A Channel-Forming Polyiodide Network in [Cu(dafone)$_3$]I$_{12}$. A Tris Chelate of Dafone and a New Planar Structure for the I$_{12}{}^{2-}$ Ion (Dafone = 4,5-Diazafluoren-9-one)

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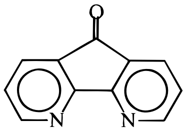
Treatment of an aqueous solution of copper(II) acetate, dafone, and KI with I_2 in CH_2Cl_2 leads to the formation of Cu(dafone)$_3$I$_{12}$ (**1**). **1** crystallizes in the orthorhombic system, space group *Pbcn*, with $a = 22.902(4)$ Å, $b = 11.104(2)$ Å, $c = 18.992(7)$ Å, and $Z = 4$. Cu(dafone)$_3{}^{2+}$ is the first tris chelate of dafone and is stabilized by a channel-forming network of planar $I_{12}{}^{2-}$ ions. Temperature dependence of the EPR spectrum indicates fluxionality of the cation.

Introduction

The remarkable ability of iodine to catenate has led to the formation of an array of polyiodides offering a wide range of structures.[1] In recent years, polyiodides have drawn considerable attention for their electrical properties[2] and tremendous structural variety.[1] Polyiodides range from the simple $I_3{}^-$ through the linear $I_4{}^{2-}$, the V-shaped $I_5{}^-$, three-pronged structures of $I_7{}^-$, $I_9{}^-$, $I_{10}{}^{2-}$, and $I_{12}{}^{2-}$, the Z-shaped $I_8{}^{2-}$, the branched $I_{16}{}^{2-}$, and the S-shaped and linear $I_{16}{}^{4-}$ species[1e−p] to infinite chains.[1d,2e,f] The size and shape of the polyiodide ion depend in an unpredictable way on the size and shape of the counterion. For example, [Mn(phen)$_3$](I$_3$)$_2$ (phen = 1,10-phenanthroline) contains only $I_3{}^-$ ions while [Mn(bipy)$_3$]I$_{6.5}$ (bipy = 2,2′-bipyridine) has $I_3{}^-$ ions as well as infinite polyiodide chains.[2f] 4,5-Diazafluoren-9-one (dafone) is structurally similar to bipy and phen. However, the presence of a rigid five-membered ring results in a much larger chelate bite for this ligand (N···N: dafone, 3.00 Å; bipy, 2.62 Å; phen, 2.64 Å). As a consequence, in all known complexes,[3] dafone chelates in a highly unsymmetrical fashion, forming one normal and one long bond. Until now, no tris chelates have been reported with this ligand. We report here Cu(dafone)$_3{}^{2+}$ included within channels formed by a polyiodide network. The shape of the $I_{12}{}^{2-}$ ion in [Cu(dafone)$_3$]I$_{12}$ (**1**) is markedly different from that found in the only other previously reported compound that contains this ion.[11] A few channel-forming polyiodide networks have been previously reported.[4] The channels in these compounds are built up around organic cations from strongly interacting I_2 and $I_3{}^-$ units. In **1**, the channels are formed by nonbonded interactions between planar $I_{12}{}^{2-}$ ions. From the structure and EPR spectra, it appears that the polyiodide channels and the cations have a symbiotic relationship which stabilizes a strained tris chelate as well as a completely planar $I_{12}{}^{2-}$ ion.



dafone

Experimental Section

Syntheses. Dafone was synthesized by a reported procedure.[5]

Cu(dafone)$_3$I$_{12}$ (1). Cu(CH$_3$CO$_2$)$_2$·H$_2$O (66.8 mg, 0.34 mmol) and dafone (183 mg, 1.0 mmol) were dissolved in 20 cm^3 of water and acidified with a few drops of 1 M H_2SO_4. Iodine (219 mg, 0.86 mmol) in 15 cm^3 of CH_2Cl_2 and KI (165 mg, 1.0 mmol) in 10 cm^3 of water were added to this solution. The mixture was stirred continuously for about 10 min, and the layers were allowed to separate. The organic layer containing the complex was extracted with excess CH_2Cl_2, and the extract was allowed to stand for 1 day. The black crystalline material that formed was recrystallized from CH_3CN to give black,

