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Studies of dicopper complexes: X-ray crystal structure of tetraaquabis(perchlorato)(*N*,*N*,*N'*,*N'*-tetrakis(benzimidazol-2-ylmethyl)-1,3-propanediamine) dicopper(II) bis(perchlorate) tetrahydrate

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Abstract

$Cu_2(PDTB)(ClO_4)_2$ (**a**), $Cu_2(PDTB)(ClO_4)_4\cdot 8H_2O$ (**b**) and $Cu_2(PDTB)(ClO_4)_3N_3$ (**c**), where PDTB = *N*,*N*,*N'*,*N'*-tetrakis(2-benzimidazolylmethyl)-1,3-propanediamine, have been synthesized. The structure of **b** has been established by X-ray diffraction to be $[Cu_2(PDTB)(ClO_4)_2(OH_2)_4](ClO_4)_2(H_2O)_4$. Its crystal data are: $M_r = 1263.7$, monoclinic, *C*2/*c*, $a = 17.581(12)$, $b = 11.604(10)$, $c = 25.90(2)$ Å, $\beta = 107.22(5)°$, $V = 5047(7)$ Å^3, $Z = 4$, $D_x = 1.663$ g cm^{-3}, $\lambda = 0.71073$ Å, $\mu = 1.147$ mm^{-1}, $F(000) = 2592$, $T = 297$ K, $R = 0.0631$, $R_w = 0.0716$ for 2262 unique reflections with $I > 3.0\sigma(I)$. In the structure there is a definite, but weak, bond between each Cu and a ClO_4^-. Resonance Raman spectra of **c** show that the values of $\nu(N_3)_{asym}$ and $\nu(Cu–N_3)_{asym}$ are in close agreement with corresponding values reported for met Hc-N_3. The values of $\nu(N_3)_{asym}$ have also been determined by FT-IR and agree with the resonance Raman data. From spectrophotometric titration of $Cu_2(PDTB)(ClO_4)_4$ with azide, the formation constant of the $Cu_2(PDTB)(ClO_4)_3N_3$ complex has been calculated to be 3.5×10^3 M^{-1}.

Introduction

The following dicopper compounds $Cu_2(PDTB)(ClO_4)_2$ (**a**), $Cu_2(PDTB)(ClO_4)_4\cdot 8H_2O$ (**b**) and $Cu_2(PDTB)(ClO_4)_3(N_3)$ (**c**), where PDTB = *N*,*N*,*N'*,*N'*-tetrakis-(2-benzimidazolylmethyl)-1,3-propanediamine and N_3 = azide, have been prepared, with **b** and **c** as possible active-site models for oxidized hemocyanin (Hc). Previously, dicopper compounds of EDTB (*N*,*N*,*N'*,*N'*-tetrakis(2-benzimidazolylmethyl)-1,2-ethanediamine) have been studied as potential models for hemocyanin [1, 2]. The purpose of the research was to investigate the dicopper compounds of PDTB as a comparison, and to determine the crystal structure of a dicopper(II) complex. Some other papers which discuss related ligands and their Cu complexes are: Takahashi *et al.* [3], McKee *et al.* [4], van Rijn *et al.* [5]. The present paper describes the crystal structure of tetraaquabis(perchlorato)(*N*,*N*,*N'*,*N'*-tetrakis(benzimidazol-2-ylmethyl)-1,3-propanediamine) dicopper(II) bis(perchlorate) tetrahydrate, the resonance Raman spectra and the formation constant of an azide complex.

Experimental

Synthesis

Propylenediamine tetraacetic acid, PDTA, was prepared by a modification of the method described by Dwyer and Garvan [6]. In the preparation of $PDTB\cdot 4H_2O$, 0.1 mol of 1,2-diaminobenzene was ground to a fine powder and intimately mixed with 0.025 mol of PDTA. The mixture was heated at 180 °C for 4 h at which stage effervescence had ceased. The mixture was dissolved in hot ethanol followed by precipitation of the crude product and recrystallyzation from hot absolute alcohol. *Anal.* Calc. for $C_{35}H_{42}N_{10}O_4$: C, 63.06; H, 6.31; N, 21.02; O, 9.61. Found: C, 62.97; H, 6.31; N, 20.86; O, 9.85%.

