Crystal Structure and Spectroscopic Properties of a Polynuclear Complex between [Bis(2-aminoethyl)amine]copper(II) and Hexacyanoferrate(III)

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The addition of $[Fe(CN)_6]^{3-}$ to $[Cu(dien)]^{2+}$ [dien = diethylenetriamine, bis(2-aminoethyl)amine] gives a polynuclear complex of formula $3[Cu(dien)]^{2+}\cdot 2[Fe(CN)_6]^{3-}\cdot 6H_2O$. The compound has been characterized by i.r., e.s.r., and reflectance spectra, and its crystal and molecular structure solved by single-crystal *X*-ray diffractometry. The dark green crystals are monoclinic, space group $P2_1/c$, with a = 20.332(6), b = 14.162(5), c = 14.932(5) Å, β = 96.29(3)°, and Z = 4. The structure has been refined by least-squares methods, using 2 518 independent reflections, to a conventional R of 0.062. It consists of two distinct ionic units. One is a polymer chain running parallel to the 2_1 screw axis and formed by cationic $\{2[Cu(dien)]\cdot[Fe(CN)_6]\}^+$ units in which the $[Cu(dien)]^{2+}$ and $[Fe(CN)_6]^{3-}$ ions are linked through cyanide bridges. In this unit, only four of the six CN^- groups around each iron are bonded to copper atoms of adjacent $[Cu(dien)]^{2+}$ molecules, thus giving rise to both linear and non-linear $Fe-C\equiv N-Cu$ linkages and to a square-based pyramidal co-ordination of nitrogen atoms around each copper atom. The other structural unit, $\{[Cu(dien)]\cdot[Fe(CN)_6]\}^-$, is an anionic monomer formed by linking the $[Cu(dien)]^{2+}$ and $[Fe(CN)_6]^{3-}$ ions through only one cyanide bridge; one of the six water molecules co-ordinates to the Cu^{2+} to give five-co-ordination. Four water molecules per asymmetric unit of the complex participate in a hydrogen-bond system, both among themselves and with some of the nearest nitrogens of the anionic unit. Each of the other two water molecules interacts only with one nitrogen of the nearest hexacyanoferrate of the anionic unit.

IT has been reported that addition of ferricyanide, $[Fe(CN)_6]^{3-}$, to galactose oxidase, an enzyme containing a single bivalent copper and which catalyzes the oxidation of galactose by molecular oxygen, causes the activation of the resting enzyme.[1] The activated enzyme, unlike its resting state, does not show any copper(II) signal in its e.s.r. spectrum down to liquid-nitrogen temperature, and is characterized by prominent optical absorption peaks at about 440 nm and between 800 and 1 000 nm. Two different explanations for the loss of e.s.r. properties were suggested, namely that the Cu^{II} is converted by the oxidant into Cu^{III} with a low-spin d^8 configuration,[1] or, alternatively, that the activated enzyme contains ferricyanide magnetically coupled to Cu^{II} in an ion-pair or charge-transfer complex, and the optical spectrum was interpreted accordingly.[2-4] The paucity of information on the interactions between ferricyanide and copper complexes, not to mention copper enzymes, has left the problem open.

On investigating copper–bis(2-aminoethyl)amine (diethylenetriamine, dien) complexes as possible models for copper-containing enzymes, it was found that on addition of ferricyanide at neutral pH a precipitate forms corresponding to the formula $3[Cu(dien)]^{2+}\cdot 2[Fe(CN)_6]^{3-}\cdot 6H_2O$. Because of its possible relevance as a higher-oxidation-state precursor of $[Cu(dien)]^{2+}$ complexes and of the possibility of elucidating the nature of the bond between ferricyanide and copper(II) complexes, this compound has been examined by *X*-ray analysis and by spectroscopy.

EXPERIMENTAL

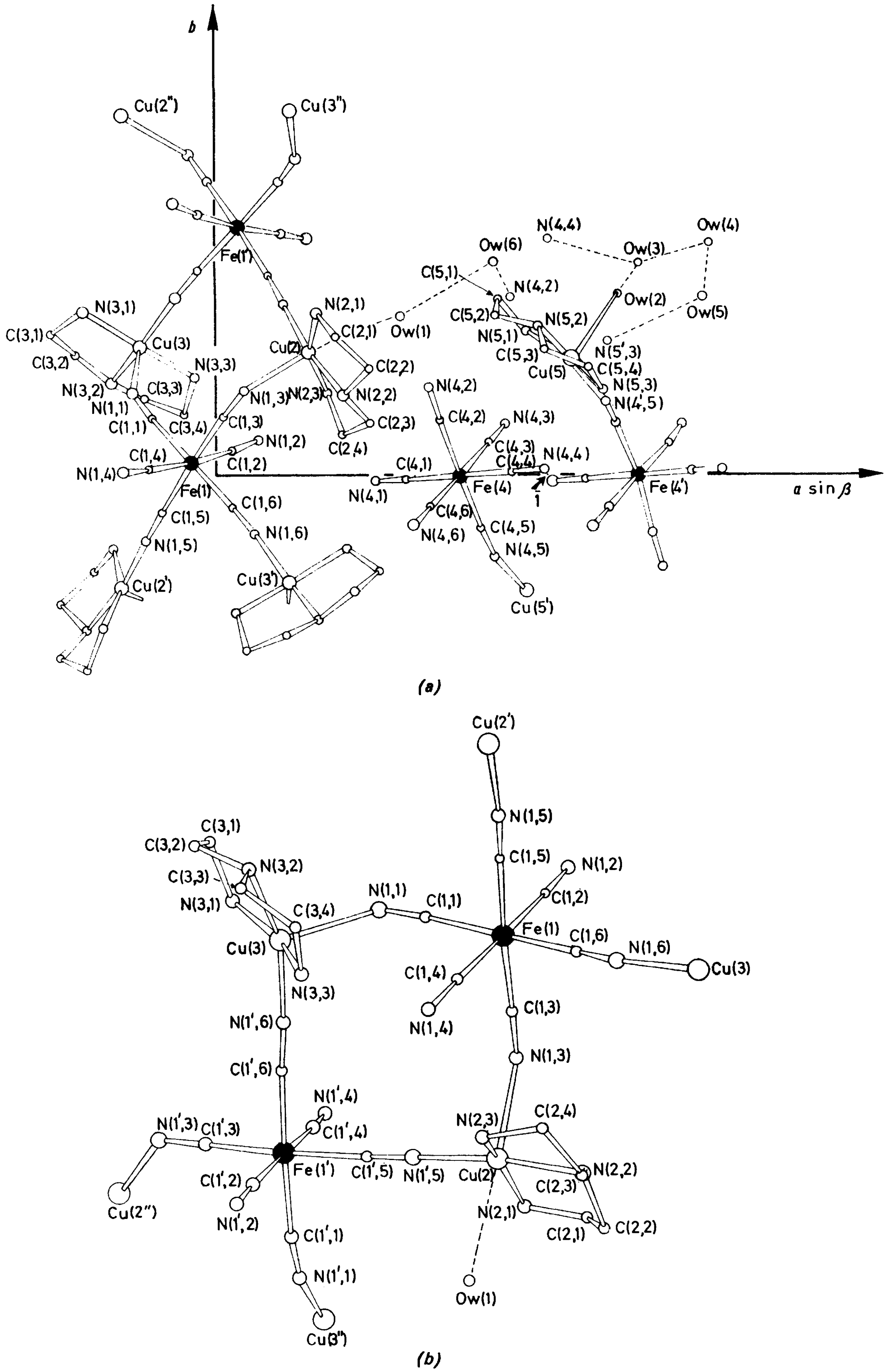
Materials.—The chemicals were commercial products; bis(2-aminoethyl)amine from Fluka A.G., $Cu[SO_4]\cdot 5H_2O$ from Merck, and $K_3[Fe(CN)_6]$ from C. Erba were used without further purification.