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Table 1. Crystallographic Data for **1**

formula	$C_{33}H_{18}CuI_{12}N_6O_3$	space group	*Pbcn* (No. 60)
fw	2132.87	T	131 K
a	22.902(4) Å	λ	0.710 73 Å
b	11.104(2) Å	ρ_{calcd}	2.933 g cm^{-3}
c	18.992(7) Å	μ	81.62 cm^{-1}
V	4829(2) Å^3	$R1$	0.0544
Z	4	w$R2$	0.1225

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_o^4)]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (0.0646P)^2]$, $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3) for **1**

atom	x	y	z	U_{eq}[a]
I(1)	7336(1)	−1979(1)	2430(1)	53(1)
I(2)	6711(1)	−178(1)	3117(1)	41(1)
I(3)	6064(1)	1812(1)	3958(1)	64(1)
I(4)	5328(1)	4094(1)	4707(1)	59(1)
I(5)	6941(1)	3093(1)	5049(1)	63(1)
I(6)	7520(1)	4538(2)	6000(1)	90(1)
Cu	5000	5668(2)	2500	26(1)
N(1)	5458(5)	4278(11)	2009(6)	25(3)
N(2)	5262(5)	6982(10)	1815(5)	22(3)
N(3)	4087(5)	5846(11)	1768(6)	33(3)
O(1)	5000	194(14)	2500	58(5)
O(2)	4171(5)	8822(10)	−17(6)	47(3)
C(1)	5911(7)	4167(16)	1558(8)	41(4)
C(2)	6121(6)	3030(14)	1389(7)	33(4)
C(3)	5875(7)	2015(16)	1643(8)	42(4)
C(4)	5412(6)	2117(14)	2080(8)	33(4)
C(5)	5000	1282(23)	2500	52(7)
C(6)	5232(5)	3267(14)	2237(7)	27(4)
C(7)	5751(6)	7590(13)	1747(7)	26(3)
C(8)	5829(7)	8500(15)	1265(9)	43(5)
C(9)	5375(7)	8820(15)	830(9)	42(4)
C(10)	4849(6)	8223(13)	901(8)	32(4)
C(11)	4289(6)	8212(14)	488(8)	30(4)
C(12)	3943(6)	7223(14)	815(9)	37(4)
C(13)	3395(6)	6770(15)	674(9)	44(4)
C(14)	3201(7)	5867(16)	1093(8)	42(4)
C(15)	3546(7)	5410(14)	1629(8)	43(4)
C(16)	4832(6)	7321(12)	1395(8)	27(3)
C(17)	4261(6)	6738(14)	1364(8)	32(4)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **1**[a]

Bond Distances			
I(1)−I(2)	2.785(2)	I(2)−I(3)	3.102(2)
I(3)−I(5)	3.217(2)	I(3)−I(4)	3.360(2)
I(4)−I(4)#1	2.746(3)	I(5)−I(6)	2.755(2)
Cu−N(2)#2	2.05(1)	Cu−N(2)	2.05(1)
Cu−N(1)#2	2.09(1)	Cu−N(1)	2.09(1)
Cu−N(3)#2	2.52(1)	Cu−N(3)	2.52(1)
Bond Angles			
I(1)−I(2)−I(3)	176.63(5)	I(2)−I(3)−I(5)	110.39(5)
I(2)−I(3)−I(4)	174.05(6)	I(5)−I(3)−I(4)	72.97(4)
I(4)#1−I(4)−I(3)	176.96(7)	I(6)−I(5)−I(3)	168.48(6)
N(2)#2−Cu−N(2)	89.0(6)	N(2)#2−Cu−N(1)#2	95.5(4)
N(2)−Cu−N(1)#2	163.7(4)	N(2)#2−Cu−N(1)	163.7(4)
N(2)−Cu−N(1)	95.5(4)	N(1)#2−Cu−N(1)	84.6(6)
N(2)#2−Cu−N(3)#2	80.6(4)	N(2)−Cu−N(3)#2	92.9(4)
N(1)#2−Cu−N(3)#2	103.2(4)	N(1)−Cu−N(3)#2	83.5(4)
N(2)#2−Cu−N(3)	92.9(4)	N(2)−Cu−N(3)	80.6(4)
N(1)#2−Cu−N(3)	83.5(4)	N(1)−Cu−N(3)	103.2(4)
N(3)#2−Cu−N(3)	171.0(6)		
Intermolecular Contacts			
I(6)⋯I(1)#3	3.851(2)	I(6)⋯I(1)#4	3.953(2)
Intermolecular Angles			
I(5)−I(6)⋯I(1)#3	155.98(6)	I(1)#4⋯I(6)⋯I(1)#3	91.75(5)
I(5)−I(6)⋯I(1)#4	88.88(5)		

