structures.[10a] The porphyrin complex possesses axial magnetic anisotropy while Fe(OEC) is rhombic. The two complexes have *different effective magnetic moments and Mössbauer spectra.* Despite this, the present results demonstrate that $\Delta\chi_{\parallel}$(para) is the same for the two complexes, confirming a tentative conclusion made from an analysis of isotropic ^{1}H chemical shifts.[10a] Any theoretical model developed to explain the electronic *differences* between $S = 1$ iron(II) porphyrins and hydroporphyrins must also account for the *similarities* in $\Delta\chi_{\parallel}$(para) values. Another tentative conclusion from our earlier work, that $\Delta\chi_{\perp}(\text{para}) = -\Delta\chi_{\parallel}(\text{para})$ for Fe(OEC), cannot be confirmed with the present data. Our inability to measure $\Delta\nu$ for samples of III precludes a calculation of $\Delta\chi_{\perp}$(para) for Fe(OEC). It is not clear at the present time why the *7,8-d*$_2$ resonance in samples of III is so broad.

The more general significance is the demonstration that magnetic anisotropies can be measured for an important class of paramagnetic transition-metal complexes. High-field ^{2}H NMR spectroscopy can now be added to the list of physicochemical techniques used to study the electronic structures of iron porphyrins. The comparison of $\Delta\chi$(para) values and their temperature dependencies for iron porphyrins and hydroporphyrins is continuing in these laboratories.

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Crystal Structure of the New Ternary Chalcogenide $Ta_2Cu_{0.80}S_6$. Relationship to Known Copper and Tantalum Chalcogenides

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In an attempt to prepare ternary phases in the system Au–Ta–S, we have unexpectedly isolated a new ternary phase in the Cu–Ta–S system.[2-5] The structure of the new compound $Ta_2Cu_{0.80}S_6$ is related to the structures of the known chalcogenides $CuTaS_3$[3] and TaS_3.[6] We report here the crystal structure of $Ta_2Cu_{0.80}S_6$, the experimental conditions that inadvertently led to the synthesis of this material, and our so far unsuccessful efforts to prepare the compound in a rational manner. The structural interrelationships of the tantalum–copper chalcogenides are described, and on this basis the physical properties of the new compound are anticipated.

Experimental Section

Synthesis. Several small (<0.3 mm in length), black, needle-shaped crystals of $Ta_2Cu_{0.80}S_6$ were isolated from a reaction of a 1:2:5 ratio of Au (AESAR, 99.95%), Ta (AESAR, 99.98%), and S (ATOMERGIC, 99.999%) powders. This charge was heated in a sealed, evacuated silica tube with ~3 μL of Br_2 for 5 days at 1000 K. The sample was then crushed, passed through a 60-mesh bronze screen, and resealed with Br_2 in a fresh silica tube that was heated for 7 days at 1125 K and then cooled. The principal product of this reaction was TaS_3, while no ternary Au–Ta–S compounds were formed. Microprobe analysis confirmed the presence of Ta, Cu, and S in the crystals and an approximate composition of 2:1:6 (Ta:Cu:S). We believe that the source of the Cu was the brass screen rather than a possible Cu impurity in the Au powder, especially since we have observed inadvertent introduction of Cu in systems where a brass screen but no Au powder was involved.[7] Direct combination reactions of Ta, Cu, and S in various ratios at temperatures between 950 and 1100 K have so far yielded $CuTaS_3$ as the only ternary product. These efforts to identify a synthetic route to $Ta_2Cu_{0.80}S_6$ have clearly been hindered by the structural similarity of the two phases (vide infra) and the apparent stability of $CuTaS_3$.

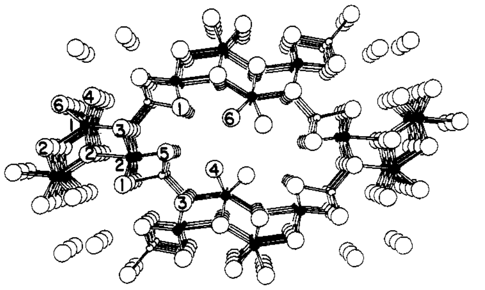

Figure 1. Perspective view of the $Ta_2Cu_{0.80}S_6$ structure along [010]. The numbering scheme is shown. Here and in Figure 2 Ta atoms are small filled circles, Cu atoms are small open circles, and S atoms are large open circles.

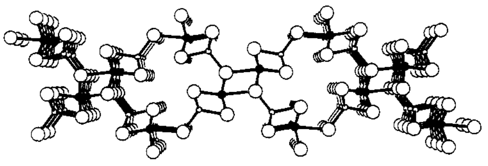

Figure 2. Perspective view of the $CuTaS_3$ structure along [010].

Crystallographic Study of $Ta_2Cu_{0.80}S_6$. Preliminary Weissenberg photographs (Cu Kα) established the orthorhombic symmetry and cell dimensions later confirmed by diffractometry. Intensity data were collected on a Rigaku AFC5-R four-circle diffractometer equipped with a 12-kW rotating-anode Cu X-ray source. Cell parameters were determined at 298 K from the setting angles of 10 accurately centered reflections in the range $10° < 2\theta(\text{Cu K}\alpha_1) < 33°$. No decay was observed in the intensities of three standard reflections monitored periodically during data collection. Cell data and crystallographic details are given in Table I.