Crystal Preparation.—The compound $3[Cu(dien)]^{2+}\cdot 2[Fe(CN)_6]^{3-}\cdot 6H_2O$ was obtained as a green precipitate by adding a cold solution of $K_3[Fe(CN)_6]$ (1.6 g) and $K_2[S_2O_8]$ (1.20 g) (to prevent reduction of ferricyanide) in water (60 cm³) to a cold solution containing $Cu[SO_4]\cdot 5H_2O$ (1.24 g) and dien (0.56 cm³) in water (40 cm³). The precipitate was separated by centrifugation, washed with cold water, and stored in a desiccator. The dry compound was ground to a fine powder which was suspended in water at 80 °C for 5 min with vigorous stirring. The green solution obtained on filtration was rapidly cooled to room temperature, and on standing dark green crystals separated (Found: C, 28.6; H, 4.8; N, 28.7. Calc. for $C_{24}H_{51}Cu_3Fe_2N_{21}O_6$: C, 27.8; H, 4.9; N, 28.5%).

Spectroscopic Measurements.—Powder reflectance spectra were measured with a Beckman DK-2 spectrophotometer equipped with a standard reflectance unit. Infrared spectra were obtained in Nujol mulls with a Perkin-Elmer 577 spectrophotometer.

Crystal Data.—$C_{24}H_{51}Cu_3Fe_2N_{21}O_6$, M = 1 032.13, dark green monoclinic prisms, a = 20.322(6), b = 14.162(5), c = 14.932(5) Å, β = 96.29(3)°, U = 4 274 Å³, D_m = 1.59(1) g cm⁻³ (by flotation), Z = 4, D_c = 1.60 g cm⁻³, $F(000)$ = 2 122.28, $\lambda(Mo\text{-}K_\alpha)$ = 0.710 7 Å, $\mu(Mo\text{-}K_\alpha)$ = 22.62 cm⁻¹, space group $P2_1/c$ (C_{2h}^5, no. 14) from systematic absences. All data were collected on a $P2_1$ Syntex automated diffractometer by the θ—2θ scan technique with graphite-monochromated Mo-K_α radiation. The intensities of 2 518 independent reflections having $I \geqslant 3\sigma(I)$ were used in the refinement. The data were corrected for background and for Lorentz and polarization effects, but no absorption correction was applied. Unit-cell dimensions were determined by least-squares analysis of diffractometer measurements on 14 reflections with $2\theta > 25°$.

Structure Solution and Refinement.—The approximate positions of the five metal atoms in the asymmetric unit were found from an E map with 277 reflections phased with the multi-solution method of the MULTAN program (P. Main, Department of Physics, University of York). The positions


b
Cu(2")
Cu(3")
Fe(1')
N(4,4)
Ow(4)
Ow(6)
Ow(3)
C(5,1)
N(4,2)
Ow(2)
N(3,1)
N(2,1)
C(5,2)
N(5,2)
Ow(5)
C(3,1)
Cu(3)
C(2,1)
Ow(1)
N(5,1)
C(5,3)
N(5',3)
C(3,2)
N(3,3)
Cu(2)
C(2,2)
Cu(5)
C(5,4)
N(3,2)
C(3,3)
N(1,3)
N(2,3)
N(2,2)
N(4,2)
N(5,3)
N(1,1)
N(4',5)
C(1,1)
C(3,4)
C(1,3)
C(2,3)
C(4,2)
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N(1,2)
C(2,4)
C(4,3)
C(1,4)
C(1,2)
C(4,1)
C(4,4)
N(4,4)
N(1,4)
Fe(1)
Fe(4)
Fe(4')
a sin β
N(4,1)
1̄
C(1,6)
C(4,6)
C(1,5)
N(4,6)
C(4,5)
N(1,6)
N(1,5)
N(4,5)
Cu(2')
Cu(3')
Cu(5')
(a)
Cu(2')
N(1,5)
C(3,1)
C(1,5)
N(1,2)
C(3,2)
N(3,2)
C(1,2)
C(3,3)
N(1,1)
C(1,1)
N(3,1)
C(3,4)
Fe(1)
C(1,6)
N(1,6)
Cu(3)
Cu(3)
C(1,4)
N(3,3)
C(1,3)
N(1,4)
N(1',6)
N(1,3)
C(1',6)
N(1',4)
C(2,4)
N(2,3)
N(1',3)
C(1',3)
C(1',4)
N(2,2)
Fe(1')
C(1',5)
N(1',5)
Cu(2)
C(2,3)
C(1',2)
N(2,1)
Cu(2")
N(1',2)
C(2,1)
C(2,2)
C(1',1)
N(1',1)
Ow(1)
Cu(3")
(b)