[a] Symmetry transformations used to generate equivalent atoms: (#1) $-x + 1, -y + 1, -z + 1$; (#2) $-x + 1, y, -z + 0.5$; (#3) $1.5 - x, 0.5 - y, 0.5 + z$; (#4) $x, -y, 0.5 + z$.

lustrous crystals. Yield: 324 mg (0.15 mmol, 88%). Mp: 200 °C. Anal. Calcd for $C_{33}H_{18}N_6O_3CuI_{12}$: C, 18.59; H, 0.85; N, 3.94. Found: C, 19.00; H, 0.86; N, 3.77. IR (KBr disk, cm^{-1}): 1732, 1585, 1410, 750, 388, 277, 235, 137, 84.

X-ray Crystallography. X-ray data were collected on a black, rectangular crystal of dimensions 0.65 × 0.36 × 0.21 mm using a Siemens P4 diffractometer with Mo Kα radiation at 131 K. A semiempirical absorption correction was applied. The structure was solved by direct methods using SHELXS-86[6a] and refined by full-matrix least-squares methods using SHELXL-93.[6b] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located at calculated positions and refined using a riding model. The data refined to a final $R1$ value of 0.0544 with w$R2$ = 0.1225 for reflections with $I > 2\sigma(I)$. Crystal data are given in Table 1, atomic coordinates in Table 2, and important bond lengths and angles in Table 3.

Spectral Measurements. IR spectra were recorded on a JASCO 5300 spectrometer (range, 4000 to 600 cm^{-1}) and a Bruker IFS 66v FT-IR spectrometer (range 500−50 cm^{-1}). CH_2Cl_2 solution electronic spectra were recorded on a JASCO 7800 spectrophotometer. A powder diffuse-reflectance spectrum was recorded on a Cary 17 UV/vis/near-IR spectrophotometer. Absorbance was recalculated using the Kubelka−Munk function.[7] Powder and single-crystal EPR spectra at room temperature and at 123 K were recorded on a JEOL FE-3X spectrometer operating at X-band frequency.

Results and Discussion

Synthesis. **1** was prepared by a two-phase synthetic route previously used in our laboratory for other polyiodides of metal tris chelate cations.[2f,g] In the literature, the general procedure employed for polyiodide synthesis involves the addition of I_2 to the iodide or triiodide of the cation in a single phase.[1] A solution of HI has also been employed in some cases.[1k] The previously reported dodecaiodide was synthesized by the addition of iodine to the iodide salt of a K^+ crown ether complex ion.[11] Our studies[2f,g] have shown that the natures of the metal and the chelating ligand strongly influence the polyiodide species formed. However, it is not possible to predict the stoichiometries that will result for a particular metal ion−ligand combination.

