Inorg. Chem. **1981**, *20*, 2165–2169 **2165**

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Coordination Chemistry of New Sulfur-Containing Ligands. 20. Preparation, Characterization, and Crystal and Molecular Structure of a Severely Distorted Copper(II) N_2S_2 Complex: [*N*,*N*′-Tetramethylenebis(methyl 2-amino-1-cyclopentenedithiocarboxylato)]copper(II)

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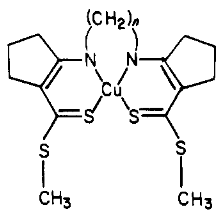
Received August 6, 1980

The copper(II) complex of the N_2S_2 tetradenate ligand *N*,*N*′-tetramethylenebis(methyl 2-amino-1-cyclopentenedithiocarboxylate) was prepared by reaction of the neutral ligand with an equivalent amount of copper acetate in methanol. The visible absorption band of the complex both in solution [9.3×10^3 cm^{-1} (ϵ 30) in DMF; 9.1×10^3 cm^{-1} (ϵ 20) in CH_2Cl] and in the solid state [9.1×10^3 cm^{-1} as mull] coupled with the observed electron spin resonance parameters ($A_{\parallel} = 145 \times 10^{-4}$ cm^{-1}, $g_{\parallel} = 2.140$, $A_0 = 55.9 \times 10^{-4}$ cm^{-1}, $g_0 = 2.066$) suggest that this complex is even more distorted from a planar complex toward a tetrahedral one than the similar complex with a three carbon backbone. A study of the exact relationships between distortion and spectral properties in a closely related series of CuN_2S_2 complexes is thus possible. The crystal and molecular structure of the title compound was solved at room temperature by a single-crystal X-ray diffraction study. The complex crystallizes in the centrosymmetric monoclinic space group $C2/c$ with $a = 16.782$ (8) Å, $b = 8.626$ (4) Å, $c = 14.621$ (8) Å, $\beta = 105.83$ (4)°, $V = 2036$ (1) Å^3, d_{obsd} (d_{calcd}) = 1.51 (1.50) g cm^{-3} for mol wt 462.2 and $Z = 4$. Full-matrix least-squares refinement of the trial structure resulted in discrepancy indices of $R_F = 4.6\%$ and "goodness-of-fit" = 1.71 for all 908 observable reflections. The molecules are monomeric, are well separated, and lie on a C_2 axis. The copper–sulfur distance is 2.221 (2) Å, and the copper–nitrogen distance is 1.955 (4) Å. Bond distances in the five-membered chelate ring indicate a surprising amount of π delocalization. The plane defined by the copper and two liganded sulfur atoms intersects the plane defined by the copper and two nitrogen atoms, forming a dihedral angle of 57.1° (90° would be ideal for a *pseudotetrahedral* N_2S_2 inner coordination sphere). The variation of spectral properties as a function of twist angle of these CuN_2 and CuS_2 planes is discussed. In addition, the possible relevance to type I copper(II) centers in metalloenzymes is presented.

Introduction

A good deal of recent excitement has centered in the area of copper(II) coordination chemistry due to the early speculation[1-13] and subsequent confirmation that type I copper(II) centers in metalloproteins existed in *pseudotetrahedral* environments.[14] The paucity of any copper(II) compounds which had similar inner coordination sphere structures has prompted a surge of interest in the design and study of distorted copper(II) compounds.[15-17] Authentic synthetic analogues of the inner coordination sphere would be invaluable to the understanding of the detailed stereoelectronic properties of copper(II) in these sites especially since a variety of "tetrahedral" sites may exist in the type I protein centers.[18]

We have explored in some detail the set of compounds represented by the Lewis structures I where n = 2–4.[15] These



I

compounds were prepared by a method recently reported by Bordas et al.[20] and Mondal et al.[21] with the hope that we could obtain soluble, distorted copper(II) complexes where solution properties could be determined and ideally, whatever distortion occurred in solution would remain unchanged in the solid state. Thus detailed crystal structure data could be related to geometry-induced spectral changes in solution.

