Crystal Structure and Spectroscopic Properties of a Polynuclear Complex between Copper(II), Diethylenetriamine, and Ferrocyanide

By **Giorgio Oscar Morpurgo,* Valeria Mosini,** and **Piero Porta,** Istituto di Chimica Generale ed Inorganica, Università di Roma, Roma, Italy
Giulia Dessy and **Vincenzo Fares,** Laboratorio di Teoria, Struttura Elettronica e Comportamento Spettrochimico dei Composti di Coordinazione, C.N.R., Via Montorio Romano 36, Roma, Italy

The addition of $[Fe(CN)_6]^{4-}$ to $[Cu(dien)]^{2+}$ (dien = diethylenetriamine) ions gives a polynuclear complex of formula $[\{Cu(dien)\}_2{\cdot}Fe(CN)_6]{\cdot}6H_2O$. The compound has been characterized by i.r., powder-reflectance, and single-crystal polarized spectra, by thermogravimetric analysis, and by its crystal and molecular structure which has been solved by single-crystal *X*-ray diffractometry. The dark green crystals are monoclinic, with space group *C2/c*, $a = 27.438(3)$, $b = 7.778(1)$, $c = 14.869(2)$ Å, $\beta = 100.9°$, and $Z = 8$; the asymmetric unit comprises half a molecule and the iron atoms at a centre of symmetry of the unit cell. The structure has been refined by least-squares methods using 1 586 independent reflections, to a conventional *R* of 0.08. The structure consists of a polymer of $[Cu(dien)]^{2+}$ and $[Fe(CN)_6]^{4-}$ ions linked together through cyanide bridges. Of the six CN^- groups around each iron, two are not bonded to copper atoms but only interact through hydrogen bonds with the water molecules present in the lattice, two are tightly bonded (Cu–N 1.97 Å) to copper atoms of adjacent $[Cu(dien)]^{2+}$ molecules giving rise to linear Fe–C≡N–Cu linkages and are co-ordinated in the equatorial plane of the square-pyramidal configuration, and the remaining two co-ordinate to copper atoms of adjacent $[Cu(dien)]^{2+}$ molecules in the apical positions of the pyramid (Cu–N 2.21 Å) leading to non-linear Fe–C≡N–Cu chains. The presence of three water molecules per asymmetric unit of the complex gives rise to an extensive hydrogen-bond system among themselves, so leading to a helix which develops one-dimensionally along the *b* axis, and also with the nitrogens of the free cyano-groups. Infrared and electronic spectral (both powder-reflectance and single-crystal polarized) and thermogravimetric results are discussed and related to the crystal structure.

INTERACTION of ferrocyanide with copper proteins may lead to electron transfer between the two metals, the copper ion(s) being reduced. It is believed that outer-sphere charge-transfer (c.t.) complexes are formed during the process. Binding in such complexes was suggested to occur *via* electrostatic interactions and hydrogen bonding, but direct information is not available.[1]

In some cases, formation of c.t. complexes without electron exchange takes place, as is the case for ferrocyanide with bovine superoxide dismutase and copper-substituted carbonic anhydrase, as well as the complex between Cu^{II} and diethylenetriamine.[2] The latter complex mimics some of the spectroscopic properties of the above copper proteins.[2] We report here the determination of its crystal structure and spectroscopic properties, in the hope that these throw some light on the actual binding modes of ferrocyanide both with copper enzymes and with copper complexes.

EXPERIMENTAL

Materials.—Diethylenetriamine (dien) from Fluka A.G., bis(2-aminopropyl)amine (Me_2dien) from K & K Laboratories, $Cu[SO_4]{\cdot}5H_2O$ from Merck, and $K_4[Fe(CN)_6]{\cdot}3H_2O$ from C. Erba were used without further purification.

Preparation of Crystals.—The complex $[\{Cu(dien)\}_2{\cdot}Fe(CN)_6]{\cdot}6H_2O$, (1), was obtained by addition of a concentrated solution of $K_4[Fe(CN)_6]{\cdot}3H_2O$ (0.844 7 g, 2 mmol) to $Cu[SO_4]{\cdot}5H_2O$ (0.998 4 g, 4 mmol) and dien (0.65 cm^3, 6 mmol) in the minimum amount of water. A dark precipitate, the yield of which could be increased by addition of ethanol, was separated by suction and recrystallized from water. The rhombic dark green crystals were dried in air; on standing or in a desiccator they tend to lose water. Elemental analysis of a sample which was apparently partially dehydrated (see Discussion section) gave 27.5% C, 5.4% H, and 26.7% N (Calc. for $[\{Cu(dien)\}_2{\cdot}Fe(CN)_6]{\cdot}4H_2O$: C, 27.3; H, 5.5; N, 27.3%).