Crystal Structure. In **1**, Cu lies on a 2-fold axis (the crystallographic b axis). Two of the ligands coordinate in an unsymmetrical fashion with one long and one short Cu−N bond, Cu−N(2) = 2.04(1) Å and Cu−N(3) = 2.52(1) Å, while the third dafone is crystallographically constrained to symmetric chelation, Cu−N(1) = 2.09(1) Å (Figure 1a). There is a strong tetrahedral distortion in the CuN_4 equatorial plane (dihedral angle 23.6(8)°). Thus, the geometry around copper is best described as a compressed tetrahedron with axial coordination, more akin to the structures observed for $[Cu(bipy)_2](BF_4)_2$ and $[Cu(bipy)_2](ClO_4)_2$[8] than to the structures of the $Cu(phen)_3^{2+}$ and $Cu(bipy)_3^{2+}$ complexes.[9] Another remarkable feature is that the chelate bite of the symmetrically coordinated dafone is significantly shorter than that of the other two ligands (N(1)⋯N(1)′ = 2.81(2) Å, prime = $-x + 1$, y, $-z + 0.5$;

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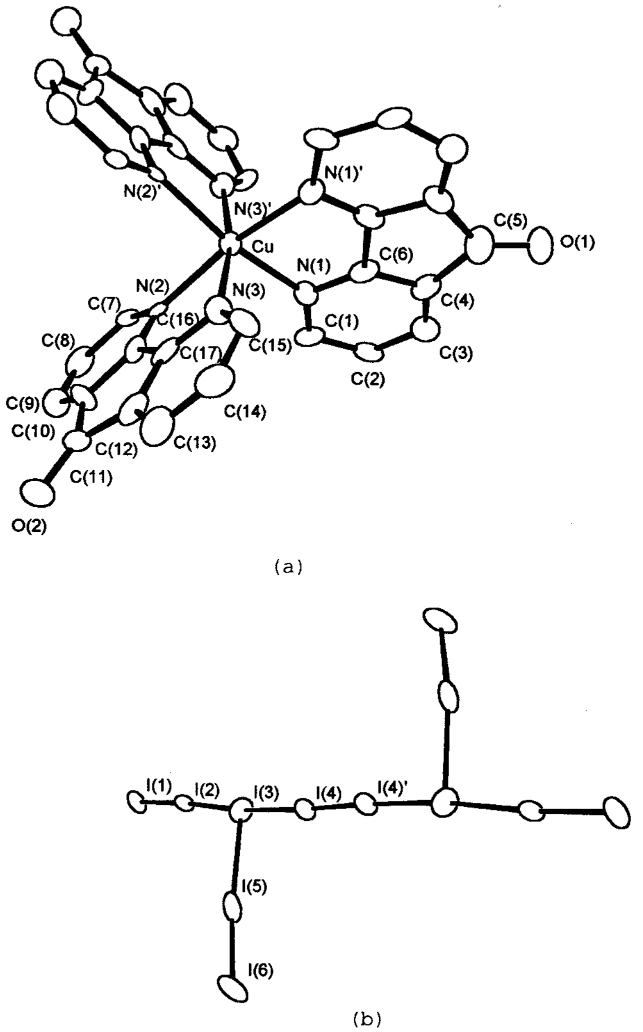


