Characterization of the Adducts formed by Cu(CN) and Cu(NCS) with Biquinoline. The Crystal Structure of the Polymeric Cyano-compound containing both Linear and Tetrahedrally Co-ordinated Copper(I), [{$Cu_3(bq)_2(CN)_3$}$_n$]†

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The salts Cu(CN) and Cu(NCS) react with 2,2′-biquinoline (bq = $C_{18}H_{12}N_2$) to give the adducts [{$Cu_3(bq)_2(CN)_3$}$_n$] (**1**) and [{$Cu_3(bq)_2(NCS)_3$}$_n$] (**2**). Complex (**1**) crystallizes in space group *C*2/*m* with cell dimensions *a* = 13.626(2), *b* = 15.322(2), *c* = 7.908(1) Å, β = 95.89(1)°, and *Z* = 2. It consists of chains of CN-bridged copper atoms, each copper being either linearly or tetrahedrally co-ordinated. The tetrahedral copper is also co-ordinated to bq. Pairs of bq molecules belonging to parallel chains stack with an interplanar spacing of 3.35 Å. Complex (**2**) is microcrystalline and from hot dimethyl sulphoxide gives crystals of [Cu(bq)(NCS)] (**3**). The polarization properties of the i.r. and electronic bands of complex (**1**) have been determined. In the optical spectrum two metal-to-ligand charge-transfer transitions could be detected. Comparison of the spectroscopic properties of the three compounds indicates a lower degree of polymerization for (**3**).

In an attempt to prepare copper(I) polymers with low-lying metal-to-ligand charge-transfer bands, we previously treated Cu(CN) and Cu(NCS) with 2,9-dimethyl-1,10-phenanthroline (dmphen) to obtain [{Cu(dmphen)X}$_n$] (X = CN or NCS).[1] Considering the higher acceptor properties of 2,2′-biquinoline (bq), as revealed by the formation of intensely magenta coloured copper(I) adducts,[2] and its structural similarity with dmphen, we have now examined the interaction of the above copper(I) salts with this ligand.

Experimental

Materials.—The chemicals were commercial products; 2,2′-biquinoline ($C_{18}H_{12}N_2$, bq) from Merck was used without further purification.

Crystal Preparations.—The complex [{$Cu_3(bq)_2(CN)_3$}$_n$] (1) was obtained by treating equimolar amounts of Cu(CN) and bq in dimethyl sulphoxide (dmso). A violet product formed which rapidly became cherry-red. The crude product was separated by centrifugation, washed with water dried in a desiccator, and recrystallized from hot dmso.

When a suspension of Cu(NCS) in a dmso solution of bq [mol ratio Cu(NCS):bq = 1:1] was left for some hours at room temperature with stirring, a violet-brown product formed. This substance, (2), was separated by suction, washed with water, and dried in a desiccator (Found: C, 52.1; H, 2.7; N, 11.2. Calc. for [{$Cu_3(bq)_2(NCS)_3$}$_n$]: C, 53.4; H, 2.75; N, 10.95%). Complex (2) is insoluble in cold dmso, but dissolves in hot dmso to give, after cooling, crystals of a different substance, (3) {Found: C, 60.0; H, 3.2; N, 11.0. Calc. for [Cu(bq)(NCS)]: C, 57.1; H, 3.25; N, 10.2%}. Complex (3) is soluble in cold dmso. Its crystals are not suitable for *X*-ray measurements owing to their decomposition upon irradiation.

Spectroscopic Measurements.—Solution visible spectra were recorded with a Perkin-Elmer 555 spectrophotometer, single-crystal polarized spectra on a Shimadzu MPS-50L spectrophotometer equipped with a microscope. I.r. polarized spectra were obtained with a Perkin-Elmer 580 B instrument using small crystals secured in a 'mosaic' fashion on a CsBr disc by use of Nujol. Iso-orientation was possible in the case of complex (1) but not (3) because of the small size of the crystals. The i.r. spectra were of good quality and consistent with those obtained for Nujol mulls.

