Structural Comparison of $(CuICH_3CN)_4$·Dibenzo-18-crown-6 (I) and $(CuICH_3CN)_x$ (II) Fluorescent Copper(I) Materials

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Abstract

The single crystal X-ray structures of $(CuICH_3CN)_4$·dibenzo-18-crown-6 (I) and $(CuICH_3CN)$ (II) have been determined at room temperature [(I) $C_{28}H_{36}Cu_4I_4N_4O_6$, monoclinic space group $P2_1/n$, $a = 10.116(4)$, $b = 18.092(8)$, $c = 22.211(9)$ Å, $\beta = 98.66(3)°$, $Z = 4$; (II) C_2H_3CuIN, orthorhombic $Pbn2_1$, $a = 13.618(8)$, $b = 8.742(2)$, $c = 4.298(2)$, $Z = 4$]. (I) exists as a distorted cube with copper and iodine at alternate corners, the fourth coordination site of copper occupied by an acetonitrile molecule coordinated through nitrogen. The cluster contains no crystallographic symmetry element and Cu–Cu distances average 2.770(5) Å. The dibenzo-18-crown-6 displays only second sphere type interactions with the cluster. (II) displays a pleated double chain type structure with distorted rectangles of alternating Cu and I atoms sharing opposite edges in infinite array. Copper displays tetrahedral geometry by coordination to three iodine atoms and a nitrogen bound acetonitrile molecule.

Introduction

Copper(I) halides react with Lewis base compounds to produce complexes of wide variation in stoichiometry and structural format. Among these are cluster compounds of stoichiometry $(Cu(I)IL)_4$, a number of which have been characterized by single crystal X-ray techniques [2]. These crystalline materials display a pseudocubic arrangement with metal and halide occupying alternate corners of a distorted cube, the electron donating ligand filling the remaining coordination site of the approximately tetrahedral copper atoms and thus projecting along the diagonals of the cube. When the electron donating ligand is an amine base [3], these clusters reportedly display a wide range of fluorescent behavior at room temperature. The nature of the electronic transition associated with the emission has not been identified. Changes in the emission maximum with temperature have been noted for $(CuIpyridine)_4$ [3a] and for $(CuImorpholine)_4$ [3b] in which the cluster displays no crystallographic symmetry elements or a two fold axis respectively, but not for $(CuIpiperidine)_4$ in which a $\bar{4}$ crystallographic symmetry element relates all Cu–ligand bonds [4]. Thus it has been suggested that observation of thermochromic fluorescence may be correlated with the lack of a four fold symmetry element in the cluster. The wavelength of the fluorescent emission changes with the identity of the halide, with the identity of the Lewis base and in one case with the presence of a crown ether in the synthetic procedure. The product of the reaction of CuI and acetonitrile reportedly displays yellow emission at 298 K and green emission at 77 K. Prepared in the presence of dibenzo-18-crown-6, the material fluoresces yellow at 298 K and pink at 77 K [5]. We have determined the single crystal X-ray structures of $(CuICH_3CN)_4$·dibenzo-18-crown-6 (I) and of $(CuICH_3CN)_x$ (II) at room temperature to ascertain the involvement of the crown ether ring with the organometallic cluster.

Experimental

Clear colorless crystals of $(CuICH_3CN)_4$·dibenzo-18-crown-6 (I) and of $(CuICH_3CN)_x$ (II) were prepared by the procedure of Hardt and Stoll [5]. A crystal of approximate dimensions 0.5 × 0.6 × 0.5 mm (I), 0.1 × 0.4 × 0.3 mm (II), was sealed in a capillary in an atmosphere of acetonitrile vapor and mounted on a Syntex P3 automated diffractometer. Unit cell dimensions were determined by least squares refinement of the best angular positions for fifteen independent reflections ($2\theta > 15°$) during normal alignment procedures. Data (11394 points (I), 1228 points (II)) were collected at room temperature using a variable scan rate, a $\theta-2\theta$ scan width of 1.2° below $K\alpha_1$ and 1.2° above $K\alpha_2$ to a maximum 2θ value of 116°. Backgrounds were measured at each side of the scan limit for a combined time equal to the total scan time. The intensities of three stan-

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dard reflections were measured after every 97 reflections and as the intensities of these reflections showed about 8% variation, corrections for decomposition were made based on the linear decay of the standard intensities. Data were corrected for Lorentz, polarization and background effects. After removal of redundent and space group forbidden data, 4399 reflections (**I**), 759 (**II**), were considered observed $[I > 3.0\sigma(I)]$.