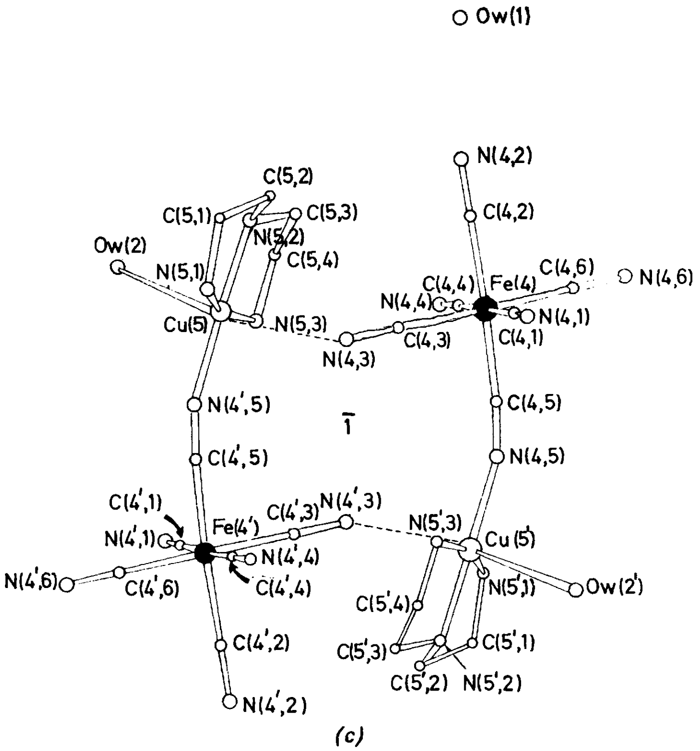

FIGURE 1 (*a*) [001] projection of part of the structure of $3[Cu(dien)]^{2+}\cdot2[Fe(CN)_6]^{3-}\cdot6H_2O$, showing the labelling of some atoms. (*b*) Perspective of part of one chain of the polymeric cation $\{2[Cu(dien)]\cdot[Fe(CN)_6]\}_n^{n+}$. (*c*) Perspective of a pair of the monomeric anions $\{[Cu(dien)]\cdot[Fe(CN)_6]\}^-$

of the other non-hydrogen atoms were obtained from subsequent Fourier syntheses. The positions and anisotropic thermal parameters were refined by a block-diagonal least-squares method. All hydrogen atoms (except those belonging to the water molecules) were included at fixed calculated positions with an isotropic temperature factor of 3.0 Å^2. The function minimized was $\Sigma w(|F_o| - k|F_c|)^2$, using the weighting scheme $w = (a + bF_o + cF_o^2)^{-1}$, where $a = 2.0$, $b = 1.0$, and $c = 0.000\,1$. The final conventional R was 0.062. Atomic scattering factors were obtained from ref. 5 and the corrections for real dispersion (heavy atoms only) from ref. 6. Calculations were made on a HP-21 MX computer of the C.N.R. Research Area (Montelibretti, Rome) and on the UNIVAC 1108 computer at Rome University using the MULTAN program for the initial solution of the structure and the set of programs of the Laboratorio di Strutturistica Chimica of the C.N.R. for its complete solution and refinement.[7]

Final parameters for the non-hydrogen atoms with their estimated standard deviations are given in Table 1, interatomic distances and angles in Table 2. Thermal parameters, calculated atomic positions for hydrogens, and observed and calculated structure factors are listed in Supplementary Publication No. SUP 22884 (19 pp.).*

RESULTS

Description of the Structure.—As shown in Figure 1(*a*) the structure of the complex of general formula $3[Cu(dien)]^{2+}\cdot2[Fe(CN)_6]^{3-}\cdot6H_2O$ consists of two distinct ionic units. One of them, Figure 1(*b*), is a polymer formed by the cationic $\{2[Cu(dien)]\cdot[Fe(CN)_6]\}^+$ units. Two of these chains run along the 2_1 screw axes at $0y\frac{1}{4}$ and $0y\frac{3}{4}$, the $[Cu(dien)]^{2+}$ and $[Fe(CN)_6]^{3-}$ starting complexes being linked through cyanide bridges. Of the six CN$^-$ groups around iron, two [namely C(1,2)≡N(1,2) and C(1,4)≡N(1,4), *trans* to each other] are bonded only to iron, whereas the other four reveal their bidentate bridging nature by forming bonds with the copper atoms of the nearest $[Cu(dien)]^{2+}$ ions, thus giving rise to four Fe–C≡N–Cu chains per loop in the chain. However, the bonding between the copper atoms and the four cyanides occurs in two different ways: two of the CN$^-$ groups, *cis* with respect to iron and labelled C(1,5)≡N(1,5) and C(1,6)≡N(1,6), co-ordinate to the two nearest copper atoms, Cu(2) and Cu(3), in the same basal plane as the diene nitrogens and form almost linear Fe–C≡N–Cu links, the angles Cu(2)–N(1,5)–C(1,5) and Cu(3)–N(1,6)–C(1,6) being 176 and 170°, respectively. The other two CN$^-$ groups, also *cis* to iron and labelled C(1,1)≡N(1,1) and C(1,3)≡N(1,3), co-ordinate to the copper atoms of the nearest $[Cu(dien)]^{2+}$ molecules almost perpendicularly to the plane formed by Cu and the diene nitrogens and give rise to non-linear Fe–C≡N–Cu sequences, the Cu(2)–N(1,3)–C(1,3) and Cu(3)–N(1,1)–C(1,1) angles being 141 and 139°, respectively. The two independent copper atoms in this unit thus acquire a square-based pyramidal co-ordination and their chromophores are of the type CuN$_5$.

Atom Cu(2) lies 0.23 Å above the mean basal plane passing through N(2,1), N(2,2), N(2,3), and N(1',5). The equation of the plane, referred to the direct cell, is $18.302\,x + 5.899\,y - 3.349\,z + 3.010 = 0$, and the nitrogen atoms are alternately below and above the plane, deviations (Å) from the latter being N(2,1) 0.08, N(2,2) − 0.09, N(2,3) 0.08, and N(1',5) − 0.07. Atom Cu(3) lies 0.32 Å above the mean basal plane passing through N(3,1), N(3,2), N(3,3), and N-

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

(1′,6). The equation of the plane, referred to the direct cell, is $5.630\,x + 8.150\,y - 11.872\,z + 1.177 = 0$, and the nitrogen atoms are alternately above and below the plane, deviations (Å) being N(3,1) −0.03, N(3,2) 0.03, N(3,3) −0.03, and N(1′,6) 0.03.