The complex $[\{Cu(Me_2dien)\}_2{\cdot}Fe(CN)_6]{\cdot}xH_2O$, (2), was obtained by the addition to $Cu[SO_4]{\cdot}5H_2O$ (0.998 4 g, 4 mmol) in water (30 cm^3) of an excess of Me_2dien sufficient to redissolve the precipitate of $Cu[OH]_2$ which forms after the initial addition of the reagent, and then of $K_4[Fe(CN)_6]{\cdot}3H_2O$ (0.844 7 g, 2 mmol) dissolved in the minimum amount of water. A turbid violet solution was obtained which, on standing at *ca.* 5 °C, gave a precipitate of needle-like green crystals. The precipitate was filtered off and recrystallized from water. The crystals appear as elongated prisms containing, along the major axis, a cylindrical channel, which incorporates some solvent. Evaporation of the solvent causes disruption of the prisms. Analysis of a sample which had been separated by suction, and maintained at room temperature in the presence of water vapour, gave 32.6% C, 5.8% H, and 25.2% N (Calc. for $[\{Cu(Me_2dien)\}_2{\cdot}Fe(CN)_6]{\cdot}4H_2O$: C, 32.2; H, 6.2; N, 25.1%).

Crystal Data for Complex (1).—$(C_7H_{19}CuFe_{0.5}N_6O_3)_n$, $M = 328.2$, dark green prisms, $a = 27.438(3)$, $b = 7.778(1)$, $c = 14.869(2)$ Å, $\beta = 100.9°$, $U = 3\ 116$ Å^3, $D_m = 1.39(1)$ g cm^{-3} (by flotation), $Z = 8$, $D_c = 1.40$ g cm^{-3}, $F(000) = 1\ 347.7$, Mo-K_α radiation, $\lambda = 0.710\ 73$ Å, graphite monochromator, μ(Mo-K_α) = 19.24 cm^{-1}, space group *C2/c* (C^6_{2h}, no. 15) from systematic absences and structure determination. Unit-cell parameters were obtained from a least-squares fit to the angular setting of 15 reflections with $2\theta \geqslant 36°$.

Structure Determination and Refinement of Complex (1).—The crystals were not stable in the *X*-ray beam and several of them were used for the data collection on a $P2_1$ Syntex automated four-circle diffractometer by the θ—2θ scan technique. The intensities of 1 586 independent reflections having $I \geqslant 3\sigma(I)$ were used for the structure determination *via* Patterson and Fourier methods, and for the refinement. The data were corrected for Lorentz and polarization effects. Given the low value of μ and the very small size of the crystals, no absorption correction was applied.

The structure was refined by full-matrix least squares using anisotropic temperature factors for all non-hydrogen atoms. The weighting scheme was $w = (\sin\theta)/\lambda$. The final refinement gave $R = 0.08$. The hydrogen atoms were included at calculated positions. Atomic scattering factors were obtained from ref. 3 and the corrections for real dispersion (heavy atoms only) from ref. 4. Calculations were made on the UNIVAC 1108 computer at Rome University using the set of programs of the Laboratorio di Strutturistica Chimica G. Giacomello, C.N.R.[5] Thermal parameters and structure factors are available as Supplementary Publication No. SUP 22750 (13 pp.).* Final atomic co-ordinates, with their estimated standard deviations, for the non-hydrogen atoms and calculated atomic positions for hydrogen atoms are given in Table 1.

TABLE 1

Atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
Fe	2 500	2 500	5 000
C(1)	2 161(4)	1 280(16)	3 973(7)
C(2)	2 170(4)	1 125(17)	5 758(7)
C(3)	1 957(4)	4 079(15)	4 813(8)
N(1)	1 929(5)	585(15)	3 332(7)
N(2)	1 978(4)	291(16)	6 218(7)
N(3)	1 614(5)	4 981(21)	4 692(9)
Cu	1 618(1)	1 292(2)	1 899(1)
N(4)	1 009(4)	−247(17)	1 749(8)
N(5)	1 156(4)	3 093(15)	2 255(8)
N(6)	2 049(4)	3 363(16)	1 766(8)
C(4)	607(5)	662(25)	2 091(12)
C(5)	642(5)	2 535(25)	1 917(12)
C(6)	1 303(6)	4 792(19)	1 968(11)
C(7)	1 844(6)	4 906(19)	2 155(10)
Ow(1)	1 255(6)	−1 963(18)	3 787(11)
Ow(2)	592(9)	−41(40)	4 700(12)
Ow(3)	660(8)	3 582(34)	4 222(18)
H(1)–N(4)	1 095	−1 353	2 111
H(2)–N(4)	896	−566	1 089
H–N(5)	1 212	3 093	2 946
H(1)–N(6)	2 396	3 138	2 098
H(2)–N(6)	2 053	3 559	1 101
H(1)–C(4)	641	459	2 771
H(2)–C(4)	275	209	1 778
H(1)–C(5)	408	3 200	2 236
H(2)–C(5)	548	2 775	1 240
H(1)–C(6)	1 154	5 717	2 306
H(2)–C(6)	1 170	4 943	1 291
H(1)–C(7)	1 973	4 959	2 835
H(2)–C(7)	1 957	5 978	1 870