Crystallography.—*Crystal data.* ($C_{39}H_{24}Cu_3N_7$)$_n$, (1), *M* = 781.29, cherry-red monoclinic prisms, *a* = 13.626(2), *b* = 15.322(2), *c* = 7.908(1) Å, β = 95.89(1)°, *U* = 1 642.3(4) Å^3, D_m = 1.57(1) g cm^{-3} (by flotation), *Z* = 2, D_c = 1.58 g cm^{-3}, *F*(000) = 788, Mo-K_α radiation, λ = 0.710 73 Å, graphite monochromator, μ(Mo-K_α) = 20.10 cm^{-1}, space group *C*2/*m* (C^3_{2h}, no. 12) from systematic absences and structure solution.

X-*Ray data collection.* A crystal (0.3 × 0.2 × 0.15 mm) was selected and mounted on a capillary glass for the data collection, at room temperature, on a Nicolet $P2_1$ four-circle autodiffractometer. The cell dimensions were refined from a least-squares fit of the setting angles of 15 computer-centred reflections ($31 \leqslant 2\theta \leqslant 43°$). The intensities of 1 436 independent reflections having $I \geqslant 3\sigma(I)$ were collected by the θ—2θ scan technique, and corrected for Lorentz and polarization effects. No absorption correction was applied as a ψ scan on two reflections showed a maximum deviation of 7%. The structure was solved by conventional Patterson and Fourier methods, and 118 parameters were refined by block-diagonal least squares to a final conventional $R\,(= \Sigma|\Delta F|/\Sigma|F_o|) = 0.033$, $R'\{= [\Sigma w(\Delta F)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$ 0.040. The quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$, with the weighting scheme $w = (\sin\theta)/\lambda$. Anisotropic thermal parameters were used for all non-hydrogen atoms and a fixed isotropic thermal parameter of 5.0 Å^2 for the hydrogen atoms, which were included at calculated positions (C–H 0.95 Å). Neutral atom scattering

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† Poly[bis(2,2′-biquinoline)tri-μ-cyano-tricopper(I)].

Supplementary data available (No. SUP 56200, 3 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Atomic co-ordinates ($\times 10^4$) with estimated standard deviations (e.s.d.s) in parentheses for $[\{Cu_3(bq)_2(CN)_3\}_n]$

Atom	*X/a*	*Y/b*	*Z/c*
Cu(1)	0	0	0
Cu(2)	3 333.7(4)	0	−1 711.7(8)
N(1)	1 249(3)	0	−635(7)
N(2)	3 549(2)	858(2)	6 295(3)
A	4 603(3)	0	−338(5)
C(1)	2 046(3)	0	−1 006(7)
C(2)	3 593(2)	1 745(2)	6 410(4)
C(3)	3 502(3)	2 134(3)	8 021(5)
C(4)	3 562(4)	3 019(3)	8 190(7)
C(5)	3 697(4)	3 553(3)	6 787(8)
C(6)	3 778(3)	3 197(3)	5 244(7)
C(7)	3 741(2)	2 286(2)	5 013(5)
C(8)	3 863(3)	1 863(3)	3 465(5)
C(9)	3 830(3)	975(3)	3 352(4)
C(10)	3 676(2)	483(2)	4 816(4)

Table 2. Bond distances (Å) and angles (°), with e.s.d.s in parentheses, for $[\{Cu_3(bq)_2(CN)_3\}_n]$