The complex with n = 3 was recently prepared and characterized.[15] The crystal structure of that complex showed a rather severe distortion about the copper(II) as measured by the angle of intersection of the planes defined by the copper and two liganded sulfur atoms and by the copper and two nitrogen atoms. That angle of 52.8° represented the largest

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twist angle of any sulfur-containing soluble copper(II) compound at that time. We report here the $n = 4$ compound and its structure, a system which is even more distorted.

Several highly distorted CuN_4 compounds are also known.[22,23] The twist angle between the two CuN_2 planes in bis((3,3′-dimethyl-2,2′-dipyridyl)amine)copper(II) of 57.4° represents the largest distortion in a soluble copper(II) complex to date.

Experimental Section

Materials. All reagents and solvents were commerically obtained, were of reagent grade, and were used without further purification.

Synthesis. The ligand *N,N′*-tetramethylenebis(methyl 2-amino-1-cyclopentenedithiocarboxylate) was prepared by the method of Bordas et al.[20] with 1,4-diaminobutane used in place of ethylenediamine. The thermal instability of the starting material, ammonium 2-amino-1-cyclopentenedithiocarboxylate, was overcome by a later method[24] (yield ≈ 70%).

The copper(II) complex was prepared in methanol by the method of Mondal et al.[21] The complex was isolated as a dark brown solid (yield ≈ 40%). Anal. Calcd for $C_{18}H_{26}N_2S_4Cu$: C, 46.77; H, 5.67; N, 6.06; S, 27.75. Found (Atlantic Microlab, Inc., Atlanta, GA): C, 46.64; H, 5.69; N, 6.04; S, 27.68.

Physical Measurements. Electron spin resonance spectra were obtained at 120 and 300 K with a Varian E-4 spectrometer operating near 9 GHz (X band). Spectra were obtained in a 50/50 (by volume) mixture of dimethylformamide/methylene chloride glass (120 K) and in solution (300 K). The spin Hamiltonian parameters were calculated as previously reported.[15] Optical spectra were determined at room temperature in methylene chloride, dimethylformamide, and Nujol mulls with a Cary 14 spectrophotometer.

Crystal Data Collection. Orange, prismatic crystals suitable for an X-ray analysis were grown by the slow evaporation of a methylene chloride solution. The crystal survey, unit cell dimension determination, and data collection were accomplished on a Syntex P$\bar{1}$ diffractometer with use of molybdenum radiation ($\lambda = 0.71069$ Å) at room temperature. The diffractometer was equipped with a graphite incident-beam monochromator mounted in the perpendicular mode. Final unit cell dimensions were obtained by a least-squares fit of 15 high-angle reflections ($2\theta > 15°$). Systematic absences indicated that the crystal belonged to the monoclinic space group *Cc* or *C*2/*c* (hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$). Because the cell dimensions and space group of this compound were very similar to the crystal parameters of the trimethylene homologue,[15] we treated the crystals of these two compounds as isomorphous. A 1-Å intensity data set was collected (maximum $(\sin \theta)/\lambda = 0.5$). One check reflection was monitored every 15 reflections and revealed no unexpected variation in intensity. Details of the crystal survey and data collection parameters are summarized in Table I.

The diffractometer output and all subsequent crystallographic calculations were processed by using subprograms of the CRYM crystallographic computer system.[25] The data processing included corrections for background, Lorentz, and polarization effects. Polarization due to the monochromator was corrected for by a method by Azaroff.[26] Processing also included the calculation of F^2 and its standard deviation for each reflection. The standard deviations were assigned on the basis of the equation: $\sigma^2(I) = S + \alpha^2(B_1 + B_2) + (dS)^2$, where S is the number of counts collected during the scan, B_1 and B_2 are the background counts, d is an empirical constant set at 0.02, and α is the scan time to total background time ratio. Data was corrected for absorption by using the correction factors for a sphere with $r = 0.13$ mm[27] (μ(Mo Kα) 15.0 cm^{-1}).