Crystal Data

(**I**) $C_{28}H_{36}Cu_4I_4N_4O_6$, M = 1286.4, monoclinic, $a = 10.116(4)$, $b = 18.092(8)$, $c = 22.211(9)$ Å, $\beta = 98.66(3)°$, $V = 4018.6(27)$ Å^3, $F(000) = 2432$, space group $P2_1/n$, $Z = 4$, $D_{calc} = 2.12$ g cm^{-3}, MoK$_\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu(\text{MoK}_\alpha) = 51.77$ cm^{-1}.

(**II**) C_2H_3CuIN, M = 231.5, orthorhombic, $a = 13.618(8)$, $b = 8.742(2)$, $c = 4.298(2)$ Å, $V = 511.6(5)$ Å^3, $F(000) = 416$, space group $Pbn2_1$, $Z = 4$, $D_{calc} = 3.00$ g cm^{-3}, MoK$_\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu(\text{MoK}_\alpha) = 100.87$ cm^{-1}.

Solution of the structures was achieved using MULTAN80 [6]. Refinement of scale factor, positional and anisotropic thermal parameters for all nonhydrogen atoms was carried out to convergence [7]. Hydrogen positional parameters for the crown ether hydrogens of (**I**) were calculated assuming normal geometry and a C–H distance of 0.97 Å. These hydrogen positional parameters were included in the final cycles of refinement. The hydrogen atoms were assigned isotropic thermal parameters of $U = 0.03$. All parameters associated with hydrogen atoms were held invariant. The hydrogen atoms of the acetonitrile groups were not located for (**I**) or (**II**). The final cycle of refinement [function minimized, $\Sigma(|F_o| - |F_c|)^2$] led to a final agreement factor, R = 7.0% (**I**), R = 8.1% (**II**). [$R = (\Sigma||F_o| - |F_c||/|F_o|) \times 100$]. Anomalous dispersion corrections were made for Cu and I. Scattering factors were taken from Cromer and Mann [8]. Unit weights were used throughout for (**I**). For (**II**) a weighting scheme was applied ($w = 10.0/F_{obs}$ if $F_{obs} > 10.0$). The average values of weighted delta F for equally populated groups of reflections partitioned according to sine theta, differed by a factor of 3.5.

Projection views of the molecules, Fig. 1, (**I**); Fig. 2, (**II**), are based on the positional parameters of Tables I and II respectively. Derived bond angles and distances (Tables III and IV) are based on the same final data.

Supplementary Material Available

Anisotropic thermal parameters for (**I**) and (**II**), hydrogen positional parameters for (**I**) and listings of observed and calculated structure factors for (**I**) and (**II**) are available from the authors on request.

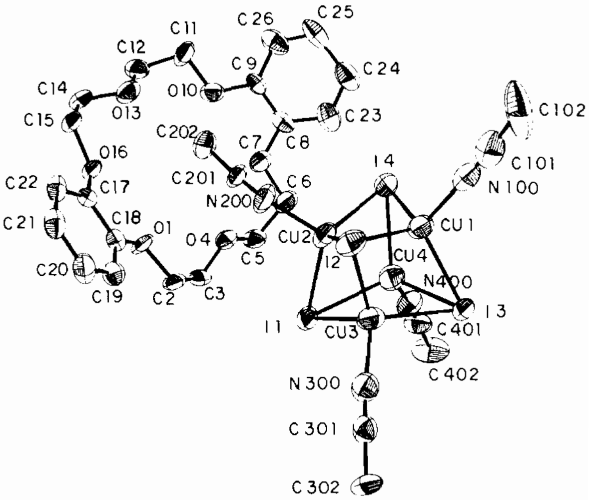

Fig. 1. Projection view of Cu_4I_4(acetonitrile)$_4$•dibenzo-18-crown-6.