Cu(1)–N(1)	1.823(4)	N(2)–Cu(2)–N(2^{II})	77.7(2)
Cu(2)–A	1.946(4)	N(2)–Cu(2)–A	103.6(2)
Cu(2)–C(1)	1.896(5)	N(2)–Cu(2)–C(1)	115.3(3)
Cu(2)–N(2)	2.096(4)	A–Cu(2)–C(1)	129.2(2)
N(1)–C(1)	1.153(6)	Cu(1)–N(1)–C(1)	178.7(5)
A–A^{I}	1.156(6)	Cu(2)–N(2)–C(10)	115.6(3)
N(2)–C(2)	1.364(5)	Cu(2)–A–A^{I}	173.6(5)
N(2)–C(10)	1.330(4)	Cu(2)–C(1)–N(1)	177.6(5)
C(2)–C(3)	1.423(5)	C(3)–C(2)–C(7)	119.2(3)
C(2)–C(7)	1.411(5)	C(2)–C(3)–C(4)	119.6(4)
C(3)–C(4)	1.365(6)	C(3)–C(4)–C(5)	120.8(5)
C(4)–C(5)	1.406(8)	C(4)–C(5)–C(6)	120.5(5)
C(5)–C(6)	1.352(8)	C(5)–C(6)–C(7)	120.8(5)
C(6)–C(7)	1.408(6)	C(2)–C(7)–C(6)	119.2(4)
C(7)–C(8)	1.410(6)	C(2)–C(7)–C(8)	116.7(4)
C(8)–C(9)	1.365(6)	C(7)–C(8)–C(9)	120.6(4)
C(9)–C(10)	1.415(5)	C(8)–C(9)–C(10)	119.0(3)
		N(2)–C(10)–C(9)	122.2(3)
		N(2)–C(10)–C(10^{II})	115.6(3)

Symmetry code: I $1 - x, y, \bar{z}$; II $x, \bar{y}, z$.

factors (f' and f'' values) were taken from ref. 3. Computations were performed on a HP 1000 computer by using a set of crystallographic programs from the Istituto di Strutturistica Chimica del C.N.R.[4]

Final atomic co-ordinates for non-hydrogen atoms with their estimated standard deviations (e.s.d.s) are given in Table 1, interatomic distances and angles in Table 2.

Results and Discussion

Description of the Structure of Complex (1).—The crystal structure of the adduct formed by Cu(CN) and bq can be described as a one-dimensional infinite polymer, developed along the *a* axis, of copper atoms bridged by CN groups in a zigzag manner and lying on the mirror plane (010). Unlike the adduct $[\{Cu(dmphen)(CN)\}_n]$,[1] the copper atoms in the chain are of two types. At the cell origin, *i.e.* at a centre of symmetry, the atom Cu(1) (type L copper) linearly co-ordinates two nitrogen atoms, N(1) and N(1^{I}), from two centrosymmetric CN groups. In a more general position (*x*, 0, *z*) another atom Cu(2) (type T copper) tetrahedrally co-ordinates two nitrogen atoms from a bq molecule and two CN groups according to the sequence $-C-N-Cu(1)_L-N-C-Cu(2)_T-(CN)-Cu(2)_T-C-N-Cu(1)_L-$ (Figure 1).