Table I. Physical Data and Data Collection Parameters

mol formula	$C_{18}H_{26}CuN_2S_4$
mol wt	462.2
crystal size, mm	spherical, with $r = 0.13$
cell dimensions	
a, Å	16.782 (5)
b, Å	8.626 (2)
c, Å	14.621 (5)
β, deg	105.83 (2)
V, Å^3	2036 (1)
space group	*C*2/*c*
molecules/unit cell	4
d_{calcd}, g/cm^3	1.50
d_{obsd},[a] g/cm^3	1.51
scan technique	θ–2θ
scan speed	2°/min in 2θ
scan width	1.2° below Kα_1 to 1.2° above Kα_2
bkgd count time	0.6 × scan time on each side of peak
no. of reflctns	1110
no. of nonzero reflctns[b]	908

[a] Density was measured by the flotation technique with use of aqueous KI. [b] All intensities with values less than 3 times the standard deviation were set equal to 0 with zero weight.

Finally, the data set was placed on an approximately absolute scale by Wilson statistics.[28] atomic scattering factors for C, N, and S were taken from ref 29, for Cu^{+2} from Cromer and Mann,[30] and for H from Stewart, Davidson, and Simpson.[31] The scattering factors for S and Cu(II) were corrected for the real anomalous scattering component.[29b]

Determination and Refinement of Structure

The appropriate coordinates from the trimethylene homologue were used to calculate the approximate phases of this tetramethylene homologue (the two compounds formed isomorphous crystals). A difference Fourier was used to locate the unique methylene carbon in the tetramethylene homologue. In both compounds the asymmetric unit contained only half a molecule. The second half was generated by a twofold axis. This trial structure refined routinely to an acceptable R index of 0.046.

The refinement was concluded by using a full-matrix least-squares technique. The quantity minimized by the least-squares precedure was $\sum w(F_o^2 - F_c^2)^2$, where $w = 1/\sigma^2(F_o^2)$. Hydrogen positions were calculated wherever required. The methyl hydrogens were located by difference Fourier techniques. While the hydrogen parameters were added to the structure factor calculations during the later stages of refinement, they were not refined. During the final cycles of refinement the scale factor, nonhydrogen coordinates, and nonhydrogen anisotropic temperature factors were located in a single matrix. Refinement of a secondary extinction coefficient proved that this correction was small. The refinement was terminated when the shifts calculated for the parameters in the least-squares cycles were all 0. A final difference Fourier revealed no missing or misplaced electron density. The data fit criteria (based on nonzero reflections) were as follows:

$$R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.046$$

$$R' = \sum w(F_o^2 - F_c^2)^2 / \sum F_o = 0.006$$

$$\text{GOF} = [\sum w(F_o^2 - F_c^2)^2/(m - s)]^{1/2} = 1.71$$

The refined coordinates were plotted with use of the ORTEP computer program of Johnson[32] (Figure 1). The final coordinates are given

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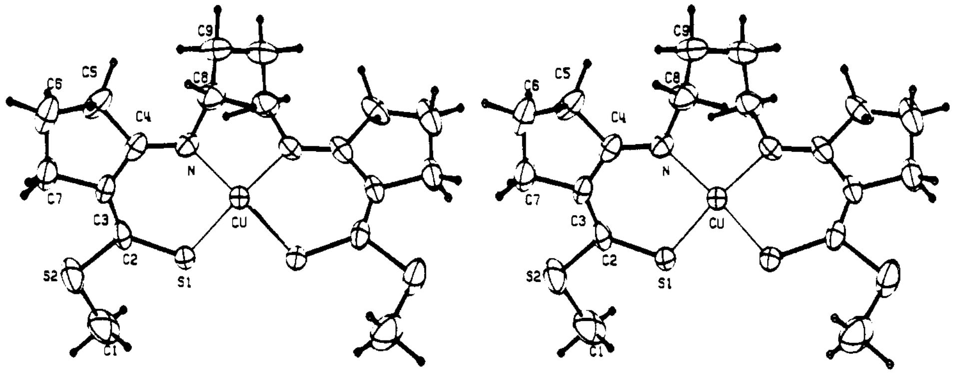

Figure 1. ORTEP diagram of Cu($S_4N_2C_{18}H_{26}$) (50% probability ellipsoids).