Spectroscopic Measurements.—Powder-reflectance spectra were recorded with a Beckman DK-2 spectrophotometer equipped with a standard reflectance unit. Single-crystal polarized spectra were obtained on a Shimadzu MPS-50L spectrophotometer up to 830 nm, the maximum of the wavelength range of the instrument. For bands in the near i.r. region, a Cary 14 spectrophotometer equipped with polarizers in both the sample and reference beam was used. Since this instrument requires sizable single crystals, which in the present case are not transparent, measurements were performed on small crystals of (1) secured, in ' mosaic ' fashion, on a quartz disc by use of stopcock grease. The spectra obtained were consistent with those for single microscopic crystals in the visible–u.v. range. Spectra of (2) were obtained only on the Shimadzu spectrophotometer, choosing microscopic crystals for which the inside channel was as narrow as possible compared with the crystal size. Infrared spectra of Nujol mulls were recorded with a Perkin-Elmer 577 spectrophotometer.

TABLE 2

Bond distances and angles with estimated standard deviations in parentheses

Distances (Å)			
Fe–C(1)	1.89(1)	N(6)–C(7)	1.49(2)
Fe–C(2)	1.90(1)	C(4)–C(5)	1.49(3)
Fe–C(3)	1.91(1)	C(6)–C(7)	1.46(3)
C(1)–N(1)	1.17(1)	Cu–N(1)	2.21(1)
C(2)–N(2)	1.14(2)	Cu–N′(2)	1.97(1)
C(3)–N(3)	1.16(2)	N(1)–Ow(1)	2.88(2)
Cu–N(4)	2.03(1)	N‴(3)–Ow(1)	2.82(3)
Cu–N(5)	2.03(1)	N(3)–Ow(3)	2.80(3)
Cu–N(6)	2.03(1)	N(4)–Ow(2)	3.06(3)
N(4)–C(4)	1.48(2)	Ow(1)–Ow(2)	2.88(3)
N(5)–C(5)	1.47(2)	Ow(2)–Ow(3)	2.92(3)
N(5)–C(6)	1.47(2)		
Angles (°)			
C(1)–Fe–C(2)	88.9(5)	Cu–N(4)–C(4)	108.7(10)
C(1)–Fe–C(3)	85.1(5)	Cu–N(5)–C(5)	108.6(10)
C(2)–Fe–C(3)	89.8(5)	Cu–N(5)–C(6)	109.4(10)
N(1)–C(1)–Fe	176.2(11)	Cu–N(6)–C(7)	109.7(10)
N(2)–C(2)–Fe	178.8(11)	N(4)–C(4)–C(5)	109.5(14)
N(3)–C(3)–Fe	177.3(12)	N(5)–C(5)–C(4)	107.5(12)
N(4)–Cu–N(5)	83.9(5)	N(5)–C(6)–C(7)	107.9(12)
N(5)–Cu–N(6)	83.2(5)	N(6)–C(7)–C(6)	108.1(12)
N(1)–Cu–N(4)	96.7(5)	C(5)–N(5)–C(6)	115.8(12)
N(1)–Cu–N(5)	93.8(5)	N(1)–Ow(1)–Ow(2)	104.1(14)
N(1)–Cu–N(6)	99.5(4)	N‴(3)–Ow(1)–Ow(2)	114.1(14)
N(1)–Cu–N′(2)	101.5(5)	N(3)–Ow(3)–Ow(2)	114.5(14)
N′(2)–Cu–N(4)	93.3(5)	N(1)–Ow(1)–N‴(3)	120.7(15)
N′(2)–Cu–N(6)	95.1(5)	Ow(1)–Ow(2)–Ow(3)	108.1(15)
Cu–N(1)–C(1)	136.2(8)	Cu–N(1)–Ow(1)	104.5(10)
Cu–N′(2)–C′(2)	174.0(8)	C(1)–N(1)–Ow(1)	113.7(10)

RESULTS

Description of the Structure of Complex (1).—The stereochemistry of the complex is shown in Figure 1 and bond distances and angles are listed in Table 2.