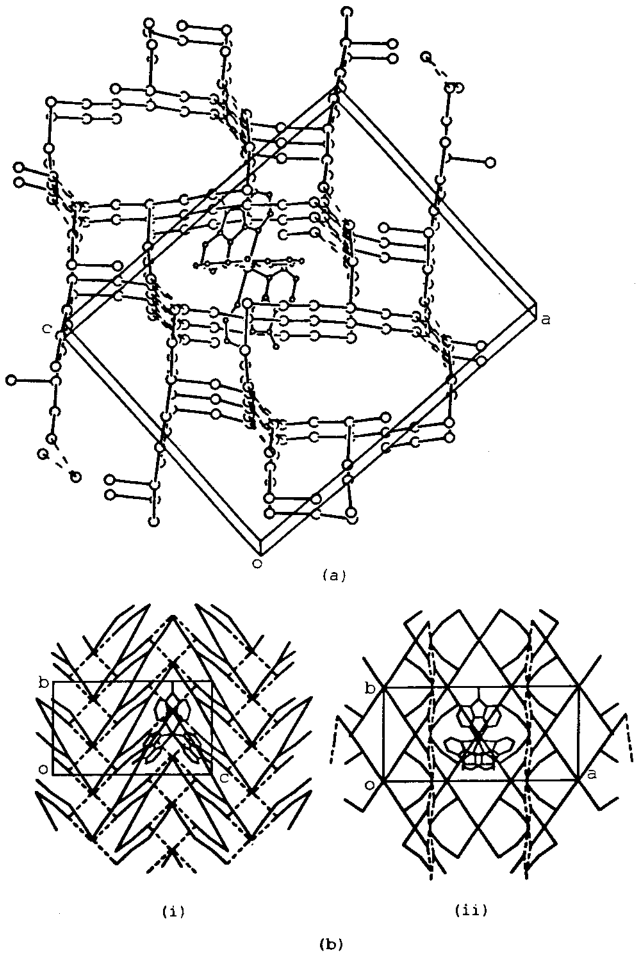
(a)

(b)

Figure 1. (a) Cu(dafone)$_3^{2+}$ in **1** (prime = $-x + 1, y, -z + 0.5$). (b) I_{12}^{2-} in **1** (prime = $1 - x, 1 - y, 1 - z$). Atoms are represented by thermal ellipsoids at 50% probability levels.

N(2)···N(3) = 2.97(2) Å). The U_{eq} value is the same for N(1) and N(2), and as expected, it is slightly larger for the weakly bound N(3). It is thus clear that while two of the ligands behave "normally", the third dafone adapts itself to symmetric chelation by reducing its bite through a slight reduction (by ~4°) in the external N−C−C bond angles. This is energetically less demanding than a static distortion about the C_2 axis, which would have resulted in three long bonds around the copper atom.

The centrosymmetric I_{12}^{2-} ion (Figure 1b) consists of an approximately linear eight-member chain having an I_2 branch on either side. A comparison of the bond lengths indicates that there are five iodine units and two I^- ions, I(3) and I(3)′ (prime = $1 - x, 1 - y, 1 - z$). As pointed out by Tebbe and Kavoosian,[11] the I_{12}^{2-} ion can be described as two V-shaped I_5^- units bridged by an I_2 molecule. However, unlike Tebbe's ion, the present I_{12}^{2-} has all the I atoms confined very nearly to a plane (root-mean-square deviation from its least-squares plane: 0.081 Å). In order to convert our planar structure to that of Tebbe, the I(2)−I(3)−I(4) angle has to be shortened from 174 to 90°. This difference arises because of the T-shaped arrangement around I(3), as opposed to the three-pronged structures observed for the I_7^- ion.[1h,i]



(a)

(i) (ii)

(b)

Figure 2. (a) Packing in **1** viewed nearly along the *b* axis showing the channel formation. (b) Two other views of the packing seen in projections down the (i) *a* axis and (ii) *b* axis. Only one cation is shown.

Intermolecular I···I interactions[10] between I(1) and I(6) assemble the I_{12}^{2-} units into a 3-dimensional network leading to a channel-like arrangement (Figure 2a). These contacts are quite long with I(6)−I(1)′ = 3.851(2) Å and I(6)−I(1)″ = 3.953(2) Å (prime = $1.5 - x, 0.5 - y, 0.5 + z$; double prime = $x, -y, 0.5 + z$). However, in view of the iodine van der Waals radius of 2.15 Å, these may be considered reasonably strong intermolecular interactions. Large six-sided and smaller four-sided channels form as a result of these van der Waals contacts. The complex cations are stacked up along the *b* axis in the larger channels. This unique arrangement of the polyiodides and the enclosed Cu(dafone)$_3^{2+}$ cations is stabilized by I···H−C contacts, whose importance in controlling the packing of molecules has been recognized.[11] I(1), I(2), I(5), and I(6) have nearest I···H contacts in the range 3.017(1)−3.59(2) Å. Previously known[4] polyiodide inclusion complexes with organic cations in channels are built from I_3^- and I_2 moieties organized in layers, pleated sheets, and chains or ladder-type bridged chains. In contrast, the channels in **1** are formed by a grill-like arrangement of I_{12}^{2-} ions. While Figure 2a gives the impression of a stack-like arrangement, in reality we have a 3-dimensional network as seen from the projections perpendicular to the channel axis (Figure 2b).