Table II. Positional Parameters and Their Standard Deviations

	x	y	z
Cu	0	50580 (14)	25000
S1	8891 (11)	32856 (20)	22784 (12)
N	896 (28)	65487 (58)	15255 (33)
S2	20700 (12)	27504 (26)	11212 (15)
C1	22649 (44)	12042 (95)	19559 (56)
C2	13321 (36)	39463 (77)	14193 (42)
C3	11631 (35)	52957 (75)	9155 (41)
C4	5712 (37)	64979 (78)	9556 (42)
C5	5804 (41)	76960 (80)	2073 (45)
C6	14123 (45)	74449 (93)	−132 (49)
C7	15984 (39)	57313 (86)	1669 (45)
C8	−4633 (39)	79014 (77)	14334 (47)
C9	−427 (47)	93100 (73)	19733 (48)
H(C1)	2547	1681	2640
H(C1)	2699	399	1737
H(C1)	1689	604	1884
H(C5)	76	7537	−425
H(C5)	536	8871	473
H(C6)	1403	7766	−729
H(C6)	1909	8132	472
H(C7)	1372	5084	−492
H(C7)	2274	5526	412
H(C8)	−986	7554	1734
H(C8)	−735	8147	692
H(C9)	−379	10351	1655
H(C9)	578	9378	1868

[a] Values have been multiplied by 10^4. [b] The temperature factors for hydrogen atoms were fixed at 2.80 A^2.

Table III.[a] Nonhydrogen Anisotropic Temperature Factors ($\times 10^4$) and Their Standard Deviations

U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
376 (7)	330 (7)	388 (6)	0 (0)	202 (5)	0 (0)
455 (11)	385 (11)	435 (11)	58 (10)	246 (9)	35 (10)
264 (32)	392 (35)	422 (34)	−18 (28)	69 (28)	18 (30)
557 (13)	905 (18)	634 (14)	237 (13)	346 (11)	−18 (13)
567 (54)	829 (66)	969 (67)	314 (49)	256 (50)	43 (57)
314 (40)	534 (49)	398 (44)	−47 (37)	181 (35)	−82 (39)
318 (39)	533 (52)	371 (40)	−131 (38)	181 (33)	−27 (39)
320 (42)	526 (48)	354 (41)	−117 (38)	89 (35)	−13 (39)
570 (50)	564 (51)	384 (43)	−187 (41)	80 (39)	124 (40)
668 (56)	869 (65)	448 (48)	−269 (50)	229 (44)	83 (46)
442 (45)	791 (59)	465 (45)	−138 (43)	278 (38)	−27 (44)
433 (45)	460 (49)	547 (47)	62 (39)	135 (39)	159 (41)
772 (54)	296 (41)	787 (55)	51 (42)	272 (52)	15 (39)

[a] The temperature factor is in the form $T = \exp[-2\pi^2 \cdot (U_{11}h^2a^{*2} + \ldots + 2U_{23}klb^*c^*)]$. Listing of atoms is the same as in Table II.