TABLE 1

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

Atom	x	y	z
Fe(1)	−348(1)	248(2)	2 895(2)
Fe(4)	3 660(1)	−10(2)	1 627(2)
Cu(2)	1 411(1)	2 599(1)	3 992(1)
Cu(3)	−1 121(1)	2 704(1)	601(1)
Cu(5)	5 430(1)	2 462(2)	157(2)
C(1,1)	−942(8)	1 195(11)	2 243(11)
C(1,2)	273(8)	503(9)	2 009(11)
C(1,3)	123(8)	1 223(11)	3 621(12)
C(1,4)	−980(9)	96(11)	3 763(12)
C(1,5)	794(8)	4 215(11)	2 812(11)
C(1,6)	−253(8)	4 315(10)	1 540(12)
C(2,1)	1 809(11)	2 936(15)	5 850(13)
C(2,2)	2 316(10)	2 238(16)	5 541(13)
C(2,3)	2 331(9)	1 090(12)	4 259(14)
C(2,4)	1 910(9)	848(12)	3 433(13)
C(3,1)	−2 451(9)	2 970(14)	−178(15)
C(3,2)	−2 088(9)	2 510(14)	−898(13)
C(3,3)	−1 052(9)	1 502(13)	−990(13)
C(3,4)	−465(9)	1 272(13)	−342(15)
C(4,1)	2 861(8)	−99(12)	797(12)
C(4,2)	3 364(9)	1 155(12)	2 127(13)
C(4,3)	4 093(10)	687(12)	723(14)
C(4,4)	4 447(10)	75(13)	2 445(13)
C(4,5)	3 979(8)	−1 125(11)	1 083(12)
C(4,6)	3 216(9)	−667(12)	2 526(13)
C(5,1)	4 246(10)	3 733(14)	−313(15)
C(5,2)	4 197(11)	3 381(16)	638(16)
C(5,3)	4 929(12)	2 662(15)	1 911(14)
C(5,4)	5 602(12)	2 284(15)	2 058(14)
N(1,1)	−1 228(7)	1 724(10)	1 809(10)
N(1,2)	639(7)	729(10)	1 522(10)
N(1,3)	431(7)	1 781(9)	4 032(9)
N(1,4)	−1 639(8)	22(11)	4 287(11)
N(1,5)	1 029(7)	3 612(11)	3 213(11)
N(1,6)	−602(7)	3 737(10)	1 264(11)
N(2,1)	1 515(8)	3 421(11)	5 073(10)
N(2,2)	1 936(7)	1 678(9)	4 805(9)
N(2,3)	1 678(8)	1 742(10)	3 019(10)
N(3,1)	−1 974(7)	3 437(10)	459(9)
N(3,2)	−1 563(7)	1 937(11)	−432(9)
N(3,3)	−306(8)	2 063(11)	308(10)
N(4,1)	2 408(7)	−145(10)	288(9)
N(4,2)	3 206(7)	1 851(10)	2 463(9)
N(4,3)	4 338(7)	1 086(9)	190(9)
N(4,4)	4 945(8)	142(9)	2 916(10)
N(4,5)	4 183(8)	−1 733(11)	715(11)
N(4,6)	2 972(7)	−1 074(10)	3 072(10)
N(5,1)	4 668(7)	3 056(11)	−747(11)
N(5,2)	4 842(8)	3 162(10)	1 028(11)
N(5,3)	5 810(7)	1 813(10)	1 260(11)
Ow(1)	2 811(14)	3 348(15)	3 599(16)
Ow(2)	6 036(7)	3 838(10)	232(11)
Ow(3)	6 338(10)	500(14)	3 625(14)
Ow(4)	7 407(12)	−61(19)	2 843(19)
Ow(5)	7 276(14)	1 243(29)	1 498(22)
Ow(6)	4 152(17)	4 436(29)	3 442(22)

The Cu−N(amine) bond distances within the two crystallographically independent pyramids are not significantly different, and their mean value (2.01 Å) is similar to those found in other mono(dien) copper complexes, namely $[Cu(dien)(NCS)_2]$,[8a] $[Cu(dien)(C_2O_4)]\cdot4H_2O$,[8b] and $[Cu(dien)(O_2CH)_2]$[8c] which also have a distorted square-based pyramidal arrangement about the copper atoms. The $Cu-N_{CN}$ distances in the basal plane are 1.96 and 2.01 Å, and in the apical position are 2.32 and 2.31 Å, for Cu(2) and Cu(3) respectively.

The other structural units of formula $\{[Cu(dien)]\cdot[Fe(CN)_6]\}^-$ occur as pairs of monomers situated around centres of symmetry and are formed [Figure 1(*c*)] by the linking of $[Cu(dien)]^{2+}$ and $[Fe(CN)_6]^{3-}$ ions through only one cyanide group. This cyanide, C(4,5)≡N(4,5), is bonded to Cu(5) in the same basal plane as the diene nitrogens [Cu(5)−N(4,5) 1.99 Å] and makes an angle Cu−N−C of about 158°. The copper atom in this unit completes its five-co-ordination with a water molecule, Cu(5)−Ow(2) 2.41 Å, and assumes a square-based pyramidal configuration with four nitrogens in the equatorial plane and an oxygen in the apical position, thus giving rise to a chromophore CuN_4O. Atom Cu(5) lies 0.10 Å below the mean basal plane passing through the nitrogen atoms. The equation of the plane, referred to the direct cell, is $13.464\,x + 10.609\,y - 1.082\,z + 9.682 = 0$, and the nitrogen atoms are alternately above and below the plane, deviations (Å) being N(5,1) − 0.07, N(5,2) 0.08, N(5,3) − 0.07, and N(4′,5) 0.07. The Cu−N(amine) bond distances within this pyramid are not significantly different, their mean value being 2.01 Å.