The structure consists of a polymer formed between the $[Cu(dien)]^{2+}$ and $[Fe(CN)_6]^{4-}$ starting complexes linked together through cyanide bridges; the resulting neutral $[\{Cu(dien)\}_2{\cdot}Fe(CN)_6]$ units occur as separate polynuclear two-dimensional arrangements of *ca.* 10 Å thickness, parallel

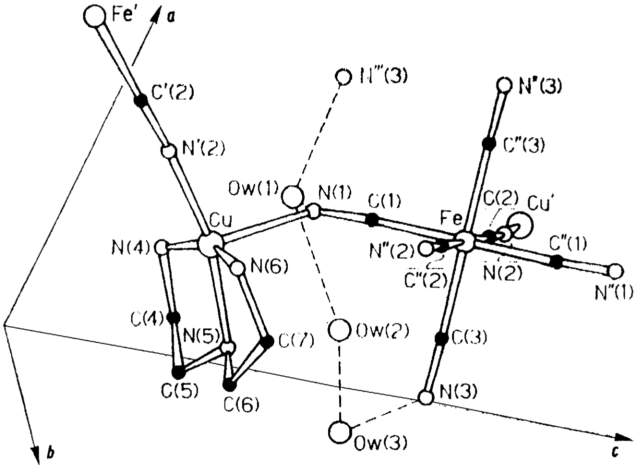

FIGURE 1 Perspective view of the molecular structure of $[\{Cu(dien)\}_2{\cdot}Fe(CN)_6]{\cdot}6H_2O$ showing the labelling of atoms

---

* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

to the *bc* plane of the crystal lattice. No interactions less than 3.8 Å are present between these two-dimensional zones.

A helix of water molecules, connected by hydrogen bonds and in groups of three for each asymmetric unit of the polynuclear complex, is present in the lattice. This develops along the *b* axis of the cell and is associated with each of the two-dimensional polynuclear zones through an extensive hydrogen-bond system involving some of the nitrogens of the hexacyanoferrate moieties. The water molecules do not, however, act as a bridging system between different zones of the two-dimensional polymers nor are they directly co-ordinated to any metal atom.

Within the polynuclear complex the iron atom of the hexacyanoferrate ion occupies a centre of symmetry of the unit cell; as shown in Figure 1, two of the six CN^- groups, namely $C(3)\equiv N(3)$ and the centrosymmetrically related one, are not bonded other than to iron and (as already mentioned) to the water molecules. The other four cyanide ligands around iron reveal their ambidentate and bridging nature, forming bonds with the copper atoms of the nearest $[Cu(dien)]^{2+}$ ions and giving rise to four-atom $Fe-C\equiv N-Cu$ sequencies. Not all of these cyanide groups, however, behave in the same way: two of them, namely $C(1)\equiv N(1)$ and the centrosymmetrical one, give non-linear $Fe-C\equiv N-Cu$ sequencies, the $Cu-N\equiv C$ angle being *ca.* 136°; the other two, *i.e.* $C(2)\equiv N(2)$ and the centrosymmetrical one, are almost linearly bonded to the nearest copper atom, the $Cu-N\equiv C$ angle being *ca.* 174°. An almost regular square-based pyramidal arrangement around each copper atom is thus present; in the basal plane the copper atom is co-ordinated by three dien nitrogen atoms and by the nitrogen atom belonging to the cyano-group linearly oriented to it, whereas the nitrogen of each non-linearly bonded cyanide is in an apical position of the square pyramid. The copper atom lies 0.28 Å out from the mean basal plane so defined by the dien nitrogens, *i.e.* N(4), N(5), and N(6), and the nitrogen N′(2), of the linearly oriented cyanide. The bond lengths and angles within each $[Fe(CN)_6]^{4-}$ and $[Cu(dien)]^{2+}$ unit do not differ significantly from values reported previously,[6,7] and the stereochemistry within the dien ligand is similar to that found for analogous complexes.[8] The bond distances between copper and the nitrogens of the bridged cyano-groups are 1.97 and 2.21 Å for the linearly and non-linearly bonded cases, respectively.

The values of the oxygen–oxygen and oxygen–nitrogen distances are *ca.* 2.9 Å and all are in the range expected for a hydrogen-bonding system.[9] A weak oxygen–nitrogen interaction, N(4)–Ow(2) 3.06 Å, is also present between a water molecule and a nitrogen from a dien ligand, but all other intermolecular distances are >3.25 Å.

Infrared Spectra.—The principal i.r.-active bands of complex (1) fall in the 3 100—3 700 and 2 000—2 100 cm^{-1} regions, the first being characteristic of ν(OH) and $\nu[NH_2(NH)]$, the other of ν(CN), Figure 2(*a*). In the first interval, the band at 3 430 cm^{-1} and a shoulder at 3 500 cm^{-1} are assigned to OH stretches. The bands at 3 320s, 3 250s, and 3 150m cm^{-1} are some of the expected $NH_2(NH)$ stretching vibrations.[10]