Table IV. Optical and ESR Spectral Features for the Ligand Series (n = 2–4)[a]

A. Position of Lowest Energy Band

	solvent		
n	DMF	CH_2Cl_2	Nujol[b]
2	12.6 (98)	12.6 (70)	12.5
3	10.5 (65)	10.5 (60)	10.5
4	9.3 (30)	9.1 (20)	9.1

B. Positions of All Spectral Features in DMF[c]

n	positions
2	12.6 (98), 17.7 sh, 21.0 sh, 25.3 sh, 26.7 (15 000), 28.0 (15 000), 31.8 (33 000), 34.5 (28 000)
3	10.5 (65), 17.7 sh, 20.5 (2600), 25.0 (10 000), 26.4 (9900), 30.9 (21 000), 34.8 (20 000)
4	9.3 (30), 18.5 (1600), 25.8 (9000), 30.8 (9000), 33.7 (22 000)

C. Positions of All Spectral Features in CH_2Cl_2

n	positions
2	12.6 (70), 20.6 sh, 25.1 sh, 26.5 (16 000), 28.9 (15 000), 31.6 (33 000), 34.0 (25 000)
3	10.5 (60), 17.9 sh, 20.5 (3300), 24.9 (15 000), 26.2 (14 000), 30.9 (29 000), 34.5 (26 000), 42.2 (18 000)
4	9.1 (20), 18.4 br, as (3000), 25.0 sh, 26.1 (12 000), 30.8 (31 000), 34.6 (34 000), 38.5 (32 000)

D. ESR Parameters[d]

n	g_0[e]	A_0[e]	g_{zz}[f]	A_{zz}[f]	$A_{N(iso)}$[e]
2	2.055	81.1	2.117	181	13.2
3	2.060	65.3	2.132	160	12.0
4	2.066	55.9	2.140	145	9.1

[a] Optical values are in 10^3 cm^{-1}; molar absorptivities are in units of M^{-1} cm^{-1}; ESR hyperfine splittings are in units of 10^{-4} cm^{-1} (A_N in G). [b] Obtained as a transmission at room temperature. [c] Key: sh = shoulder, br = broad, as = asymmetrical band. [d] Obtained in 50/50 DMF/CH_2Cl_2. Solvent coordination was checked by collecting data in toluene. Similar gross features resulted but the resolution was superior in the DMF/CH_2Cl_2 glass. [e] Ambient room temperature. [f] Frozen glass, 100 K.

in Table II; thermal parameters are presented in Table III.

Results and Discussion

Spectral Properties. We as well as others have been interested in copper(II) compounds with N_2S_2 inner coordination sphere ligand atoms.[33-35] As noted above, this interest has been generated in large part by the finding that the type I copper(II) site in metalloenzymes, as represented by plastocyanin, consists of a pseudotetrahedral array of two nitrogen atoms from imidazoles, a sulfur atom from a methionine residue, and a thiol sulfur atom from a cysteine residue. The series of CuN_2S_2 compounds we chose to study have two important structural features which we initially felt would be required to produce a distorted copper environment. First,

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Table V. Bond Distances (Å) for $Cu(S_4N_2C_{18}H_{26})$ ($n = 4$)[a] and $Cu(S_4N_2C_{17}H_{24})$ ($n = 3$)

	$n = 4$	$n = 3$[15]
Cu-S1	2.221 (2)	2.222 (1)
Cu-N	1.955 (5)	1.950 (3)
C1-S2	1.777 (8)	1.757 (6)
C2-S1	1.722 (6)	1.722 (4)
C2-S2	1.755 (7)	1.772 (4)
C2–C3	1.365 (9)	1.359 (6)
C3–C7	1.520 (9)	1.526 (5)
C3–C4	1.448 (9)	1.429 (6)
C7–C6	1.519 (11)	1.518 (7)
C6–C5	1.532 (11)	1.526 (6)
C5-C4	1.508 (9)	1.510 (5)
C4-N	1.310 (8)	1.310 (5)
N–C8	1.474 (8)	1.495 (5)
C8–C9	1.515 (9)	1.516 (6)
C9–$C9_a$	1.507 (9)	

[a] "a" atom generated by the symmetry operation $-x, y, \frac{1}{2} - z$.