Initial calculations were performed on a VAX 11/730 computer with the use of the TEXSAN[8] crystallographic computing package. The structure was solved by direct methods (MITHRIL[9]) in space group *Pnma*. An *E* map revealed the location of all independent atoms. All subsequent calculations were performed on a Harris 1000 computer, employing standard programs and methods.[10] Initial refinements of the data indicated that the Cu site is only partially occupied; subsequent refinements included a variable occupancy factor for the Cu atom. A full anisotropic refinement was attempted; anisotropic thermal parameters for several atoms became nonpositive definite. Probably this results from a somewhat inaccurate correction for absorption. We were unable to measure accurately the dimensions of the extremely small crystal, and as the absorption coefficient is very high, the absorption correction is significant. Accordingly, the final cycle of refinement of the 521 unique F_o^2 values included an isotropic parameter for each atom. From the refined occupancy of the Cu atom, the composition of the crystal used is $Ta_2Cu_{0.797(9)}S_6$. The height of the largest peak in the final difference electron density map is 3.5% that of a Ta atom. Final agreement indices are given in Table I. Final positional parameters are presented in Table II.

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Table I. Crystallographic Data for $Ta_2Cu_{0.80}S_6$

mol wt	605.1
a, Å	9.422 (5)[a]
b, Å	3.406 (1)
c, Å	21.548 (7)
V, Å^3	691.6
Z	4
density (calcd), g/cm^3	5.81
space group	D_{2h}^{16}-$Pnma$
T of data collection, K	298
radiation	monochromated Cu Kα from 12-kW rotating-anode source ($\lambda(K\alpha_1)$ = 1.540 562 Å)
cryst shape	needle bound by {101}, $(10\bar{1})$, $(\bar{2}01)$, and {010}; approx dimens 0.004 × 0.012 × 0.29 mm
cryst vol, mm^3	7.5×10^{-6}
linear abs coeff, cm^{-1}	757
transmission factors	0.446–0.810 (analytical method)[b]
data limits, deg	$4 \le 2\theta(\mathrm{Cu}\ K\alpha_1) \le 110$
takeoff angle, deg	6
bkgd counts	50% of scan time
data collection speed, deg/min	8.0 in ω with a max of 2 additional rescans for weak reflectns
p for calculation of $\sigma(F_o^2)$	0.03
no. of unique data (including $F_o^2 < 0$)	521
no. of unique data with $F_o^2 > 3\sigma(F_o^2)$	313
no. of variables	29
$R(F^2)$	0.115
$R_w(F^2)$	0.122
R on F_o ($F_o^2 > 3\sigma(F_o^2)$)	0.052
error in observn of unit wt, e^2	1.38

[a] Refined angles were α = 90.02 (3)°, β = 90.00 (4)°, and γ = 89.99 (3)°. [b] de Meulenaer, J.; Tompa, H. *Acta Crystallogr.* **1965**, *19*, 1014–1018.

Table II. Positional Parameters and Isotropic Thermal Parameters for $Ta_2Cu_{0.80}S_6$

atom	x	y	z	B, Å^2
Ta(1)	0.169 81 (22)	$^1/_4$	0.457 92 (10)	0.76 (5)
Ta(2)	0.053 35 (22)	$^1/_4$	−0.317 70 (11)	0.84 (5)
Cu[a]	0.318 16 (86)	$^1/_4$	0.269 08 (38)	1.3 (2)
S(1)	0.267 9 (10)	$^1/_4$	0.164 97 (47)	0.5 (2)
S(2)	0.023 9 (10)	$^1/_4$	−0.441 15 (49)	0.5 (2)
S(3)	0.136 4 (10)	$^1/_4$	0.337 43 (48)	0.3 (2)
S(4)	0.142 0 (11)	$^1/_4$	−0.072 52 (56)	1.2 (2)
S(5)	0.025 1 (11)	$^1/_4$	−0.214 86 (51)	1.2 (2)
S(6)	0.192 8 (12)	$^1/_4$	0.020 65 (52)	1.3 (2)

[a] Occupancy = 0.797 (9).