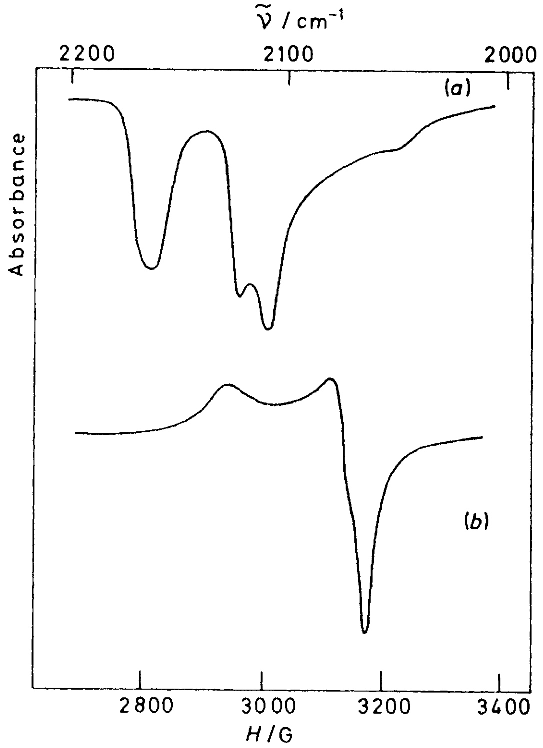

FIGURE 2 Spectra of $3[Cu(dien)]^{2+}\cdot2[Fe(CN)_6]^{3-}\cdot6H_2O$: (*a*) i.r.; (*b*) e.s.r. at 77 K, $\nu = 9.15$ GHz (1 G = 10^{-4} T)

As regards the six water molecules present for each complex formula unit, it must be noted that: (*i*) four of them, Ow(2), Ow(3), Ow(4), and Ow(5) in Figure 1(*a*), are linked together through hydrogen bonds, with average Ow−Ow distances of 2.72 Å; (*ii*) Ow(2) is bonded, as already mentioned, to Cu(5); (*iii*) Ow(3) interacts with N(4,4), a nitrogen belonging to the hexacyanoferrate moiety of the anionic unit, Ow(3)−N(4,4) 2.96 Å; (*iv*) Ow(5) interacts with another diene nitrogen, Ow(5)−N(5,3) 3.08 and Ow(5)−H-[N(5,3)] 2.18 Å. The other two water molecules, Ow(1) and Ow(6), each interact with only one cyanide nitrogen of the nearest hexacyanoferrate of the anionic complex, the distances Ow(1)–N(4,2) and Ow(6)–N(4,3) being 2.89 and 2.71 Å, respectively.

Infrared Spectrum.—In the region between 3 000 and 3 700 cm^{-1} the i.r. spectrum is remarkably similar to that obtained for $[\{Cu(dien)\}_2\cdot Fe(CN)_6]\cdot 6H_2O$.[9] ν(OH) bands occur at 3 630 and 3 760(sh) cm^{-1}, while the ν[NH_2(NH)] stretching vibrations appear at 3 360, 3 400, 3 430, and 3 510 cm^{-1}.[10] In the region between 2 100 and 2 200 cm^{-1}, three bands arising from the lowering of symmetry from the T_{1u} modes of ferricyanide in O_h are observed: two of them (at 2 109 and 2 122 cm^{-1}) are assigned to terminal CN stretching modes, the other (at 2 162 cm^{-1}) to the intermetallic linear –C–N– stretching vibrations.[11] No band due to an intermetallic non-linear –C–N– bond was present [Figure 2(*a*)].

Reflectance Spectrum.—The electronic reflectance spectrum of the title compound shows bands with maxima at 590, 435, 340, and about 290(sh) nm. The broad band with a maximum at 590 nm is an envelope of several transitions due to the $[Cu(dien)]^{2+}$ chromophore in tetragonally distorted environments.[12] The remaining bands cannot be so readily assigned, as for such a compound a number of transitions of different origin can be expected: iron(III) *d–d* transitions, charge transfer (c.t.) from ligand (CN) to iron, and c.t. between copper and iron in either direction. The assignment is further complicated by the non-equivalence of the ferricyanide ions in the crystal.

TABLE 2

Bond distances (Å) and angles (°) with their estimated standard deviations in parentheses

(*a*) Distances

Fe(1)–C(1,1)	1.99(2)	Fe(4)–C(4,1)	1.94(2)
Fe(1)–C(1,2)	1.97(2)	Fe(4)–C(4,2)	1.94(2)
Fe(1)–C(1,3)	1.95(2)	Fe(4)–C(4,3)	1.96(2)
Fe(1)–C(1,4)	1.94(2)	Fe(4)–C(4,4)	1.91(2)
Fe(1)–C(1,5)	1.97(2)	Fe(4)–C(4,5)	1.93(2)
Fe(1)–C(1,6)	1.93(2)	Fe(4)–C(4,6)	1.94(2)
C(1,1)–N(1,1)	1.12(2)	C(4,1)–N(4,1)	1.13(2)
C(1,2)–N(1,2)	1.15(2)	C(4,2)–N(4,2)	1.17(2)
C(1,3)–N(1,3)	1.15(2)	C(4,3)–N(4,3)	1.14(3)
C(1,4)–N(1,4)	1.18(2)	C(4,4)–N(4,4)	1.17(3)
C(1,5)–N(1,5)	1.12(2)	C(4,5)–N(4,5)	1.13(2)
C(1,6)–N(1,6)	1.13(2)	C(4,6)–N(4,6)	1.16(3)
Cu(2)–N(2,1)	1.99(1)	N(3,1)–C(3,1)	1.45(2)
Cu(2)–N(2,2)	2.01(1)	N(3,2)–C(3,2)	1.46(2)
Cu(2)–N(2,3)	2.02(1)	N(3,2)–C(3,3)	1.49(2)
Cu(2)–N(1,3)	2.32(1)	N(3,3)–C(3,4)	1.50(2)
Cu(2)–N(1′,5)	1.96(1)	C(3,1)–C(3,2)	1.52(3)
N(2,1)–C(2,1)	1,43(2)	C(3,3)–C(3,4)	1.52(3)
N(2,2)–C(2,2)	1.50(2)	Cu(5)–N(5,1)	2.00(2)
N(2,2)–C(2,3)	1.47(2)	Cu(5)–N(5,2)	2.00(2)
N(2,3)–C(2,4)	1.47(2)	Cu(5)–N(5,3)	2.03(2)
C(2,1)–C(2,2)	1.54(3)	Cu(5)–N(4′,5)	1.99(1)
C(2,3)–C(2,4)	1.47(3)	Cu(5)–Ow(2)	2.41(1)
Cu(3)–N(3,1)	2.02(1)	N(5,1)–C(5,1)	1.49(3)
Cu(3)–N(3,2)	2.02(1)	N(5,2)–C(5,2)	1.41(3)
Cu(3)–N(3,3)	1.99(1)	N(5,2)–C(5,3)	1.49(3)
Cu(3)–N(1,1)	2.31(1)	N(5,3)–C(5,4)	1.47(3)
Cu(3)–N(1′,6)	2.01(1)	C(5,1)–C(5,2)	1.52(3)
		C(5,3)–C(5,4)	1.47(3)