there must be some systematic way whereby the distortion from a planar toward a *pseudotetrahedral* geometry could be controlled. Ideally, no other structural features should change. Secondly, the presence of some electronic delocalization in each CuNS portion of the ligand should keep that half of the ligand planar and inhibit any relaxation back toward an overall planar geometry by the terminal ligand atoms (S here). By increasing the length of the diamine bridge, it has been possible to prepare a series of compounds whose spectral properties vary smoothly in such a way as to suggest a more distorted complex exists at $n = 4$ than at $n = 2$. Table IV lists both the detailed visible–ultraviolet spectral features for this complete series as well as the electron spin resonance spectral parameters. The visible band at 9.1×10^3 cm^{-1} for the $n = 4$ compound is near that found for some type I copper(II) centers, and yet the $A_{\parallel}$ value is still far outside the range of all type I copper(II) centers ($<100 \times 10^{-1}$ cm^{-1}).[1] Recent crystal field calculations for copper(II) in an N_2S_2 environment where the geometry was varied from *pseudo square planar* to *pseudotetrahedral* have shown that the position of the highest energy "d–d" band varies only little with distortion between ~60 and ~90°.[36] Only the lower energy, more difficult to observe, "d–d" bands vary dramatically in this region. Thus, the similarily in position of the band at 9.1×10^3 cm^{-1} with those in type I centers is neither unexpected nor informative. It is, however, worth noting the rather large effect on $A_{\parallel}$ in going from $n = 3$ to $n = 4$. It would be most interesting to know quantitatively the structural or bonding features which bring about this change.

Description of Structure

The structure of this CuN_2S_2 complex with $n = 4$ consists of discrete, well-separated monomers with a distorted inner coordination sphere as predicted from the spectral data. The molecules have crystallographically dictated $C_2(2)$ symmetry. An ORTEP diagram, which indicates the labeling of the atoms, is shown in Figure 1. Table V lists the nonhydrogen bond distances along with those of the $n = 3$ complex for comparison. Table VI lists the bond angles. The twist angle, as measured by the intersection of the CuN_2 and Cu(S-ligand atom)$_2$ planes is 57.1°.

It is remarkable that, within experimental error, only one bond length *within* the ligand has changed in going from the $n = 3$ to the $n = 4$ compound (Table V), that being C1 to S2. Other than a modest decrease in the Cu–N bond distance, all other distances are similar. Again, as noted before,[15,21] a good deal of resonance π delocalization must exist in the six-membered ring including the metal. This is evident in the very short formal C2–C3 single bond and long formal C3–C4 double bond.

Table VI. Bond Angles (Deg) for $Cu(S_4N_2C_{18}H_{26})$[a]

N–Cu–S1	99.1 (2)	C4–C3–C2	129.2 (6)
N–Cu–$S1_a$	138.6 (1)	C7–C3–C2	122.0 (6)
N–Cu–N_a	98.3 (2)	C7–C3–C4	108.8 (5)
C2–S1–Cu	108.6 (2)	C3–C4–N	126.8 (6)
C4–N–Cu	128.7 (4)	C5–C4–N	124.7 (6)
C8–N–Cu	114.5 (4)	C5–C4–C3	108.6 (5)
C8–N–C4	116.8 (5)	C6–C5–C4	104.3 (6)
C2–S2–C1	106.3 (3)	C7–C6–C5	104.9 (6)
S2–C2–S1	117.4 (4)	C6–C7–C3	104.4 (6)
C3–C2–S1	127.5 (5)	C9–C8–N	113.3 (6)
C3–C2–S2	115.1 (5)	$C9_a$–C9–C8	115.6 (5)

[a] "a" atom generated by symmetry operation $-x, y, \frac{1}{2} - z$.