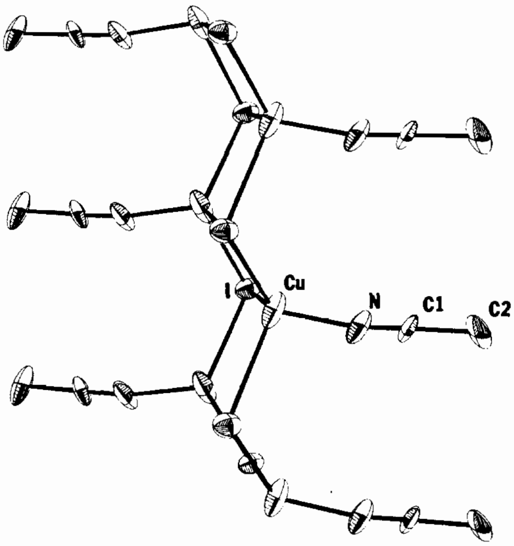

Fig. 2. Packing of asymmetric units in the monoclinic cell.

Discussion

CuI and acetonitrile alone form a complex that is unexpectedly different from that formed by CuI and acetonitrile in the presence of dibenzo-18-crown-6. $(CuICH_3CN)_4$•dibenzo-18-crown-6 (**I**) (Fig. 1) displays the expected pseudocubic Cu_4I_4 cluster with one acetonitrile group coordinated to each copper atom via electron pair donation from nitrogen. The acetonitrile groups thus project from alternate corners of the 'cube' roughly along the cubic diagonals. The average Cu–Cu distance (2.770(5) Å is long in comparison to that observed in other similar clusters; 2.690(5) Å average [3a] in (CuIpyridine)$_4$ (**III**); 2.65(3) Å average in (CuImorpholine)$_4$

TABLE I. Positional Parameters for $Cu_4I_4(CH_3CN)_4 \cdot$Dibenzo-18-Crown-6 (I).

Atom	$x(\sigma(x))$	$y(\sigma(y))$	$z(\sigma(z))$	U_{equiv}
I1	0.1516(2)	0.1688(1)	0.2046(1)	5.15
I2	−0.2292(2)	0.0434(1)	0.2339(1)	5.66
I3	0.0757(2)	−0.0263(1)	0.0840(1)	4.96
I4	0.1561(2)	−0.0624(1)	0.2717(1)	5.68
Cu1	−0.0245(3)	−0.0545(2)	0.1979(1)	5.77
Cu2	0.0102(3)	0.0640(2)	0.2697(1)	5.91
Cu3	−0.0234(3)	0.0914(2)	0.1499(1)	5.89
Cu4	0.2080(3)	0.0249(2)	0.1739(1)	1.99
N100	−0.1278(21)	−0.1497(12)	0.2067(9)	5.47
C101	−0.2010(29)	−0.1967(15)	0.2120(13)	7.13
C102	−0.3065(32)	−0.2531(16)	0.2240(15)	12.15
N200	−0.0015(23)	0.0994(12)	0.3554(9)	6.50
C201	0.0255(23)	0.1090(12)	0.4025(9)	4.60
C202	0.0540(25)	0.1172(15)	0.4651(10)	6.10
N300	−0.0855(21)	0.1627(12)	0.0909(9)	6.10
C301	−0.1061(24)	0.2013(13)	0.0529(10)	5.14
C302	−0.1287(26)	0.2493(15)	0.0016(11)	6.38
N400	0.3965(21)	0.0274(13)	0.1323(9)	6.16
C401	0.4985(24)	0.0369(15)	0.1035(11)	6.12
C402	0.6250(24)	0.0492(18)	0.0619(12)	8.22
O1	0.1202(14)	0.2973(8)	0.4223(6)	4.59
C2	0.1712(24)	0.2972(12)	0.3581(9)	4.65
C3	0.3047(24)	0.2670(13)	0.3459(10)	4.81
O4	0.3023(14)	0.1931(8)	0.3633(6)	4.44
C5	0.4253(23)	0.1579(14)	0.3442(10)	9.93
C6	0.4091(26)	0.0778(15)	0.3556(11)	5.70
O7	0.3816(16)	0.0657(9)	0.4207(7)	5.27
C8	0.3620(23)	−0.0054(12)	0.4422(11)	4.82
C9	0.3274(21)	−0.0117(12)	0.5060(10)	3.89
O10	0.3127(16)	0.0540(9)	0.5369(6)	5.13
C11	0.2547(24)	0.0494(14)	0.5995(10)	6.11
C12	0.2318(23)	0.1259(13)	0.6249(9)	5.33
O13	0.1314(16)	0.1597(9)	0.5962(6)	5.50
C14	0.0820(25)	0.2255(14)	0.6259(8)	5.38
C15	−0.0276(23)	0.2558(11)	0.5973(9)	4.55
O16	0.0301(14)	0.2803(8)	0.5368(6)	4.00
C17	−0.0605(22)	0.3090(10)	0.5034(9)	3.63
C18	−0.0090(19)	0.3185(11)	0.4405(9)	3.99
C19	−0.0903(25)	0.3481(13)	0.4026(10)	4.67
C20	−0.2164(30)	0.3675(15)	0.4231(11)	6.28
C21	−0.2671(20)	0.3577(13)	0.4848(10)	4.88
C22	−0.1873(20)	0.3283(12)	0.5244(8)	4.33
C23	0.3742(25)	−0.0709(18)	0.4075(11)	6.52
C24	0.3571(28)	−0.1380(14)	0.4338(14)	7.22
C25	0.3208(27)	−0.1434(14)	0.4954(12)	6.85
C26	0.3110(26)	−0.0824(15)	0.5315(12)	6.26
H201	0.1114(0)	0.2677(0)	0.3364(0)	
H202	0.1698(0)	0.3482(0)	0.3423(0)	
H301	0.3410(0)	0.2721(0)	0.3027(0)	
H302	0.3632(0)	0.2953(0)	0.3692(0)	
H501	0.4556(0)	0.1680(0)	0.3010(0)	
H502	0.4933(0)	0.1772(0)	0.3673(0)	
H601	0.3340(0)	0.0592(0)	0.3356(0)	
H602	0.4892(0)	0.0507(0)	0.3373(0)	
H1101	0.1688(0)	0.0230(0)	0.6042(0)	
H1102	0.3137(0)	0.0213(0)	0.6230(0)	
H1201	0.2067(0)	0.1248(0)	0.6690(0)	
H1202	0.3169(0)	0.1538(0)	0.6161(0)	