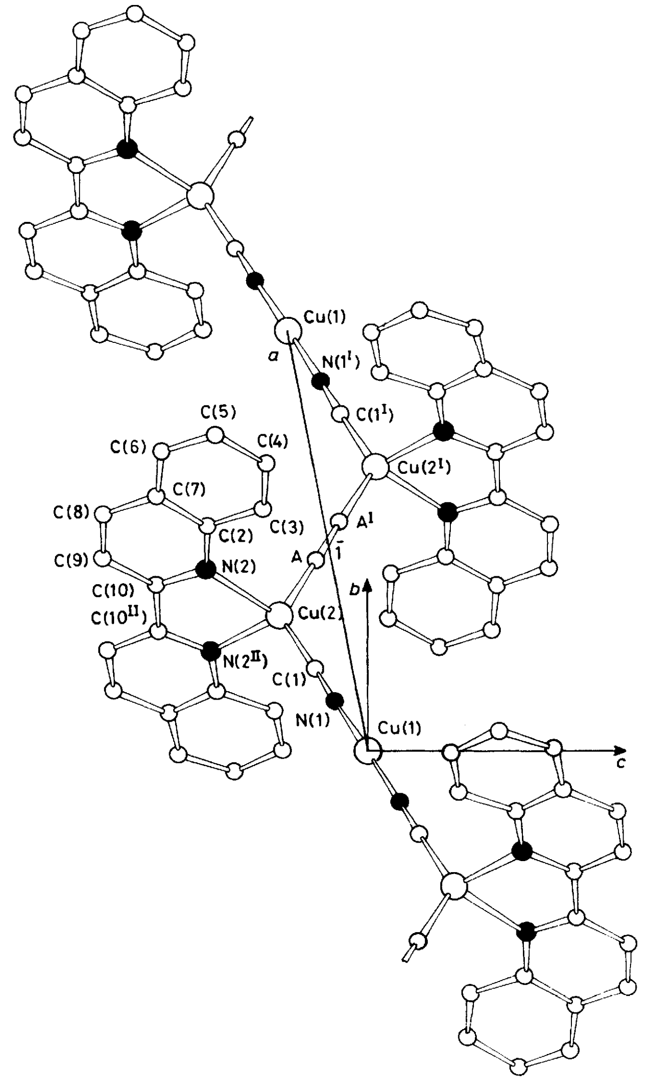

Figure 1. Atomic arrangement of $[\{Cu_3(bq)_2(CN)_3\}_n]$ referred to the unit-cell directions

The CN group bridging two Cu_T atoms is required to be disordered by symmetry (A–A^{I} in the Figure) as it lies on a centre of inversion. Consequently the Cu_T–A distance of 1.946(4) Å is intermediate between Cu_T–C 1.897(12) Å and Cu_T–N 2.008(11) Å found in $[\{Cu(dmphen)(CN)\}_n]$.[1] The other Cu_T–C(CN) and Cu_T–N(bq) bond distances of 1.896(5) Å [Cu(2)–C(1)] and 2.096(4) Å [Cu(2)–N(2)] are in excellent agreement with literature data.[1,5] The type L copper atom shows a strictly linear co-ordination: it represents a rather unusual case in the solid-state chemistry of copper(I), the sole reported examples being a $CuCl_2^-$ group in the mixed-valence polymeric compound bis(bipyridyl)copper(II) bis[dichlorocuprate(I)][6] and the CuN_2 groups in the mixed-valence cluster $[Cu^I_{10}Cu^{II}_2(Me\overline{NCH{=}CHN{=}CS}^-)_{12}(MeCN)_4][BPh_4]_2\cdot 4MeCN$.[7] Angles X–Cu–X in the range 140—175° were found in other copper(I) complexes with bidentate ligands.[8,9] In the present case, since the atom $Cu(1)_L$ lies at a centre of symmetry, the N–Cu–N co-ordination is perfectly linear. The Cu–N distance of 1.823(4) Å is the first between an *sp*-hybridized copper atom and the nitrogen atom belonging to a CN group. Its shortening with respect to the $Cu(sp^3)$–N (CN) distance of

2.008 Å in [{Cu(dmphen)(CN)}$_n$] is 0.185 Å.[1] A similar shortening (0.199 Å) is found between Cu(sp^3)–Cl (2.339 Å) and Cu(sp)–Cl (2.140 Å) bonds of the above mentioned bis[dichlorocuprate(I)].[6]

The bq molecules are normal to the (010) mirror plane and nearly parallel to the (100) plane. Pairs of them, belonging to symmetry-related parallel chains shifted by a *c*-unit translation, are formed, with an interplanar spacing of 3.35 Å (Figure 2). The degree of superposition is high, the two central phenyl rings being perfectly eclipsed. Between this polymeric system developing in the (x, 0, z) plane and the equivalent one in the (x, $\frac{1}{2}$, z) plane (III in Figure 2) exist weak interactions, the biquinoline interplanar spacing being 3.28 Å, but with a sliding of molecules relative to each other (degree of superposition *ca.* 20%). The interactions between the eclipsed conjugated systems probably stabilize this crystalline form and the unusual copper sequence.