Table VII. $A_{\parallel}$ Values for Typical Type I Copper(II) Centers and Predicted Twist Angles

protein	$10^4 A_{\parallel}$, cm^{-1}	twist angle, deg
Rhus vernicifera		
stellacyanin	35	88
umecyanin	35	88
Pseudomonas		
aeruginosa azurin	60	81
spinach plastocyanin	63	80
Polyporus versicolor		
laccase	90	73
Rhus vernicifera		
laccase	43	86

While we must be careful not to over interpret any small differences in these two sets of data, it is equally important not to overlook any potentially important differences. As noted above, the only statistically different distances involving the inner coordination sphere is the Cu–N bond. The more distorted compound ($n = 4$) has a somewhat longer Cu–N bond than the less distorted one ($n = 3$). That this difference is real can be verified from the values for the ^{14}N superhyperfine values observed in the ESR spectra of 12.0 and 9.1 G for the $n = 3$ and $n = 4$ complexes, respectively. As the bond distance becomes longer, less unpaired electron density from the copper will exist at the N center. This is certainly a result of a mismatch of symmetry of the copper-based and nitrogen-based atomic orbitals. At the same time, the Cu–S bond in the more distorted complex *might* be slightly shortened.[37] Since the N and S atoms, as a result of the twist, can no longer compete as effectively for the π orbital of copper(II), then the "softer" sulfur atom might be expected to dominate as the better π-bonding ligand atom. Perhaps even shorter Cu–S bond distances will result as the twist angle increases. Clearly more structural data on similar compounds is needed to verify this observation.

If we assume that no real significance can be given on any of the differences between the two ligands, then the changes in bond distances (if real) and certainly the changes in spectral parameters are *only a function of twist angle*. This compound and the $n = 3$ compound therefore allow us the unique opportunity to judge how important the twist angle is to these properties. The change is *only* 4.3° (52.8 to 57.1°). Yet a change in $A_{\parallel}$ of 15×10^{-4} cm^{-1} is brought about by the increased distortion; that is, 3.5×10^{-4} cm^{-1} deg.$^{-1}$ If we use this as a rough measure, then we can expect that twist angles of near 80° will be required to yield an $A_{\parallel}$ of 64×10^{-4} cm^{-1}, a value typical of type I copper(II) centers.[38] Since this twist

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(36) Bereman, R. D.; Bordner, J.; Dorfman, J.; McCarthy, P.; Rillema, D. P.; Shields, G. D. *J. Inorg. Biochem.*, in press.

(37) The Cu–S distance in the less distorted $n = 2$ compound[36] is significantly *larger* than that for the $n = 3$ or $n = 4$ compound.

(38) Blumberg, W. E.; Peisach, J. *Biochim. Biophys. Acta* **1966**, *126*, 269–273.

angle is near the value found for plastocyanin,[39] it suggests that the $A_{\|}$ value of type I copper(II) centers is a very good measure of twist angle regardless of the ligand atom type. The thioketone sulfur is apparently adequate to mimic ESR parameters of the protein. The d–d optical features of type I centers however appear to depend more heavily on ligand atom identity.[36]

While it is speculative, it is also a useful exercise to attempt to predict the twist angles in other type I copper(II) centers. Table VII lists representative examples of other type I centers and the predicted twist angles. It is interesting to note that even the *very low* value of stellacyanin can be accommodated within this approach.

Acknowledgment. R.D.B. acknowledges support from a Camille and Henry Dreyfus Teacher–Scholar Grant and the Research Corp. We thank the computing center at North Carolina State University for an allocation of computer time.

Registry No. $Cu(S_4N_2C_{18}H_{26})$ ($n = 4$), 77110-99-7; $Cu(S_4N_2C_{16}H_{22})$ ($n = 2$), 63665-42-9; $Cu(S_4N_2C_{17}H_{24})$ ($n = 3$), 70814-01-6.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

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(39) Freeman, H. C., personal communication.

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X-ray Crystal Structure of Triiodine(1+) Hexafluoroarsenate(V), I_3AsF_6

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Received August 19, 1980

The crystal structure of the compound I_3AsF_6 has been determined from three-dimensional X-ray counter data. Crystals are triclinic with $a = 8.054$ (3) Å, $b = 5.942$ (1) Å, $c = 10.503$ (2) Å, $\alpha = 103.08$ (2)°, $\beta = 88.95$ (2)°, $\gamma = 100.35$ (2)°, and $V = 481$ Å^3. The structure was refined in the space group $P\bar{1}$ to a conventional R factor of 0.091 for 1268 independent reflections with $I \geq 3\sigma(I)$. The structure consists of discrete I_3^+ cations and AsF_6^- anions with some cation–anion interaction. The iodine–iodine distances are 2.660 (2) and 2.669 (2) Å with a bond angle of 101.75 (6)°.