$Cu_2(PDTB)(ClO_4)_2$ was prepared by mixing 20 ml of hot ethanol solution containing 2 mmol of PDTB and 2 ml of hot acetonitrile solution containing 4 mmol $Cu(CH_3CN)_4(ClO_4)$ under N_2. After drying *in vacuo* at 50 °C, white powders were obtained. $Cu_2(PDTB)(ClO_4)_4\cdot 8H_2O$ was prepared by mixing ethanolic solutions of $Cu(ClO_4)_2\cdot 6H_2O$ and PDTB (2:1) and the precipitate collected. The mixture was

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TABLE 1. Summary of crystal data and intensity collection

Empirical formula	$C_{35}H_{50}N_{10}O_{24}Cl_4Cu_2$
Color, habit	bluish green, chunk
Crystal size (mm)	0.35 × 0.36 × 0.50
Space group	monoclinic; *C*2/*c*
Unit cell dimensions	
a (Å)	17.581(12)
b (Å)	11.604(10)
c (Å)	25.90(2)
β (°)	107.22(5)
Volume (Å^3)	5047(7)
Z	4
Formula weight	1263.7
Density (calc.) (Mg/m^3)	1.663
Absorption coefficient (mm^{-1})	1.147
F(000)	2592
Diffractometer used	Nicolet R3m/V
Radiation	Mo Kα (λ = 0.71073 Å)
Temperature (K)	297
Monochromator	highly oriented graphite crystal
2θ Range (°)	2.5 to 50.0
Scan type	$\theta/2\theta$
Scan speed	variable; 2.93 to 14.65°/min in ω
Scan range (ω)	0.96° plus Kα-separation
Background measurement	stationary crystal and stationary counter at beginning and end of scan, each for 50.0% of total scan time
Standard reflections	3 measured every 50 reflections
Index ranges	$-20 \leqslant h \leqslant 0$, $0 \leqslant k \leqslant 11$, $-29 \leqslant l \leqslant 30$
Reflections collected	9189 ($2352 > 3.0\sigma(I)$)
Independent reflections	4185 ($2262 > 3.0\sigma(I)$)
Hydrogen atoms	riding model, fixed isotropic *U*
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0132F^2$
Final *R* indices (obs. data) (%)	$R = 6.31$, $R_w = 7.16$
Goodness-of-fit	0.80
Largest and mean Δ/σ	0.030, −0.001
Data-to-parameter ratio	6.3:1
Largest difference peak (e Å^{-3})	0.68
Largest difference hole (e Å^{-3})	−0.47

dissolved in hot ethanol followed by precipitation of the crude product and recrystallization. $Cu_2(PDTB)(ClO_4)_3(N_3)$ was prepared by adding 1 mmol NaN_3 to a solution containing 1 mmol $Cu_2(PDTB)(ClO_4)_4 \cdot 8H_2O$ in 60 ml of 95% ethanol and 5 ml water. *Anal.* Calc. for $Cu_2(PDTB)(ClO_4)_2$: C, 45.6; H, 3.7; N, 15.2; Cl, 7.7; O, 13.9; Cu, 13.8. Found: C, 45.2; H, 3.8; N, 15.1; Cl, 7.9; O, 14.3; Cu, 14.3%. Calc. for $Cu_2(PDTB)(ClO_4)_4 \cdot 8H_2O$: C, 33.3; H, 4.0; N, 11.1; Cl, 11.2; Cu, 10.1. Found: C, 33.6; H, 4.0; N, 11.2; Cl, 11.1; Cu, 10.5%. Calc. for $Cu_2(PDTB)(ClO_4)_3(N_3)$: C, 39.6; H, 3.0; N, 17.2; Cu, 11.99). Found: C, 38.9; H, 3.6; N, 17.3; Cu, 11.26%.