(continued overleaf)

TABLE 1 *(continued)*

Atom	$x(\sigma(x))$	$y(\sigma(y))$	$z(\sigma(z))$	U_{equiv}
H1401	0.0527(0)	0.2163(0)	0.6695(0)	
H1402	0.1545(0)	0.2631(0)	0.6233(0)	
H1501	−0.0952(0)	0.2168(0)	0.5946(0)	
H1502	−0.0734(0)	0.2965(0)	0.6209(0)	
H19	−0.0553(0)	0.3551(0)	0.3587(0)	
H20	−0.2741(0)	0.3889(0)	0.3947(0)	
H21	−0.3609(0)	0.3711(0)	0.5000(0)	
H22	−0.2235(0)	0.3223(0)	0.5679(0)	
H23	0.3974(0)	−0.0670(0)	0.3613(0)	
H24	0.3726(0)	−0.1833(0)	0.4071(0)	
H25	0.3021(0)	−0.1930(0)	0.5130(0)	
H26	0.2903(0)	−0.0881(0)	0.5768(0)	

TABLE II. Positional Parameters for $(CuICH_3CN)_x$ (**II**).

Atom	$x(\sigma(x))$	$y(\sigma(y))$	$z(\sigma(z))$
I1	0.8623(1)	0.4684(2)	0.3509
Cu1	0.0516(2)	0.4089(3)	0.3418(21)
N1	0.0826(17)	0.1896(21)	0.379(10)
C1	0.1027(16)	0.0648(21)	0.379(11)
C2	0.1350(18)	0.9025(26)	0.340(11)

[3b] (**IV**) and 2.657(2) Å average in $(CuIpiperidine)_4$ (**V**) [4]. Notable also is the 2.845(5) Å distance between Cu1 and Cu3 as compared with the average of the five other similar distances (2.755(5) Å). This distance is the longest observed in any of the reported tetrameric CuI clusters with nitrogen bases, but it is shorter than the 2.78 Å average distance reported for $(CuIEt_3As)_4$, the 2.92 Å average for $(CuIEt_3P)_4$ and the distances in excess of 3.1 Å

TABLE III. Bond Angles (°) and Distances (Å) for $Cu_4I_4(CH_3CN)_4$•Dibenzo-18-Crown-6.