The ν(CN) stretching modes of $[Fe(CN)_6]^{4-}$ appear in the 2 000—2 100 cm^{-1} region. Two main band systems of comparable intensity are observed: one at 2 097 cm^{-1}, which is assigned to the intermetallic linear C–N stretching vibration,[11] and another which is split with maxima at 2 042 and 2 034 cm^{-1} is assigned to terminal CN stretching modes. The three bands are derived from the T_{1u} species of ferrocyanide in O_h point group (2 046 cm^{-1}) by lowering of the symmetry.[12]

Complex (2), Figure 2(*b*), shows bands at 3 120(sh), 3 140, 3 230, 3 290, and 3 320(sh) cm^{-1} due to the $NH_2(NH)$ stretching vibrations, and at 3 450 and 3 560 cm^{-1} assigned to OH stretches. A broad band centred at 2 045 cm^{-1} is due to the terminal CN stretching vibration, while the shoulders at 2 075 and 2 100 cm^{-1} may be assigned to intermetallic linear bridging CN.

Binding of Water Molecules.—Thermal analysis of (1) shows that two main weight losses occur: between 60 and 160 °C corresponding to 12% of the total weight and between 165 and 220 °C accounting for 7—8% of the initial weight. The second weight loss is rather ill defined because of the coexistence, at the higher-temperature limit, of other losses due to thermal decomposition of the sample. The two losses are attributed to water (see below). Samples of (1) which lose water rather slowly on standing in air or in a desiccator, if exposed to NH_3 vapour and then left *in vacuo* over $CaCl_2$ for 24 h, lose *ca.* 11% of their initial weight. The amount of water lost corresponds to four molecules out of six of the hydrated compound, and is accompanied by the following changes in the i.r. spectrum: (*a*) a strong decrease in the absorbance at 3 500 cm^{-1}; (*b*) a shift of the band at 3 430 cm^{-1} of the hydrated compound to *ca.* 3 400 cm^{-1}; (*c*) a decrease in absorbance at 2 097 cm^{-1}; and (*d*) a shift to lower frequency (2 040 cm^{-1}) and broadening of the band assigned to terminal CN, which now exhibits several submaxima. Both the weight and i.r. spectrum of the fully hydrated compound can be restored by exposing the sample to a water-saturated atmosphere. Heating (1) at 140 °C causes total and irreversible water loss, which can be monitored by the disappearance of the bands at 3 500 and 3 430 cm^{-1}.

Complex (2) also lost water following the above treatment

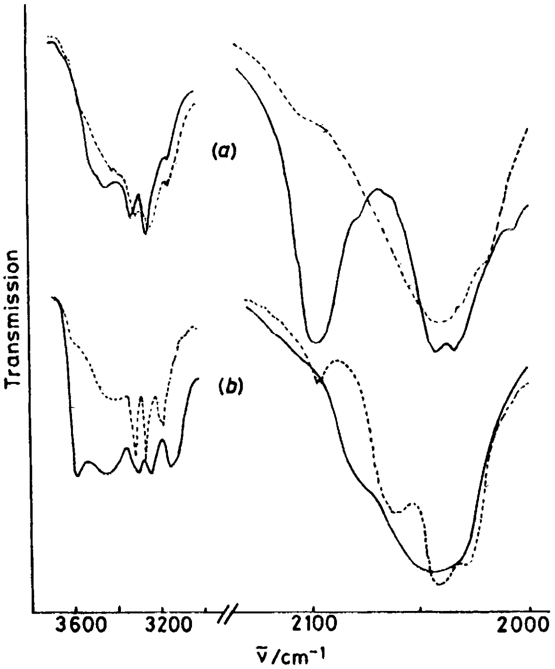

FIGURE 2 Infrared spectra of (*a*) $[\{Cu(dien)\}_2\cdot Fe(CN)_6]\cdot 6H_2O$ and (*b*) $[\{Cu(Me_2dien)\}_2\cdot Fe(CN)_6]\cdot 6H_2O$, in their hydrated (——) and partially dehydrated forms (– – – –)

(NH_3 and vacuum), and exhibited an i.r. spectrum in which the band at 3 560 cm^{-1} has almost completely disappeared while that at 3 450 cm^{-1} shifted to 3 410 cm^{-1}. The i.r. spectrum of the original hydrated species can be restored in the presence of water vapour. Dehydration causes the band at 2 045 cm^{-1} to split into three well separated components (2 060, 2 040, and 2 028 cm^{-1}), and results in the disappearance of the band at 2 060 cm^{-1} and reduction of the absorbance at 2 100 cm^{-1} to a weak peak at 2 096 cm^{-1}.