(*b*) Other interatomic contacts

Distances		Angles	
Cu(2)–Ow(1)	3.16(3)	N(1,3)–Cu(2)–Ow(1)	166.4(8)
Cu(5)–N(4,3)	2.83(2)	N(1,5)–Cu(2)–Ow(1)	87.1(8)
Ow(2)–Ow(3)	2.71(3)	N(4,3)–Cu(5)–N(4′,5)	93.3(8)
Ow(3)–Ow(4)	2.70(3)	N(4,3)–Cu(5)–N(5,1)	82.0(8)
Ow(4)–Ow(5)	2.72(3)	N(4,3)–Cu(5)–N(5,2)	85.0(7)
Ow(1)–Ow(6)	3.16(4)	N(4,3)–Cu(5)–N(5,3)	87.1(8)
Ow(3)–N(4,4)	2.96(4)	N(4,3)–Cu(5)–Ow(2)	168.8(7)
Ow(5)–N(5′,3)	3.08(4)	Ow(2)–Ow(3)–Ow(4)	139.2(15)
Ow(1)–N(4,2)	2.89(4)	Ow(3)–Ow(4)–Ow(5)	95.9(14)
Ow(6)–N(4,3)	2.71(4)	Ow(2)–Ow(3)–N(4,4)	94.4(14)
		N(4,4)–Ow(3)–Ow(4)	125.5(14)
		Ow(4)–Ow(5)–N(5,3)	106.2(14)
		N(4,2)–Ow(1)–Ow(6)	90.9(15)

TABLE 2 (*continued*)

(*c*) Angles

C(1,1)–Fe(1)–C(1,6)	176.4(6)	C(4,1)–Fe(4)–C(4,4)	179.9(7)
C(1,2)–Fe(1)–C(1,4)	175.6(6)	C(4,2)–Fe(4)–C(4,5)	176.7(8)
C(1,3)–Fe(1)–C(1,5)	177.2(6)	C(4,3)–Fe(4)–C(4,6)	178.3(8)
C(1,1)–Fe(1)–C(1,2)	86.9(7)	C(4,1)–Fe(4)–C(4,2)	91.6(7)
C(1,1)–Fe(1)–C(1,3)	91.7(7)	C(4,1)–Fe(4)–C(4,3)	90.1(8)
C(1,1)–Fe(1)–C(1,4)	89.5(7)	C(4,1)–Fe(4)–C(4,5)	88.6(7)
C(1,1)–Fe(1)–C(1,5)	91.1(7)	C(4,1)–Fe(4)–C(4,6)	89.4(8)
C(1,2)–Fe(1)–C(1,3)	86.0(7)	C(4,2)–Fe(4)–C(4,3)	91.1(8)
C(1,2)–Fe(1)–C(1,5)	93.9(7)	C(4,2)–Fe(4)–C(4,4)	88.5(8)
C(1,2)–Fe(1)–C(1,6)	89.9(8)	C(4,2)–Fe(4)–C(4,6)	87.3(8)
C(1,3)–Fe(1)–C(1,4)	91.7(7)	C(4,3)–Fe(4)–C(4,4)	90.0(8)
C(1,3)–Fe(1)–C(1,6)	89.6(7)	C(4,3)–Fe(4)–C(4,5)	85.6(8)
C(1,4)–Fe(1)–C(1,5)	88.6(7)	C(4,4)–Fe(4)–C(4,5)	91.3(7)
C(1,4)–Fe(1)–C(1,6)	93.9(7)	C(4,4)–Fe(4)–C(4,6)	90.5(9)
C(1,5)–Fe(1)–C(1,6)	87.7(7)	C(4,5)–Fe(4)–C(4,6)	96.0(9)
Fe(1)–C(1,1)–N(1,1)	172.5(16)	Fe(4)–C(4,1)–N(4,1)	177.5(17)
Fe(1)–C(1,2)–N(1,2)	174.2(13)	Fe(4)–C(4,2)–N(4,2)	176.9(16)
Fe(1)–C(1,3)–N(1,3)	176.4(15)	Fe(4)–C(4,3)–N(4,3)	179.1(18)
Fe(1)–C(1,4)–N(1,4)	178.7(14)	Fe(4)–C(4,4)–N(4,4)	177.0(18)
Fe(1)–C(1,5)–N(1,5)	177.7(14)	Fe(4)–C(4,5)–N(4,5)	174.6(16)
Fe(1)–C(1,6)–N(1,6)	175.3(15)	Fe(4)–C(4,6)–N(4,6)	177.6(17)
N(2,1)–Cu(2)–N(2,2)	83.5(6)	Cu(3)–N(1,1)–C(1,1)	140.6(14)
N(2,1)–Cu(2)–N(2,3)	158.2(6)	Cu(3)–N(1′,6)–C(1′,6)	170.1(15)
N(2,2)–Cu(2)–N(2,3)	82.9(6)	N(1,1)–Cu(3)–N(1′,6)	98.3(6)
Cu(2)–N(2,1)–C(2,1)	112.2(16)	N(1,1)–Cu(3)–N(3,1)	103.8(6)
N(2,1)–C(2,1)–C(2,2)	107.5(14)	N(1,1)–Cu(3)–N(3,2)	101.7(5)
C(2,1)–C(2,2)–N(2,2)	104.5(14)	N(1,1)–Cu(3)–N(3,3)	92.9(6)
C(2,2)–N(2,2)–C(2,3)	116.0(14)	N(1′,6)–Cu(3)–N(3,1)	94.4(6)
N(2,2)–C(2,3)–C(2,4)	107.2(15)	N(1′,6)–Cu(3)–N(3,2)	159.8(6)
C(2,3)–C(2,4)–N(2,3)	106.6(14)	N(1′,6)–Cu(3)–N(3,3)	92.0(6)
C(2,4)–N(2,3)–Cu(2)	108.4(14)	N(5,1)–Cu(5)–N(5,2)	82.7(6)
Cu(2)–N(2,2)–C(2,2)	107.3(11)	N(5,1)–Cu(5)–N(5,3)	164.7(7)
Cu(2)–N(2,2)–C(2,3)	108.7(11)	N(5,2)–Cu(5)–N(5,3)	85.6(7)
Cu(2)–N(1,3)–C(1,3)	139.0(13)	Cu(5)–N(5,1)–C(5,1)	111.2(12)
Cu(2)–N(1′,5)–C(1′,5)	175.6(15)	N(5,1)–C(5,1)–C(5,2)	107.3(16)
N(1,3)–Cu(2)–N(1′,5)	95.6(6)	C(5,1)–C(5,2)–N(5,2)	107.7(18)
N(1,3)–Cu(2)–N(2,1)	106.8(6)	C(5,2)–N(5,2)–C(5,3)	119.0(18)
N(1,3)–Cu(2)–N(2,2)	93.5(6)	N(5,2)–C(5,3)–C(5,4)	108.9(18)
N(1,3)–Cu(2)–N(2,3)	91.1(6)	C(5,3)–C(5,4)–N(5,3)	113.1(17)
N(1′,5)–Cu(2)–N(2,1)	93.1(6)	C(5,4)–N(5,3)–Cu(5)	107.5(13)
N(1′,5)–Cu(2)–N(2,2)	170.9(6)	Cu(5)–N(5,2)–C(5,2)	110.8(12)
N(1′,5)–Cu(2)–N(2,3)	97.7(6)	Cu(5)–N(5,2)–C(5,3)	108.7(12)
N(3,1)–Cu(3)–N(3,2)	83.8(6)	Cu(5)–N(4′,5)–C(4′,5)	161.2(12)
N(3,1)–Cu(3)–N(3,3)	161.0(6)	N(4′,5)–Cu(5)–N(5,1)	97.3(7)
N(3,2)–Cu(3)–N(3,3)	84.0(6)	N(4′,5)–Cu(5)–N(5,2)	178.3(7)
Cu(3)–N(3,1)–C(3,1)	110.0(11)	N(4′,5)–Cu(5)–N(5,3)	94.3(7)
N(3,1)–C(3,1)–C(3,2)	108.6(15)	N(4′,5)–Cu(5)–Ow(2)	97.1(7)
C(3,1)–C(3,2)–N(3,2)	106.9(15)	N(5,1)–Cu(5)–Ow(2)	92.6(6)
C(3,2)–N(3,2)–C(3,3)	116.0(14)	N(5,2)–Cu(5)–Ow(2)	84.6(6)
N(3,2)–C(3,3)–C(3,4)	106.9(15)	N(5,3)–Cu(5)–Ow(2)	96.1(6)
C(3,3)–C(3,4)–N(3,3)	106.8(14)		
C(3,4)–N(3,3)–Cu(3)	111.1(10)		
Cu(3)–N(3,2)–C(3,2)	107.8(10)		
Cu(3)–N(3,2)–C(3,3)	109.1(10)		