Cu1–Cu2	2.724(5)	I2–Cu1–I3	108.6(1)
Cu1–Cu3	2.845(5)	I2–Cu1–I4	114.6(1)
Cu1–Cu4	2.739(5)	I3–Cu1–I4	113.9(1)
Cu2–Cu3	2.775(4)	I1–Cu2–I2	111.8(1)
Cu2–Cu4	2.783(4)	I1–Cu2–I4	110.9(1)
Cu3–Cu4	2.754(5)	I2–Cu2–I4	113.8(1)
		I1–Cu3–I2	110.2(1)
Cu1–I2	2.750(4)	I1–Cu3–I3	116.2(1)
Cu1–I3	2.628(3)	I2–Cu3–I3	107.7(1)
Cu1–I4	2.635(4)	I1–Cu4–I3	113.6(1)
Cu2–I1	2.665(4)	I1–Cu4–I4	110.6(1)
Cu2–I2	2.685(4)	I3–Cu4–I4	109.6(1)
Cu2–I4	2.724(4)		
Cu3–I1	2.685(4)	Cu2–I1–Cu3	62.5(1)
Cu3–I2	2.718(4)	Cu2–I1–Cu3	62.1(1)
Cu3–I3	2.690(4)	Cu3–I1–Cu4	61.2(1)
Cu4–I1	2.728(4)	Cu1–I2–Cu2	60.1(1)
Cu4–I3	2.725(4)	Cu1–I2–Cu3	62.7(1)
Cu4–I4	2.672(4)	Cu2–I2–Cu3	61.8(1)
		Cu1–I3–Cu3	64.7(1)
I1–I2	4.432(3)	Cu1–I3–Cu4	61.5(1)
I1–I3	4.562(3)	Cu3–I3–Cu4	61.1(1)
I1–I4	4.440(3)	Cu1–I4–Cu2	61.1(1)
I2–I3	4.369(3)	Cu1–I4–Cu4	62.1(1)
I2–I4	4.532(3)	Cu2–I4–Cu4	62.1(1)
I3–I4	4.411(3)		
		N100–C101–C102	173.5(28)
Cu1–N100	2.01(2)	N200–C201–C202	176.0(24)

(continued on facing page)