Spectroscopic Characterization.—Some i.r. bands of complexes (**1**)—(**3**), their correlation, and probable assignment are reported in Table 3. The vibrational assignment was based on those reported for pyridine, biphenyl, bipyridine, and quinoline, and assisted by the i.r. polarized spectra of complex (**1**) measured along the a' and c' directions of Figure 2. The part of the spectrum of complex (**1**) due to bq is interpreted in terms of C_{2v} symmetry of [Cu(bq)]$^+$ as was done for the dmphen part of [{Cu(dmphen)(CN)}$_n$].[1] The spectra of complexes (**1**) and (**2**) show, however, a splitting of some of the bands, attributed to vibrational interaction of the polymeric chains within the unit cell, which is absent or reduced in the spectrum of (**3**). This observation, together with the presence of a medium-intensity band at 695 cm^{-1}, perhaps due to ν(C–S) of a sulphur-bridging thiocyanate (footnote *g* of Table 3), suggests a different structure for (**3**).

The polarized electronic single-crystal spectra of complex (**1**), measured along a' and c', closely correspond to those of [{Cu(dmphen)(CN)}$_n$] measured along [010] and [101] respectively, and are assigned accordingly.[1] Thus one band at 18 500 cm^{-1} is the $d_{yz}\rightarrow\varphi_\pi$ ligand-to-metal charge transfer (l.m.c.t.), while the other at 21 200 cm^{-1} is the d_{z^2} or $d_{x^2-y^2}\rightarrow\varphi_\pi$ (lowest unoccupied molecular orbital of bq). In dmso solutions these transitions are found at 18 500 cm^{-1} (ε = 900 dm^3 mol^{-1} cm^{-1}) and *ca.* 23 000 cm^{-1}. The high-energy band, the molar intensity of which increases with concentration and decreases with temperature, is associated with the stacking of the [Cu(bq)]$^+$ groups. In the polarized crystal spectrum of complex (**3**) this band is barely detectable at 19 000 cm^{-1} in one of the two extinction directions and it is completely absent in its

Table 3. Some i.r. bands (cm^{-1}) of complexes (**1**)—(**3**). The spectrum of (**2**) was measured on a Nujol mull

(1)	Mode[a]	(2)	(3)	Assignment	Ref.
3 130	A_1		3 120	Symmetric C–H stretch	
3 090	A_1		3 080		
3 050	A_1		3 060		
3 010	A_1		3 010		
2 160	Mixed	2 146		C–N(CN,NCS) stretch	*b*
2 140	Mixed	2 126			
2 124	Mixed	2 116	2 113		
2 085	Mixed	2 112			
1 620	A_1	1 615	1 620	Ring stretch	*b*—*d*
1 615	Mixed				
1 600	B_2	1 590	1 590		
1 595	A_1				
1 540	A_1		1 540	In-plane ring def.	*d*
1 425	A_1		1 430	C–H def.	*d*
1 245	A_1	1 245		In-plane C–H bend	*d*
1 175	A_1	(1 170)	1 170	C–H def.	*d*
1 130	A_1	1 125	1 142	In-plane ring def.	*d*
1 019	A_1	1 016	1 016	Ring def.	*d*
1 013	B_2				
965	A_1	965	968	Ring stretch (breathing)	*d*
		912	910	First overtone (NCS) bend	*b*
895	A_1			In-plane ring def.	*d*
830	B_2	830	822	Out-of-plane C–H bend of heteroatom ring	*e*
810		822			
790	B_2	779	783		
778		776	778		
747	B_2	747	745	Out-of-plane C–H bend of carbocyclic ring	*e*
725		738	(743)	or ring def.	*f*
			695	Symmetric (C–S) stretch	*g*
652	A_1	656	656	In-plane ring def.	*d*,*f*
648		650	650		
620		630	630		
		453	453	(NCS) bend	*b*
		444			
440	A_1			Symmetric Cu–N(bq) stretch	*b*
400	B_2	400	400	Out-of-plane ring def.	*d*

[a] Assuming C_{2v} for bq. [b] G. O. Morpurgo, G. Dessy, and V. Fares, *J. Chem. Soc., Dalton Trans.*, 1984, 785 and refs. therein. [c] G. Zerbi and S. Sandroni, *Spectrochim. Acta, Part A*, 1968, **24**, 483. [d] E. Castellucci, L. Angeloni, N. Neto, and G. Sbrana, *Chem. Phys.*, 1979, **43**, 365. [e] C. Karr, jun., P. A. Estep, and A. J. Papa, *J. Am. Chem. Soc.*, 1959, **81**, 152. [f] N. Neto, M. Muniz-Miranda, L. Angeloni, and E. Castellucci, *Spectrochim. Acta, Part A*, 1983, **39**, 97. [g] S. M. Nelson, F. S. Esho, and M. G. B. Drew, *J. Chem. Soc., Chem. Commun.*, 1981, 388.