Structure amplitudes (×10) are listed in Table III.[11]

Results and Discussion

The structure of $Ta_2Cu_{0.80}S_6$ is shown in Figure 1. It is closely related to that of $CuTaS_3$,[3] shown in Figure 2. Both structures contain units of infinite chains of CuS_4 tetrahedra and TaS_6 octahedra running parallel to the b axis. The $CuTaS_3$ structure is realized by the simple linking of these chains to form a crisscross pattern of tetrahedra and octahedra in the a–c plane. In $Ta_2Cu_{0.80}S_6$, this network is interrupted by chains of Ta-centered bicapped trigonal prisms. As in $CuTaS_3$, the chains are linked so as to form open channels parallel to b, though the nature of the channels is different in the two compounds. The coordination geometries within the Ta(2) octahedron and Cu tetrahedron in the present compound (Table IV) are remarkably similar to those found in $CuTaS_3$.[3] Of note is the unusually short Cu–Ta(2) distance, 2.804 (7) Å, across the edge shared by neighboring polyhedra. This distance is only ~0.10 Å longer than the sum of the metallic radii of Cu and Ta.[12] In addition, atom Ta(2) is displaced from the center of the octahedron toward the vertex occupied by atom S(5). The resultant Ta(2)–S(5) distance, 2.232 (11) Å, is very short for a Ta–S bond. These metrical data and the analogous values for $CuTaS_3$[3b,13] are indicative of some interaction between the Cu and Ta atoms in these compounds. Any effect of the ~20% Cu vacancies in $Ta_2Cu_{0.80}S_6$ on such an interaction is not reflected in the observed structure.

Table IV. Selected Bond Distances (Å) and Angles (deg) for $Ta_2Cu_{0.80}S_6$

Cu–S(1)	2.293 (14)	Ta(1)–S(3)	2.615 (10)
Cu–S(3)	2.259 (13)	Ta(2)–2S(1)	2.426 (7)
Cu–2S(5)	2.281 (9)	Ta(2)–2S(3)	2.505 (7)
Cu–2Ta(2)	2.804 (7)	Ta(2)–S(2)	2.675 (10)
Ta(1)–2S(2)	2.522 (8)	Ta(2)–S(5)	2.232 (11)
Ta(1)–2S(4)	2.545 (8)	S(4)–S(6)	2.064 (18)
Ta(1)–2S(6)	2.531 (8)	S(2)–S(2)	3.088 (17)
Ta(1)–S(2)	2.573 (11)		
S(1)–Cu–S(3)	118.8 (5)	S(2)–Ta(1)–S(3)	140.8 (3)
S(1)–Cu–2S(5)	106.4 (4)	S(2)–Ta(1)–2S(2)	74.6 (3)
S(3)–Cu–2S(5)	113.1 (4)	S(2)–Ta(1)–2S(6)	79.7 (3)
S(5)–Cu–S(5)	96.6 (5)	S(1)–Ta(2)–S(3)	89.6 (2)
S(2)–Ta(1)–S(6)	89.6 (3)	S(1)–Ta(2)–S(3)	161.3 (3)
S(2)–Ta(1)–S(4)	90.9 (2)	S(1)–Ta(2)–S(1)	89.2 (3)
S(4)–Ta(1)–S(6)	48.0 (4)	S(2)–Ta(2)–S(5)	167.2 (3)
S(2)–Ta(1)–S(2)	84.9 (3)		

The trigonal prism in $Ta_2Cu_{0.80}S_6$ has an S–S bond in each trigonal face. The distance S(4)–S(6), 2.06 (2) Å, is consistent with similar interactions in the materials TaS_3[6] and NbS_3.[14] Indeed, the bicapped-trigonal-prismatic geometry about atom Ta(1) is closely related to that found in the infinite chains in TaS_3.[6]

Electrical conductivity measurements of crystals of $CuTaS_3$ have shown the material to be an insulator.[3b] This behavior may be accounted for on the basis of either of two simple valence descriptions. As there are no S–S distances in $CuTaS_3$ indicative of S–S bonding, we may assign S the formal valence –II. The metal atoms are then considered to be either d^0 Ta^V and d^{10} Cu^I or d^1 Ta^{IV} and d^9 Cu^{II}, in which case a pairing of electrons consistent with the short Ta–Cu distance would be possible. With either description, we would anticipate the presence of a large energy gap between filled orbitals and higher empty states that would afford an insulating behavior for this material. By contrast, TaS_3 is a metallic conductor above 240 K, a direct consequence of the S_2^{2-} pairs and the resultant partial reduction of the Ta valence from V to IV.[6] As the trigonal prisms in $Ta_2Cu_{0.80}S_6$ also possess S_2^{2-} pairs, the Ta atoms in these chains should have a formal valence of IV, thus imparting metallic properties to the compound. Moreover, the MQ_3 (M = Nb, Ta; Q = S, Se) materials are noted for charge-density wave behavior and attendant Peierls distortions.[6,15] Similar phenomena have also been observed in compounds of the Nb_3FeSe_{10} structural type.[16] Trigonal-prismatic Nb chains that contain Se_2^{2-} pairs are believed to be the locus of charge-density wave behavior in these materials.[17] The similar structural features of $Ta_2Cu_{0.80}S_6$ raise the possibility that this compound may also display unusual physical properties.

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Registry No. $Ta_2Cu_{0.80}S_6$, 106946-94-5; Ta, 7440-25-7; S, 7704-34-9; Br_2, 7726-95-6; bronze, 12597-70-5.

Supplementary Material Available: A table of structure amplitudes (×10) for $Ta_2Cu_{0.80}S_6$ (Table III) (3 pages). Ordering information is given on any current masthead page.

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(11) Supplementary material.

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