C_2 axis passing through the Cu atom of the connecting CuCl$_4^{2-}$ ion, are essentially parallel to each other. The Cu atom in Cu(DAPDH$_2$)Cl$^+$ is bonded to the three nitrogen atoms of DAPDH$_2$ and to Cl$^-$ to give a nearly planar local CuN$_3$Cl polyhedron. There are four distinct Cu–Cl distances in the compound: 2.193 Å in the Cu(DAPDH$_2$)Cl$^+$ groups, 2.220 and 2.270 Å in the CuCl$_4^{2-}$ ion, and 2.604 Å between Cu of Cu(DAPDH$_2$)Cl$^+$ and the bridging chlorine. The compound crystallizes in orthorhombic group *Pccn*, with a = 10.463 (2) Å, b = 12.514 (12) Å, c = 20.275 (3) Å, V = 2654 (3) Å^3, and Z = 4. The three Cu(II) centers are ferromagnetically coupled (J = 3.0 K).

Introduction

Many studies of electron spin interactions in magnetically concentrated compounds have focused on copper(II). The principal reasons for this are (1) the electronic configuration of the copper(II) ion, d^9, effectively quenches the orbital contribution to the magnetic moment of the ion, thus allowing one to treat electron spin interactions as spin-only interactions; (2) the stereochemistry of copper complexes is extremely diverse; and (3) Cu(II) readily forms a rich variety of dimers and oligomers.

In magnetic studies of complex compounds, a heavy accent has been put on compounds with antiferromagnetically coupled metal atoms. The most thoroughly studied copper complexes are dimeric. Of them, "less than 5% ... are reported as ferromagnetically coupled and in some cases the result may be questioned".[1] A large number of magnetic studies on trimeric copper compounds have also been reported.[2] To the best of our knowledge, in all of them the copper ions are antiferromagnetically coupled. We report here on the structure, low-temperature magnetic susceptibility, and ESR spectrum of a novel trimeric copper complex in which the copper ions are ferromagnetically coupled. The trimer consists of a CuCl$_4^{2-}$ anion sandwiched between two CuLCl$^+$ cations, where L is the ligand 2,6-diacetylpyridine dioxime, hereafter DAPDH$_2$ (Figure 1).

Experimental Section

Preparations. Unless otherwise noted all chemical used were of reagent grade quality and were used as commercially obtained.

2,6-Diacetylpyridine Dioxime (DAPDH$_2$). This ligand was synthesized in the manner described by Vasilevsky et al.[3]

Bis[(2,6-diacetylpyridine dioxime)chlorocopper(II)] Tetrachlorocuprate ([Cu(DAPDH$_2$)Cl]$_2$CuCl$_4$). Method 1. Crystals suitable for X-ray and magnetic measurements were obtained by diffusion. To a mixture of 2,6-diacetylpyridine dioxime (0.39 g, 2.0 mmol) and tetraethylammonium chloride (1.9 g, 12.0 mmol) in 30 mL of acetonitrile was added trifluoroacetic acid dropwise until all the ligand dissolved. The solution was poured in a 30-mL beaker and several milliliters of acetonitrile was added so that the beaker was full. It was then placed in an 80-mL beaker. Solid cupric chloride dihydrate (1.02 g, 6.0 mmol) was placed in the annulus in the bottom of the 80-mL beaker, and acetonitrile was then slowly and carefully added to the 80-mL beaker until the lip of the smaller beaker was covered with approximately 0.5 cm of solvent. At this point, the mouth of the 80-mL beaker was covered with Parafilm, and the nested beakers were allowed to sit at room temperature. Over the course of several days dark green, long, prismatic crystals formed. The crystals were collected by filtration, washed with acetonitrile, and air dried. Yield: 0.695 g (88%). Anal. Calcd. for C$_{18}$H$_{22}$N$_6$O$_4$Cl$_6$Cu$_3$: C, 27.39; H, 2.81; N, 10.65; Cl, 26.95; Cu, 24.15. Found: C, 27.46; H, 2.84; N, 10.47; Cl, 26.55; Cu, 24.4. Principal IR absorptions in a Nujol mull: 690 m, 740 w, 815 s, 835 m, 1058 vs. 1143 s, 1267 s, 1300 s, 1325 sh, 1585 s, 3350 s, br cm^{-1}.

Method 2. Trifluoroacetic acid was added dropwise to a suspension of DAPDH$_2$ (0.19 g, 1.0 mmol) in 20 mL of absolute methanol until the ligand dissolved. To this solution was then added a solution of CuCl$_2$·2H$_2$O (0.34 g, 3.0 mmol) and LiCl (0.15 g, 6.0 mmol). The walls of the beaker were scratched with a glass rod. Several hours later a green crystalline precipitate was filtered off, washed with several milliliters of absolute methanol, and air-dried. Yield: 90 mg. Slow evaporation of

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(1) Kahn, O. *Comments Inorg. Chem.* **1984**, *3*, 105.
(2) (a) Grigereit, T. E.; Ramakrishna, B. L.; Place, H.; Willett, R. D.; Pellacani, G. C.; Manfredini, T.; Menabue, L.; Bonamartini-Corradi, A.; Battaglia, L. P. *Inorg. Chem.* **1987**, *26*, 2235. (b) Chiari, B.; Piovesana, O.; Tarantelli, T.; Zanazzi, P. F. *Inorg. Chem.* **1985**, *24*, 4615. (c) Fletcher, R.; Hansen, J. J.; Livermore, J.; Willett, R. D. *Inorg. Chem.* **1983**, *22*, 330. (d) Epstein, J. M.; Figgis, B. N.; White, A. H.; Willis, A. C. *J. Chem. Soc., Dalton Trans.* **1974**, 1954. (e) Figgis, B. N.; Martin, D. J. *J. Chem. Soc., Dalton Trans.* **1972**, 2174. (f) Beckett, R.; Colton, R.; Hoskins, B. F.; Martin, R. L.; Vince, D. G. *Aust. J. Chem.* **1969**, *22*, 2527. (g) Gruber, S. J.; Harris, C. M.; Sinn, E. *J. Chem. Phys.* **1968**, *49*, 2183. (h) Costes, J.-P.; Dahan, F.; Laurent, J.-P. *Inorg. Chem.* **1986**, *25*, 413. (i) Hulsbergen, F. B.; ten Hoedt, R. W. M.; Verschoor, J. C.; Reedijk, J.; Spek, A. L. *J. Chem. Soc., Dalton Trans.* **1983**, 539. (j) Journaux, Y.; Sletten, J.; Kahn, O. *Inorg. Chem.* **1986**, *25*, 439. (k) Kokozska, G. F.; Padula, F.; Goldstein, A. S.; Venturini, E. L.; Azevedo, L.; Siedle, A. R. *Inorg. Chem.* **1988**, *27*, 59.
(3) Vasilevsky, I.; Stenkamp, R. E.; Lingafelter, E. C.; Rose, N. J. *J. Coord. Chem.* **1988**, *19*, 171.

0020-1669/89/1328-2619$01.50/0