Free $K_3[Fe(CN)_6]$ shows a band at 415 nm, which had been identified as a $T_{2g} \longleftarrow L(CN^-)_g$ symmetry-forbidden c.t. allowed by the mixing of ligand (CN) orbitals with higher orbitals of opposite parity to those of iron, by odd vibrations.[13] It is suggested that the present band at 435 nm, which has an intensity comparable to the copper *d–d* transitions, has the same origin. Its low intensity could be explained if further symmetry restrictions, due to the mixing of copper *d* orbitals with those of CN^-, are taken into account. In that case the transition is better described as a one-electron charge transfer from an *e* orbital of copper (*i.e.* $d_{x^2-y^2}$) to a *t* orbital of iron.[14]

The other two weak bands are identified as iron(III) crystal-field transitions. The band at 340 nm compares with the $^2A_2$ $(t^4e) \leftarrow {}^2T_2(t^5)$ transition of $[Fe(CN)_6]^{3-}$ at 320 nm, while that at 290 nm, which also occurs with other hexacyanoferrate complexes, compares with the $^2E_g(t^4e) \leftarrow {}^2T_2(t^5)$ transition occurring at 280 nm and is assigned accordingly.

E.S.R. Spectra.—The e.s.r. spectra [Figure 2(*b*)] obtained on polycrystalline powdered samples of the title compound, at *X*-band in the range 77—300 K, yielded three values, $g_1 = 2.050$, $g_2 = 2.067$, and $g_3 = 2.210$, which, due to the misalignment of both the CuN_5 and CuN_4O chromophores, represent crystal parameters. The e.s.r. signal, which seems to be due to a single species, is identical to that obtained for $[\{Cu(dien)\}_2\cdot Fe(CN)_6]\cdot 6H_2O$,[15] where only the CuN_5 chromophore is present. It is also similar to the signal of other dien copper complexes with distorted square-pyramidal geometry [12] and $d_{x^2-y^2}$ ground state. The spectrum is attributed either to the CuN_5 chromophores, the copper of CuN_4O being antiferromagnetically coupled to Fe^{III}, or to both chromophores which are spectroscopically equivalent.