Reflectance and Single-crystal Spectra.—Reflectance spectra of (1) and (2) are reported in Figure 3. Absorbances at *ca.* 460 nm for (1) and 475 nm for (2) are assigned to $Fe^{2+}\rightarrow Cu^{2+}$ c.t.,[2,6] while the other bands are due to Cu^{2+} *d–d* transitions. The presence of a more intense band maximum at *ca.* 640 nm and of an ill defined shoulder at *ca.* 900 nm for both compounds makes the spectra rather similar to that of tetragonally distorted square-pyramidal $[Cu(dien)X(Y)]\cdot zH_2O$ complexes with $d_{x^2-y^2}$ as ground state.[13]

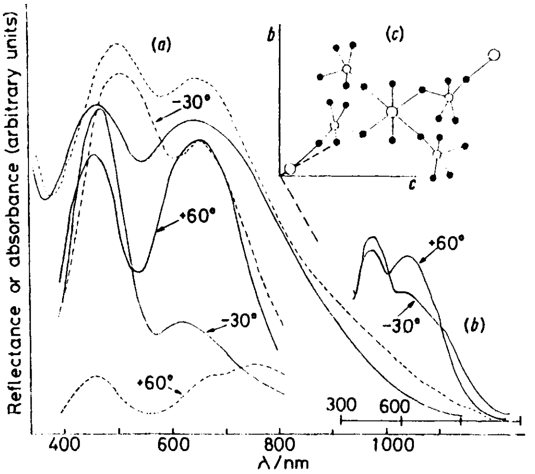

FIGURE 3 (*a*) Polarized single-crystal and electronic reflectance spectra of $[\{Cu(dien)\}_2\cdot Fe(CN)_6]\cdot 6H_2O$ (——) and $[\{Cu(Me_2\text{-}dien)\}_2\cdot Fe(CN)_6]\cdot 6H_2O$ (– – – –). (*b*) Polarized crystal electronic spectrum of a ' mosaic-like ' arrangement of iso-oriented crystals of $[\{Cu(dien)\}_2\cdot Fe(CN)_6]\cdot 6H_2O$. (*c*) Projection of the crystal structure of $[\{Cu(dien)\}_2\cdot Fe(CN)_6]\cdot 6H_2O$ on to the *bc* plane showing the extinction direction of the electronic spectrum

The polarized single-crystal electronic spectrum of (1) was recorded at room temperature with the planes of polarization parallel to the only well developed face (100), along the extinction directions which are at −30° and +60° to the *c* axis, *i.e.* roughly in the *xy* plane and *z* directions of the chromophore. On passing from −30 to +60° the following changes are detectable in the spectrum (Figure 3): (*a*) the c.t. band at 465 nm decreases in intensity and shifts to 450 nm; (*b*) the shoulder at 615 nm (*d–d* transition) is replaced by a broad and more intense band at *ca.* 645 nm; (*c*) a shoulder persists at *ca.* 780 nm; and (*d*) absorbance decreases at 900 nm.

The electronic selection rules for copper(II) *d–d* transitions in C_{2v} symmetry, which is suggested in the present case, allow transitions in *x* ($d_{xz}\rightarrow d_{x^2-y^2}$), *y* ($d_{yz}\rightarrow d_{x^2-y^2}$), and *z* ($d_{z^2}\rightarrow d_{x^2-y^2}$) polarization, while the $d_{xy}\rightarrow d_{x^2-y^2}$ is forbidden. As far as the c.t. bands are concerned, considering only the linear CuN_3–CN–Fe chromophore of C_{2v} symmetry with *y* as principal axis (this assumption is based on the persistency of c.t. bands in solution where the non-linear Cu–NC bond is absent), two allowed ' te ' transitions[6] are expected: in *x* [Fe^{2+} $d_{xy}(B_1)\rightarrow Cu^{2+}$ $d_{x^2-y^2}$ (A_1)] and *z* [Fe^{2+} $d_{yz}(B_2)\rightarrow Cu^{2+}$ $d_{x^2-y^2}$ (A_1)] polarization. Accordingly, the following assignments can be made:

Transition	λ/nm	ν/cm⁻¹
$d_{z^2}\rightarrow d_{x^2-y^2}$	900	11 110
$d_{xy}\rightarrow d_{x^2-y^2}$	780	12 820
$d_{xz}\rightarrow d_{x^2-y^2}$	650	15 410
$d_{yz}\rightarrow d_{x^2-y^2}$	615	16 200
Fe $d_{yz}\rightarrow$Cu $d_{x^2-y^2}$	465	21 500
Fe $d_{xy}\rightarrow$Cu $d_{x^2-y^2}$	435	22 980