Introduction

The I_3^+ cation was the first of the homoatomic cations of the halogens to be identified.[1,2] In 1938 its existence was postulated by Masson from his studies of aromatic iodinations,[3] and subsequently its presence in 100% sulfuric[4] and fluorosulfuric acid[5] was confirmed from detailed conductometric and cryoscopic measurements. The solids I_3SO_3F,[6] I_3AlCl_4,[7] I_3AsF_6,[8] and I_3SbF_6[9] have also been prepared. A bent structure for I_3^+ has been deduced from Raman[9] and NQR spectra.[7] The crystal structures of various triatomic interhalogen cations have been reported, as well as those of the iodine polyatomic cations I_2^+ and I_5^+ in $I_2Sb_2F_{11}$[10] and $I_{15}(SbF_6)_3$.[11] However, no crystal structure has been reported for any trihalogen homoatomic cation. In the course of our work, we readily obtained good crystals of I_3AsF_6 and report its crystal structure below.

Experimental Section

I_3AsF_6 was prepared quantitatively in SO_2 solution by the reaction of stoichiometric quantities of I_2 and AsF_5, as previously described.[8] Highly crystalline material was obtained upon removal of all volatiles.

X-ray Data Collection. A well-formed crystal was mounted, under dry nitrogen, in a capillary tube as previously described.[12] Preliminary unit cell parameters were obtained from precession photographs which showed the crystal system to be triclinic. The crystal was mounted on a Picker FACS-I diffractometer equipped with a molybdenum tube ($\lambda(K\alpha) = 0.71069$ Å) and a graphite monochromator. Final cell dimensions were obtained by a least-squares fit to the coordinates of 20 well-centered reflections.

Intensity data were collected with use of an ω–2θ scan of 2° (2θ) corrected for dispersion of the Kα doublet. Backgrounds were estimated from a stationary count for 1/10 of the scan time at each end of the scan. If the net intensity was greater than $2\sigma(I)$, then an analysis was made of the scan profile, and those portions not part of the peak were included in the background estimate. Data were collected for $2\theta \leq 50°$ which resulted in 1694 unique reflections of

Table I. Crystal Data for I_3AsF_6

fw	569.6	temp of data collection	20 °C
d_{calcd}	3.93 Mg m^{-3}	λ(Mo Kα)	0.710 69 Å
Z, formula units/unit cell	2	scan range	2.0°
crystal size	0.20 × 0.22 × 0.07 mm	scan rate	2° (2θ) min^{-1}
		maximum 2θ	50°
a	8.054 (3) Å	no. of unique reflections	1694
b	5.942 (1) Å		
c	10.503 (2)	no. of unique reflections with $I \geqslant 3\sigma(I)$	1268
α	103.08 (2)°		
β	88.95 (2)°		
γ	100.35 (2)°		
V	481 Å^3		

Table II. Atomic Coordinates[a] for I_3AsF_6 (×10^4)

atom	x	y	z
I(1)	8297 (1)	8175 (1)	2157 (1)
I(2)	6199 (1)	10962 (2)	1785 (1)
I(3)	7627 (1)	7785 (2)	4604 (1)
As(1)	7753 (1)	5525 (2)	8065 (1)
F(1)	7430 (19)	7497 (26)	7166 (14)
F(2)	8753 (18)	7814 (24)	9269 (13)
F(3)	5903 (16)	5765 (29)	8787 (15)
F(4)	8112 (21)	3602 (28)	8952 (16)
F(5)	9624 (15)	5402 (24)	7337 (16)
F(6)	6800 (24)	3331 (28)	6848 (20)

[a] Standard deviations in parentheses.

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