DISCUSSION

Many examples have been reported of the formation of inorganic polynuclear complexes when polycyano-compounds are added to other complexes; they arise because of the bidentate and bridging nature of the CN^- group which leads to four-atom $M_A-C\equiv N-M_B$ sequences.[16-20] A similar formation of polynuclear species between ferrocyanide and metal enzymes has also been suggested recently on the basis of optical and e.s.r. spectroscopic evidence.[4,21,22]

In a previous investigation the formation has been demonstrated, in both the solid state and in solution (by comparison of the optical spectra), of μ-cyano-polynuclear species between $[Fe(CN)_6]^{4-}$ and $[Cu(dien)]^{2+}$ ions.[9]

The present study provides definitive evidence that the addition of ferricyanide to mono(diethylenetriamine) copper ions likewise gives rise to a polynuclear complex of formula $3[Cu(dien)]^{2+}\cdot 2[Fe(CN)_6]^{3-}\cdot 6H_2O$. However, unlike the previously investigated complex, the present compound is formed from two separate ionic units of formulae $\{2[Cu(dien)]\cdot[Fe(CN)_6]\}^+$ and $\{[Cu(dien)]\cdot[Fe(CN)_6]\}^-$ respectively. The cationic unit is a polymer chain running parallel to the 2_1 screw axis and in which: (*a*) four cyanides from each hexacyanoferrate provide both linear and non-linear linkages with the nearest $[Cu(dien)]^{2+}$ ions; and (*b*) the linearly and non-linearly oriented cyanides co-ordinate to copper atoms in, respectively, the equatorial and apical positions of their square-pyramidal configurations. The anionic unit is a binuclear monomer where the linkage between $[Fe(CN)_6]^{3-}$ and $[Cu(dien)]^{2+}$ ions is provided by only one of the six CN^- groups around iron. It is interesting to note that in this unit the cyanide is bonded in the equatorial plane of the copper square-based pyramidal configuration but the angle Cu–N–C (158°) is half-way between the average values found in the cationic unit for linear (173°) and non-linear (140°) Cu–N–C chains.

As well as forming hydrogen bonds between themselves, the water molecules interact with some of the nitrogens of the anionic unit. One of them, however, is also tightly bonded to the copper atom in the anionic monomer to form a chromophore CuN_4O. It should be noted that one water molecule, Ow(1), is pointing almost perpendicularly toward the basal plane of the pyramid around Cu(2) of the cationic unit and makes a very weak interaction with it, the distance Cu(2)–Ow(1) being 3.16 Å [see Figure 1(*a*) and 1(*b*)]. If this is regarded as a true (but weak) interaction, this water molecule, which is also hydrogen bonded to a nitrogen of the anionic unit [see Table 2 and Figure 1(*a*)], thus links the two ionic structural units present in the cell, and the chromophore for Cu(2) may (tentatively) be considered as CuN_5O with a highly tetragonally distorted octahedral configuration.

A second cyanide group, belonging to the hexacyanoferrate of the anionic monomer [C(4,3)≡N(4,3) in Figure 1(*a*) and 1(*c*)], occupies a similar position in relation to the nearest copper atom, Cu(5), and appears to make a weak interaction with it; the distance Cu(5)–N(4,3) is 2.83 Å and the angle Cu(5)–N(4,3)–C(4,3) 137°. If this is a real (but weak) bond, Cu(5) may (tentatively) be considered as six co-ordinated with a chromophore CuN_5O, the cyanide involved acting as a bridge between the two monomers related by the centre of symmetry, so producing a weakly bound dimer.

A comparison between the present cationic polynuclear complex $\{2[Cu(dien)]\cdot[Fe(CN)_6]\}^+$ and that previously studied by us, $[\{Cu(dien)\}_2\cdot Fe(CN)_6]\cdot 6H_2O$,[9] which have the same formula but different oxidation state for iron, leads to the following conclusions. (*i*) In both complexes, linear and non-linear Fe–C≡N–Cu sequences are present; however, *cis* cyanides occur in the present cationic unit in both linear and non-linear orientation to copper atoms, whereas it is the *trans* cyanides which occur in linear and bent linkages in the previous compound. This leads to one- and two-dimensional polymers, respectively. (*ii*) Despite the above structural differences, the average Cu–N–C angles, both linear and bent, are comparable (174 and 136°, 173 and 140°, respectively, for the ferrocyanide and the ferricyanide complexes), and so, too, are the average linear Cu–N distances, 1.97 and 1.98 Å. The only difference is found in the non-linear Cu–N distance which is 2.21 Å in the previously studied ferrocyanide compound and 2.32 Å in the present structure.

Finally, it may be noted that all other distances and angles within the $[Fe(CN)_6]^{3-}$ and $[Cu(dien)]^{2+}$ units are comparable to those reported in the literature for similar compounds,[8,19,23] and also found by us in the previous investigation.[9]

The chromophores of copper found in solid $3[Cu(dien)]^{2+}\cdot 2[Fe(CN)_6]^{3-}\cdot 6H_2O$, namely square-pyramidal CuN_5 and CuN_4O, and the two different ways by which $[Fe(CN)_6]^{3-}$ is bound to copper in the diene plane (linear or bent Cu–N–C chains), prevent any detailed discussion of the optical spectrum. The general features of tetragonally distorted five-co-ordinate $[Cu(dien)]^{2+}$ complexes, *i.e.* the large asymmetric band with maximum around 16 000 cm^{-1} and a ' tail ' on its low-energy side, are preserved when ferricyanide is co-ordinated. The reflectance spectrum of copper then resembles that observed for $[\{Cu(dien)\}_2 \cdot Fe(CN)_6] \cdot 6H_2O$,[9] apart from the small shift to higher energy of all the *d–d* transitions of Cu^{2+}. In copper ferricyanide,[14] however, the bonding of $[Fe(CN)_6]^{3-}$ to copper does not produce the large changes in the copper spectrum that are observed in ferricyanide-treated galactose oxidase. This difference suggests that, unless variations of copper stereochemistry are admitted, one may question the hypothesis that the spectral change in the ferricyanide-treated galactose oxidase is due to complex formation. Analogous conclusions are reached from e.s.r. measurements. The signal observed for $3[Cu(dien)]^{2+} \cdot 2[Fe(CN)_6]^{3-} \cdot 6H_2O$, similar to that obtained for $[\{Cu(dien)\}_2 \cdot Fe(CN)_6] \cdot 6H_2O$,[15] and typical of distorted square-pyramidal complexes, indicates that no antiferromagnetic coupling occurs when the mode of ligation of the ferricyanide anion to copper is either linear equatorial or bent apical $Fe{-}C{\equiv}N{-}Cu$. The possibility of antiferromagnetic coupling through bent equatorial bonds is at present under investigation.

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