The discrimination between the transitions in the 600 nm region, which can be hazardous on the basis of the polarized spectrum of (1), was aided by recording the polarized spectrum of (2) along the extinction directions at −30 and +60° to the major axis of the almost rectangular faces of its channelled crystals. At +60° (Figure 3) almost no c.t. absorbance and a small absorbance at 760 nm are detectable, while at −30° two distinct bands are apparent, a c.t. band at 500 nm and a *d–d* band at 660 nm. Apparently the two spectra were taken along *y*, where c.t. bands are forbidden and where, in the *d–d* region, the $d_{xz}\rightarrow d_{x^2-y^2}$ might be visible (760 nm), and along *x*, where the c.t. transitions Fe^{2+} $d_{xy}\rightarrow Cu^{2+}$ $d_{x^2-y^2}$ and Cu^{2+} $d_{xy}\rightarrow d_{x^2-y^2}$ are allowed. Thus, given the similarity of the spectra of (1) and (2), if $d_{xz}\rightarrow d_{x^2-y^2}$ occurs at 650—660 nm, the $d_{yz}\rightarrow d_{x^2-y^2}$ transition should fall at higher energy and is very likely the small band which is left over at 615 nm in *z* polarization. Thus, the one-electron energy sequence is $d_{x^2-y^2} > d_{z^2} > d_{xy} > d_{xz} > d_{yz}$ analogous to that found for other Cu–dien complexes with square-pyramidal stereochemistry and low tetragonal distortion.[13]

Partial dehydration of both (1) and (2) causes the c.t. bands in the reflectance spectra to shift to lower energy [460 to 485 nm for (1), 465 to 470 nm for (2)] while *d–d* transitions increase in energy [from 635 to 615 nm and from 630 to 620 nm for the more intense bands of (1) and (2), respectively]. This is in keeping with the observation that decreasing the acceptor properties of the solvent in the outer sphere of hexacyanoferrate results in an increase in the donor properties of this ion,[14] thus making easier the c.t. to copper and at the same time destabilizing its $d_{x^2-y^2}$ atomic orbital. The effect is weaker for (2) than for (1) as in the former compound partial dehydration is likely to cause loss of water less tightly bound to that water molecule which is attached to CN^-, as revealed by ν(OH) occurring at 3 560 cm^{-1}.

Solution spectra of the trinuclear species show c.t. bands at 460 nm ($\varepsilon_{max.}$ = 430 dm^3 mol^{-1} cm^{-1} for Fe, extrapolated value from Job's plots) and *d–d* transitions at 585 nm ($\varepsilon_{max.}$ = 120 dm^3 mol^{-1} cm^{-1} for Fe, extrapolated value from Job's plot and corrected for the absorbance due to the c.t. band), in good agreement with reported data. There is no shoulder on the low-energy side of the main *d–d* transition, thus indicating a stronger tetragonal distortion in solution, even stronger than that operating in $[Cu(dien)]^{2+}$ (maximum at 610 nm, $\varepsilon_{max.}$ = 80 dm^3 mol^{-1} cm^{-1}, and asymmetry on the low-energy side of the *d–d* band) whose spectrum was attributed to a square-planar complex.[15]

DISCUSSION

The formation of extended polymers through cyanide bridges often occurs when polycyano-compounds are added to other complexes. The ambidentate co-ordination of cyanide has been shown from the literature to lead to a four-atom $M_A-C\equiv N-M_B$ sequence which may be connected in different ways to form a crystal lattice.[16] The co-ordination behaviour of the two different metal ions determines whether there will be a one-, two-, or three-dimensional linkage. Examples of typical chains are represented by the crystals of $[Ni(en)_2{\cdot}Pd(CN)_4]$ [17] and occurrence of a two-dimensional linkage has been observed in the sheets of the cyanide–ammonia clathrates,[18] but the majority of polynuclear cyanides has a three-dimensional framework structure.[6] The $M_A-C\equiv N-M_B$ linkages are usually linear but often deviate from linearity, as occurs in $KCu_2(CN)_3$.[19] Polynuclear species formed between hexacyanoferrate and copper or cobalt complexes (or enzymes) have also been suggested recently on the basis of optical and e.s.r. spectroscopic evidence.[2,20,21]

The present work has conclusively demonstrated the formation in the solid state and, by comparison of the optical spectra, also in solution of µ-cyano-polynuclear species comprising $[Fe(CN)_6]^{4-}$ and $[Cu(dien)]^{2+}$ ions. It is important to point out, however, that the cyanide groups of the hexacyanoferrate complex do not behave similarly: (*i*) two are not bonded to copper but only interact, through hydrogen bonds, with the water molecules present in the lattice; (*ii*) two are tightly bonded (Cu–N 1.97 Å) to copper atoms of adjacent $[Cu(dien)]^{2+}$ molecules giving rise to *linear* $Fe-C\equiv N-Cu$ linkages and are co-ordinated in the equatorial plane of the square-pyramidal configuration; and (*iii*) the remaining two co-ordinate to copper atoms of the nearest $[Cu(dien)]^{2+}$ ions in the apical positions of the pyramid (Cu–N 2.21 Å) leading to *non-linear* $Fe-C\equiv N-Cu$ chains.