TABLE III *(continued)*

Cu2–N200	1.99(2)	N300–C301–C302	177.4(24)
Cu3–N300	2.00(2)	N400–C401–C402	175.4(28)
Cu4–N400	1.99(2)		
		I2–Cu1–N100	99.5(6)
N100–C101	1.12(3)	I3–Cu1–N100	112.3(5)
N200–C201	1.13(3)	I4–Cu1–N100	107.0(6)
N300–C301	1.14(3)	I1–Cu2–N200	103.8(6)
N400–C401	1.14(3)	I2–Cu2–N200	113.6(7)
		I4–Cu2–N200	102.0(7)
C101–C102	1.47(4)	I1–Cu3–N300	104.7(6)
C201–C202	1.47(3)	I2–Cu3–N300	111.7(6)
C301–C302	1.48(3)	I3–Cu3–N300	106.3(6)
C401–C402	1.48(3)	I1–Cu4–N400	104.1(7)
		I3–Cu4–N400	102.1(6)
		I4–Cu4–N400	116.6(6)
		C18–O1–C2	118.5(16)
O1–C2	1.44(2)	O1–C2–C3	111.8(18)
C2–C3	1.44(3)	C2–C3–O4	109.5(18)
C3–O4	1.39(3)	C3–O4–C5	112.0(16)
O4–C5	1.40(3)	O4–C5–C6	108.8(18)
C5–C6	1.48(4)	C5–C6–O7	108.7(20)
C6–O7	1.45(3)	C6–O7–C8	119.0(18)
O7–C8	1.38(3)	O7–C8–C23	115.2(19)
C8–C9	1.41(3)	O7–C8–C9	115.2(19)
C9–O10	1.37(3)	C9–C8–C23	118.0(20)
O10–C11	1.43(2)	C8–C9–O10	115.1(18)
C11–C12	1.50(3)	C8–C9–C26	118.5(20)
C12–O13	1.42(3)	O10–C9–C26	126.4(20)
O13–C14	1.42(3)	C9–O10–C11	115.8(17)
C14–C15	1.46(3)	O10–C11–C12	109.3(18)
C15–O16	1.45(2)	C11–C12–O13	108.0(19)
O16–C17	1.37(3)	C12–O13–C14	112.3(17)
C17–C18	1.42(3)	O13–C14–C15	110.4(18)
C18–O1	1.36(2)	C14–C15–O16	106.9(17)
C18–C19	1.37(3)	C15–O16–C17	114.2(16)
C19–C20	1.33(4)	O16–C17–C18	113.7(17)
C20–C21	1.40(3)	O16–C17–C22	126.4(17)
C21–C22	1.39(3)	C22–C17–C18	119.9(19)
C22–C17	1.34(3)	C17–C18–O1	116.6(18)
C8–C23	1.41(4)	C17–C18–C19	118.9(18)
C23–C24	1.34(4)	O1–C18–C19	124.5(18)
C24–C25	1.36(4)	C18–C19–C20	121.6(21)
C25–C26	1.36(4)	C19–C20–C21	119.5(25)
C26–C9	1.40(3)	C20–C21–C22	120.4(20)
		C21–C22–C17	119.8(17)
		C8–C23–C24	121.6(23)
		C23–C24–C25	119.8(25)
		C24–C25–C26	121.2(24)
		C25–C26–C9	120.6(24)

reported for the $(CuBr)_4$ and $(CuCl)_4$ clusters with trialkyl phosphorous donor ligands [2b, 2c].

The atoms of the cluster are unrelated by a crystallographic symmetry element and the cluster thus resembles cluster (**III**). It is unlike structure (**IV**) in which a two fold crystallographic axis penetrates one set of opposing cluster faces and unlike cluster (**V**) where the tetrameric structure is centered on a $\bar{4}$ center of symmetry.

As expected, deformation of the cubic faces to bring copper atoms at opposite corners of faces into closer proximity results in greater separation of iodide atoms at alternate corners. Thus those (CuInitrogen donor)$_4$ clusters which show relatively shorter Cu–Cu separations, display relatively longer I–I separations: 4.508(3) Å in (**III**); 4.515 Å in (**V**) and 4.458(3) Å in the title structure (**I**). Cu–I bonding distances remain relatively constant; 2.703(4) Å in (**III**),

TABLE IV. Bond Angles (°) and Distances (Å) for $(\mathrm{CuICH_3CN})_x$.

I1–Cu1'	2.630(5)
I1–Cu1''	2.704(10)
I1–Cu1'''	2.641(10)
I1–I1''''	4.358(4)
I1–I1$^{\mathrm{V}'}$	4.298(2)
Cu1'–Cu1'''	3.022(10)
Cu1'–Cu1$^{\mathrm{V}''}$	4.298(13)
Cu1–N1	1.97(2)
N1–C1	1.12(3)
C1–C2	1.50(3)
Cu1'–I1–Cu1''	69.0(2)
Cu1'–I1–Cu1'''	69.9(2)
Cu1''–I1–Cu1'''	107.0(4)
I1–Cu1'–I1''''	111.5(3)
I1–Cu1'–I1$^{\mathrm{V}}$	109.5(3)
I1''''–Cu1–I1$^{\mathrm{V}}$	107.0(3)
I1–Cu1'–N1'	113.7(8)
I1''''–Cu1'–N1'	111.4(6)
I1$^{\mathrm{V}}$–Cu1'–N1'	103.2(6)
Cu1–N1–C1	175.2(9)
N1–C1–C2	175.2(9)

Symmetry relationships

' = 1.0 + *x*, *y*, *z*
'' = 1.0 – *x*, 1.0 – *y*, –0.5 + *z*
''' = 1.0 – *x*, 1.0 – *y*, 0.5 + *z*
'''' = 2.0 – *x*, 1.0 – *y*, –0.5 + *z*
V = 2.0 – *x*, 1.0 – *y*, 0.5 + *z*
V' = *x*, *y*, 1.0 + *z*
V'' = 1.0 + *x*, *y*, 1.0 + *z*