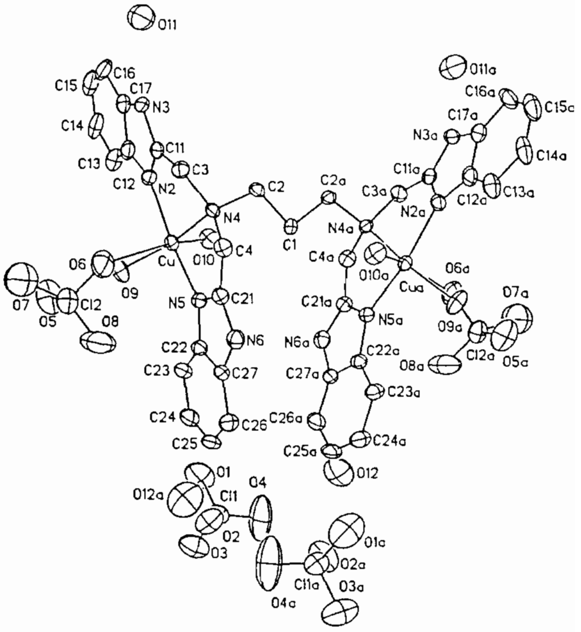

Fig. 1. ORTEP drawing and the atomic number scheme for $[Cu_2(PDTB)(ClO_4)_2(OH_2)_4](ClO_4)_2(H_2O)_4$.

Caution: although we have had no difficulties with the perchlorate salts, these are potentially explosive, and one should be careful by making only small quantities.

X-ray diffraction study of $Cu_2(PDTB)(ClO_4) \cdot 8H_2O$

A crystal and molecular structure determination of the title compound was carried out by the X-ray diffraction method. Crystal data and details of the intensity collection are summarized in Table 1. Lattice constants were determined from a least-squares fit to the automatically centered settings for 17 reflections with $11.60 \leqslant 2\theta \leqslant 29.45°$. A Micro VAXII computer-controlled Nicolet R3m/V diffractometer equipped with a graphite monochromator (Mo Kα radiation) was used for intensity data collection. The intensities were corrected for Lorentz and polarization effects. No absorption correction was applied ($T_{max}/T_{min} = 0.838/0.820$).

The space group *C*2/*c* was unambiguously determined from the systematic absences: *hkl*, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$. The structure was solved by a direct method using SHELXTL PLUS [7]. Full matrix least-squares refinement based on *F* with anomalous-dispersion terms for atoms with atomic number greater than 16 was used. Neutral-atom scattering form factors were taken from the International Tables for X-ray Crystallography [8]. The positions of all non-hydrogen atoms were located from *E*-maps. All of the hydrogen atoms which were included in the refinement were placed in idealized

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$)

	x	y	z	U_{eq}[a]
Cu	3724(1)	343(1)	6254(1)	45(1)
Cl(1)	2811(2)	7374(3)	7423(2)	88(1)
Cl(2)	3948(2)	1929(3)	4979(1)	89(1)
O(1)	2267(7)	6467(12)	7249(6)	193(8)
O(2)	3384(6)	7393(10)	7157(4)	131(5)
O(3)	2291(7)	8350(11)	7239(6)	167(8)
O(4)	3096(8)	7407(19)	7955(5)	254(13)
O(5)	3127(5)	1915(31)	4905(12)	144(14)
O(5A)	3559(20)	2721(19)	5220(11)	118(15)
O(6)	4292(7)	988(8)	5301(3)	148(5)
O(7)	3784(22)	1508(26)	4451(5)	200(16)
O(7A)	3312(18)	1600(27)	4535(11)	151(12)
O(8)	4236(22)	2845(16)	5333(9)	183(21)
O(8A)	4488(9)	2513(17)	4770(9)	115(11)
O(9)	2750(4)	1154(8)	5815(3)	91(3)
O(10)	3116(5)	174(6)	6897(3)	80(3)
O(11)	4574(9)	−4776(8)	5471(4)	155(7)
O(12)	3668(7)	6068(13)	8907(5)	178(8)
C(3)	4783(6)	−1387(8)	6063(4)	61(4)
N(2)	3385(4)	−1194(6)	5971(3)	51(3)
N(3)	3696(7)	−2909(7)	5736(3)	74(4)
C(4)	5473(5)	353(8)	6519(4)	57(3)
N(5)	4391(4)	1690(6)	6523(3)	53(3)
N(6)	5582(5)	2486(7)	6749(3)	62(3)
C(1)	5000	−297(11)	7500	48(4)
C(2)	4958(5)	−1096(7)	7022(3)	44(3)
N(4)	4832(4)	−498(5)	6498(2)	42(2)
C(11)	3949(6)	−1853(8)	5925(3)	56(4)
C(12)	2685(7)	−1862(10)	5806(3)	71(4)
C(13)	1911(6)	−1630(11)	5788(4)	76(4)
C(14)	1358(8)	−2505(14)	5609(4)	94(6)
C(15)	1546(10)	−3549(15)	5472(5)	109(7)
C(16)	2342(9)	−3801(11)	5482(4)	93(6)
C(17)	2884(8)	−2965(10)	5660(4)	70(5)
C(21)	5161(5)	1513(8)	6610(3)	50(3)
C(22)	4287(5)	2870(8)	6607(3)	52(3)
C(23)	3639(7)	3529(8)	6569(4)	72(5)
C(24)	3732(11)	4679(11)	6680(5)	101(7)
C(25)	4518(12)	5139(10)	6811(5)	105(8)
C(26)	5178(9)	4539(10)	6856(4)	83(5)
C(27)	5056(7)	3372(8)	6744(3)	66(4)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 3. Bond lengths (Å)