Another interesting features of the crystal structure is the presence of three water molecules (per asymmetric unit of the complex) which form an extensive hydrogen-bonded system among themselves, so leading to a helix which develops one-dimensionally along the *b* axis, as well as with the nitrogens of the free cyano-groups, *i.e.* those of class (*i*), belonging to a polynuclear two-dimensional zone. It is worth emphasizing that one water molecule [Ow(1) in Table 2 and in Figure 1] has a greater involvement in the intermolecular hydrogen-bonding system than the other two since it interacts with two nitrogens [N(1) and N(3)] whereas both Ow(2) and Ow(3) interact with only one nitrogen atom [N(4) and N(3) respectively].

Thermogravimetric results are in agreement with the above findings; it is likely that on heating Ow(2) and Ow(3) are lost at lower temperature than Ow(1). Molecule Ow(1) plays a special role in stabilizing the crystalline structure of (1) since its removal results in the breakdown of the complex. This role can be explained by considering the angles Cu–N(1)–Ow(1) and Cu–N(1)–C(1), which are 105 and 136° respectively, and the fact that N(1) lies on the plane formed by Ow(1), Cu, and C(1), suggesting a sp^2 hybridization for the nitrogen atom. If this is the case, then one would expect that the negative charge density on the trigonally hybridized nitrogen atom could be relieved by the acceptor properties of water, on the one hand, and by the metal on the other; the loss of this water, favouring a shift of charge back to Fe^{2+}, would then also weaken the Cu–N bond. Unfortunately, the above qualitative picture cannot be confirmed by the bond distances, since all the Fe–C and C–N are of the same order of magnitude, within experimental error.

Regarding the ferrocyanide charge-transfer complexes of bovine superoxide dismutase which form at low pH, and of copper-substituted bovine carbonic anhydrase, the present findings confirm the suggestion that the ferrocyanide is directly bound to copper in both enzymes,[2] while the alternative possibility of bridging cyanides bonded to water molecules in the inner co-ordination sphere of Cu^{2+} now seems less likely.

The authors thank Mr. A. Piccotti for technical assistance with the *X*-ray measurements, Mr. A. Maltese for the drawings, and Professor M. Valigi for help in the thermogravimetric analysis. This work was supported, in part, by Consiglio Nazionale delle Ricerche.

[9/1006 *Received, 27th June,* 1979]

REFERENCES

[1] M. Goldberg and I. Pecht, *Biochemistry*, 1976, **15**, 4197.

[2] L. Morpurgo, I. Mavelli, L. Calabrese, A. Finazzi, and G. Rotilio, *Biochem. Biophys. Res. Comm.*, 1976, **70**, 607.

[3] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[4] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

[5] R. Spagna, unpublished work.

[6] A. Ludi and H. U. Gudel, *Structure and Bonding*, 1973, **14**, 1.

[7] G. Davey and F. S. Stephens, *J. Chem. Soc.* (*A*), 1971, 103.

[8] B. J. Hathaway, 'Essays in Chemistry,' 1971, vol. 2, pp. 61—92.

[9] W. C. Hamilton and J. A. Ibers, 'Hydrogen Bonding in Solids,' W. A. Benjamin, New York, 1968.

[10] H. H. Schmidtke and G. Garthoff, *Inorg. Chim. Acta*, 1968, **2**, 357.

[11] D. A. Dows, A. Haim, and W. K. Wilmarth, *J. Inorg. Nuclear Chem.*, 1961, **21**, 33.

[12] D. F. Shriver, S. H. Shriver, and S. E. Anderson, *Inorg. Chem.*, 1965, **4**, 725.

[13] M. J. Bew, B. J. Hathaway, and R. F. Fereday, *J.C.S. Dalton*, 1972, 1229; M. J. Bew, R. J. Fereday, G. Davey, and B. J. Hathaway, *Chem. Comm.*, 1970, 887.

[14] V. Gutmann, 'The Donor-Acceptor Approach to Molecular Interactions,' Plenum, New York and London, 1978, p. 117, 128 and refs. therein.

[15] C. J. Jørgensen, 'Inorganic Complexes,' Academic Press, London and New York, 1963, p. 67.

[16] D. F. Shriver, *Structure and Bonding*, 1966, **1**, 32.

[17] M. Ruegg and A. Ludi, *Theor. Chim. Acta*, 1971, **20**, 193.

[18] J. H. Rayner and H. M. Powell, *J. Chem. Soc.*, 1952, 319.

[19] D. T. Cromer and A. C. Larson, *Acta Cryst.*, 1962, **15**, 397.

[20] P. Machill, N. Blackburn, and H. S. Mason, 'Iron and Copper Proteins,' eds. K. T. Yasunobu, H. F. Mower, and O. Hayaishi, Plenum, New York, 1976, p. 470.

[21] S. Bagger and K. Gibson, *Acta Chem. Scand.*, 1973, **27**, 3227.