Solution Chemistry and Electronic Spectroscopy. Absorption spectra in dichloromethane show bands due to iodine (505

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nm) and triiodide species (330 nm), indicating the break-up of the polyiodide in solution.[12] The powder diffuse-reflectance spectrum is nearly featureless in the visible region, implying electronic delocalization over the entire polyiodide network. Reflectance studies usually reveal a broad band covering the entire visible range.[2f,13] The delocalization in the present case, probably via the nonbonded intermolecular contacts, is manifested in the lustrous appearance of the crystals. This kind of a reflectance spectrum has been reported previously in an infinite-chain polyiodide.[2e] In both solution and the solid state, the d−d transitions of the cation are not clearly resolved, due to low concentration of the cation in the former case and other absorptions in the region in the latter case. EPR in dilute solutions and in frozen solutions gave broad signals, which prevented assignments to any particular species. Therefore, it is not possible to know definitely the exact species existing in solution. One might expect the formation of species like $Cu(dafone)_2(I)_2$ as well as solvent-substituted species especially in acetonitrile, although there is no evidence for these species from our studies. On the other hand, the compound can be recrystallized without decomposition from solvents like acetonitrile and dichloromethane. It is insoluble in water and is not decomposed by prolonged contact with it.

EPR. The polyiodide network in **1** serves to magnetically isolate the Cu(II) ions. The closest Cu···Cu neighbors, at a distance of 9.6 Å from each other, are separated by the polyiodide network. Although the cations are aligned along the *b* axis with no intervening polyiodide units, the distance of 11.1 Å between copper atoms is sufficient to preclude any significant magnetic interactions. This results in well-resolved EPR spectra, with axial **g** and **A** tensors. At 300 K, $g_{\parallel} = 2.247$, $g_{\perp} = 2.078$, $A_{\parallel} = 136.4 \times 10^{-4}$ cm^{-1}, and $A_{\perp} \leq 23 \times 10^{-4}$ cm^{-1}, while at 123 K, $g_{\parallel} = 2.262$, $g_{\perp} = 2.067$, $A_{\parallel} = 163.7 \times 10^{-4}$ cm^{-1}, and $A_{\perp} \leq 18 \times 10^{-4}$ cm^{-1}. The $A_{\parallel}$ value is temperature dependent, increasing from 136.4×10^{-4} cm^{-1} at 300 K to 163.7×10^{-4} cm^{-1} at 123 K, while the other parameters are less sensitive. The $A_{\parallel}$ value is expected to be correlated to the extent of tetrahedral distortion.[14] Planar structures have larger $A_{\parallel}$ values than tetrahedrally compressed systems. Since the diffraction data were collected at 131 K, the structure corresponds to the low-temperature EPR data.