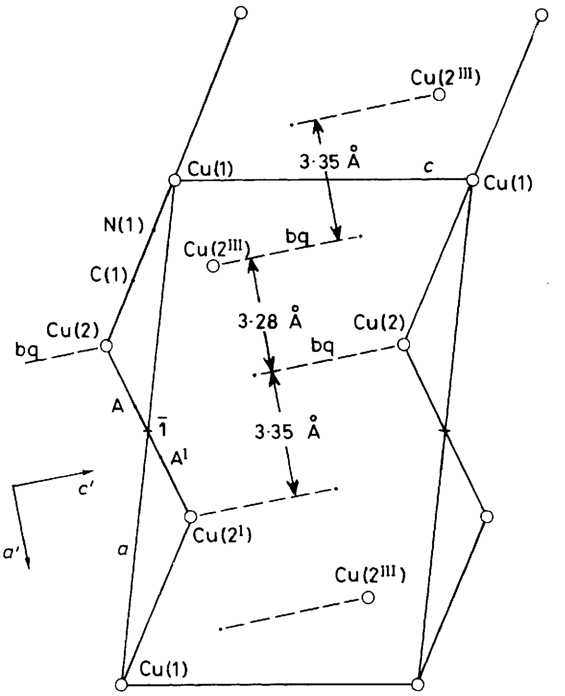

Figure 2. Schematic view of the crystal packing of $[\{Cu_3(bq)_2(CN)_3\}_n]$ projected onto the (010) plane. Roman numeral superscripts are defined in Table 2 and in the text; *a′* and *c′* indicate the extinction directions

dmso solution, where only the $d_{yz} \rightarrow \varphi_\pi$ l.m.c.t. is present at 18 000 cm^{-1} (ε = 820 dm^3 mol^{-1} cm^{-1}). The solubility of (**3**) and its spectral properties indicate a different mode of polymerization, probably due to the absence of $[Cu(bq)]^+$ stacking. A dimeric S-bridged form is in accord with the reported spectroscopic data.

Conclusions

Of the characteristic co-ordination modes of Cu^I, the two-co-ordinate one is of particular interest, since extended *X*-ray absorption fine structure indicates its presence in deoxyhaemocyanin.[10] Structural studies carried out so far on a number of inorganic model compounds have revealed that nitrogen atoms seem very effective in stabilizing linear co-ordination of Cu^I.[9] However, linear co-ordination is invariably found to occur in synthetic polynuclear compounds having rather complicated structures, where the more usual tetrahedral structure for Cu^I is prevented by steric effects. Examination of the polymeric structures obtained in our laboratory shows the tendency for the planar aromatic ligands of Cu^I to stack face to face to form a repeating pattern of coupled π systems.[1] In compound (**1**), tetrahedral copper and a regular Cu–CN chain would have led to a regular stacking of bq molecules, instead of the preferred coupled-unit structure. The latter can be obtained only if one copper out of three is depleted of bq, and thus two-co-ordinated and nitrogen stabilized. In the case of $[\{Cu(dmphen)(CN)\}_n]$ and $[\{Cu(dmphen)(NCS)\}_n]$, the less extended organic ligand allows, by the inclination of the dmphen molecular plane with respect to the (010) and $(\bar{1}0\bar{1})$ planes, the tetrahedral co-ordination of every Cu^I and the formation of rather well separated dmphen pairs.[1] The spectroscopic measurements suggest a different situation for complex (**3**). The non-linearity of the CuSC group prevents [Cu(bq)(NCS)] from forming stable extended polymeric NCS-bridged systems, because of the consequent steric interactions between the bq molecules.

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