2.700(1) Å in (**V**) and 2.692 Å in this work (**I**), as do average Cu–N bonding distances: 2.04(2) Å in (**III**), 2.02(4) Å in (**IV**), 2.052(7) Å in (**V**) and 2.00(2) Å in this work, despite the differences in hybridization of the donor nitrogen (sp, this work (**I**); sp^2 in (**III**); and sp^3 in (**IV**) and (**V**)). I–Cu–N angles display considerable variation (maximum range 12.8° per copper atom) indicating the asymmetry of acetonitrile binding to the cluster. The acetonitrile groups are unbent (average C–C–N angle 175.6(26)°). The dibenzo-18-crown-6 group is ordered and displays normal bond angles and distances. The oxygen atoms of the crown ether display numerous contact distances of 3.22(3)–3.41(3) Å to the terminal carbon atoms, C202, C302 and C402 of acetonitrile groups. These may be thought of as weak hydrogen bonds involving hydrogen atoms made acidic by hyperconjugation involving the adjacent cyano group. Further evidence for this interaction comes from comparison of the torsion angles for the dibenzo-18-crown-6 ring with those observed for the crown ether in a complexed and in a noncomplexed state [9]. Thus Table V shows the torsion angles calculated for the crown ether in (**I**) to resemble those of other complexed crown ethers and not to resemble those of the crown ether uninvolved with a positively charged species.

Copper iodide and acetonitrile in the absence of the crown ether, form a pleated double chain structure (Fig. 2) in which parallelograms of alternating copper and iodide atoms share opposite sides in an infinite series, each copper atom tetrahedrally bound

TABLE V. Torsion Angles for Dibenzo-18-Crown-6.

	Uncomplexed	This work	Dibenzo-18-crown-6·Na$^+$	
			Molecule A	Molecule B
O1–C2	74.1	–174.6(18)	174.2	172.3
C2–C3	77.3	63.8(24)	61.1	63.7
C3–O4	–103.4	171.1(18)	176.5	178.5
O4–C5	–176.0	–171.2(19)	–179.0	–179.3
C5–C6	–164.3	–66.1(25)	–69.9	–67.1
C6–O7	158.7	179.6(14)	–176.7	–174.1
O7–C8	–174.1	–176.1(20)	–178.5	176.1
C8–C9	–5.0	2.7(28)	–1.3	–1.5
C9–O10	155.0	169.1(20)	177.7	170.4
O10–C11	–74.1	–174.0(19)	179.3	–177.7
C11–C12	–77.3	67.1(22)	65.5	68.1
C12–O13	103.4	167.2(17)	174.7	176.0
O13–C14	176.0	–176.1(17)	–179.6	–175.7
C14–C15	164.3	–67.6(2)	–61.7	–59.3
C15–O16	–158.7	178.8(17)	–166.6	–171.8
O16–C17	174.1	–167.6(16)	172.5	176.5
C17–C18	5.0	0.8(21)	–1.0	–1.5
C18–O1	–155.0	172.3(17)	180.0	–176.0

to three iodide atoms and a nitrogen donor acetonitrile group. The Cu–I distances average 2.658(8) Å. The Cu–Cu distance across the parallelogram is 3.022(10) Å whereas the Cu–Cu distance across the fold of the chain is longer, 4.298(13) Å. I–I distances across the fold are shorter (4.298(2) Å) than those across the four sided figure (4.358(4) Å). The Cu–N distance is 1.97(2) Å.

This structural format is not without precedent. $(CuBrCCN)_x$, $(CuClCCN)_x$, $(CuX\text{benzonitrile})_x$ X = Cl or Br, $(CuX\textit{trans}\text{-acrylonitrile})_x$ X = Br or Cl also crystallize in this pleated double chain structure [10–13]. Thus the difference in thermochromic behavior reported for clusters **(I)** and **(II)** may stem from alteration of the donicity of the nitrile nitrogen atom due to the 'second sphere' type interaction of the crown ether with the acetonitrile group or from the differing structural motif of the clusters themselves.

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