For analysis of single-crystal EPR data, the molecular *x* axis is taken along the crystal *b* axis on which the copper atom lies. The normal to the mean equatorial plane is taken as the molecular *z* axis, which forms angles of 4.5° with the Cu−N(3) vector and 49.5° with the *a* axis. Figure 3 shows the single-crystal EPR spectra at two temperatures with the magnetic field making an angle of 45° with the *a* axis in the *ac* plane. In this orientation one of the two magnetically nonequivalent molecules has its *z* axis nearly along the field, while the other molecule has it orthogonal to the field. The *g* and *A* values measured from the low-temperature spectrum agree with the corresponding powder EPR parameters within experimental error. The 300 K spectrum (Figure 3a), on the other hand, shows broadening due to additional splitting, implying that the orientation of the molecule with respect to the magnetic field is different although the crystal orientation is unchanged. This observation indicates that the Cu(II) complex trapped in the polyiodide network is fluxional. On the basis of the observed low-temperature structure, three possibilities arise: (a) tetrahedral distortion in the CuN(1)N(1)′N(2)N(2)′ plane may increase on going from 130 to 300 K; (b) there being two types of dafone ligands, they may dynamically exchange positions at higher temperatures; (c) a phase transition may occur between 130 and 300 K. The following observation strongly favors case a over the other two. The room-temperature unit cell is also orthorhombic, and the space group is unchanged. This rules out the possibility of a phase transition. The room-temperature cell parameters ($a = 23.08(2)$ Å, $b = 11.12(2)$ Å, $c = 19.34(2)$ Å) show that the increases in a ($\Delta a = 0.18$ Å) and c ($\Delta c = 0.35$ Å) are respectively 9 and 17 times the increase in b ($\Delta b = 0.02$ Å). The *z* axis lies approximately midway between the crystal axes in the *ac* plane. The observed cell expansion is therefore consistent with increase in the tetrahedral distortion, which takes place along the molecular *z* axis. Unresolved disorders are usually manifested in the thermal ellipsoids of vibration.[15] The low precision of the refined *U* values prevents a detailed analysis of the anisotropic vibration amplitudes. The differential amplitudes for the coordinated atoms (ΔU_i, i = molecular x, y, z) are within one standard deviation for all except ΔU_z for N(1) and N(1)′, which is 0.019(8) Å^2. This indicates dynamic or static disorder of these atoms along the *z* direction. On the other hand, the large distortions required for a dynamic switch between the different dafone ligands would probably destabilize the polyiodide network around the cation. We therefore conclude that the temperature dependence of the EPR spectrum as well as the highly anisotropic thermal expansion of the unit cell is a consequence of tetrahedral distortion of the coordination polyhedron. The decrease in the $A_{\parallel}$ value at 300 K is consistent with such a distortion,[14] while the additional splitting would indicate crystallographic disorder, resulting from this distortion. The driving force for the above fluxionality is most likely the release of strain involving the symmetric chelation of dafone.

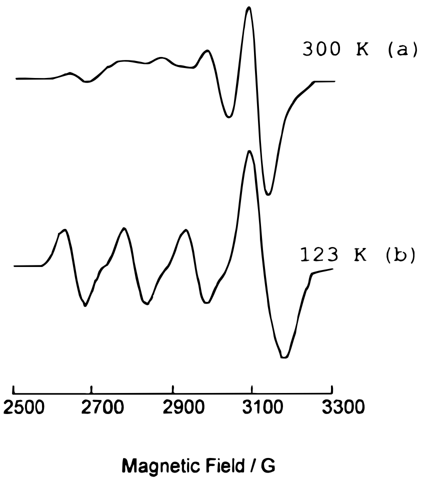

Figure 3. Single-crystal EPR spectra of **1** with **B** midway between the axes in the *ac* plane ($\nu = 9.17$ GHz).

Conclusions

(i) The polyiodide network stabilizes an "unwilling" tris chelate complex of dafone. The network of the planar I_{12}^{2-} ions is in turn stabilized by the cation. (ii) A new, discrete polyiodide species, the planar I_{12}^{2-} ion, is observed in **1** that differs in structure and packing from the previously reported nonplanar I_{12}^{2-} ion.[11] This highlights the role of the cation (a tris chelate of Cu(II) in the former case and a potassium crown ether in the

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latter) in determining the structure of the polyiodide species. (iii) Dafone appears to overcome its preference for unsymmetric chelation when its tris chelate is stabilized by an extensive polyiodide network. The cation Cu(dafone)$_3^{2+}$ undergoes a temperature-dependent structural disorder due to tetrahedral distortion.

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Supporting Information Available: Tables S1−S5, listing crystal data, atomic coordinates, temperature factors, bond distances and angles, and intermolecular contacts (8 pages). Ordering information is given on any current masthead page.

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