Cu–O(9)	1.990(7)	Cu–O(10)	2.236(9)
Cu–N(2)	1.953(7)	Cu–N(5)	1.955(7)
Cu–N(4)	2.102(7)	Cu–O(6)	3. 019
Cl(1)–O(1)	1.403(13)	Cl(1)–O(2)	1.378(13)
Cl(1)–O(3)	1.445(13)	Cl(1)–O(4)	1.321(13)
Cl(2)–O(5)	1.398(10)	Cl(2)–O(5A)	1.398(31)
Cl(2)–O(6)	1.398(9)	Cl(2)–O(7)	1.398(17)
Cl(2)–O(7A)	1.398(26)	Cl(2)–O(8)	1.398(20)
Cl(2)–O(8A)	1.398(21)	O(5)–O(5A)	1.322(38)
O(5)–O(7A)	1.157(44)	O(5A)–O(8)	1.147(50)
O(7)–O(7A)	0.924(51)	O(7)–O(8A)	1.723(35)
O(8)–O(8A)	1.689(38)	C(3)–N(4)	1.511(11)
C(3)–C(11)	1.503(14)	N(2)–C(11)	1.285(13)
N(2)–C(12)	1.410(13)	N(3)–C(11)	1.346(12)
N(3)–C(17)	1.384(17)	C(4)–N(4)	1.488(11)
C(4)–C(21)	1.498(13)	N(5)–C(21)	1.322(11)
N(5)–C(22)	1.406(12)	N(6)–C(21)	1.339(12)
N(6)–C(27)	1.380(14)	C(1)–C(2)	1.531(11)
C(1)–C(2A)	1.531(11)	C(2)–N(4)	1.482(10)
C(12)–C(13)	1.374(16)	C(12)–C(17)	1.408(16)
C(13)–C(14)	1.387(19)	C(14)–C(15)	1.332(24)
C(15)–C(16)	1.422(25)	C(16)–C(17)	1.343(18)
C(22)–C(23)	1.353(15)	C(22)–C(27)	1.418(15)
C(23)–C(24)	1.365(16)	C(24)–C(25)	1.426(27)
C(25)–C(26)	1.328(25)	C(26)–C(27)	1.388(15)

positions (C–H = 0.96 Å, <H–C–H = 109.4°) and refined with a fixed U value of 0.08 $Å^2$. A final difference map showed no other features. The agreement factors were $R = 0.0631$ and $R_w = 0.076$. All calculations were performed on a Micro VAX II based Nicolet SHELXTL PLUS software system.

Spectroscopic measurements

Resonance Raman spectra were obtained on a Spex 1403 double spectrometer. The synthetic compounds were examined in the solid state (KBr pellet) and spun at room temperature, in order to minimize the problem of achieving a homogeneous mixture. Infrared spectra of the synthetic compounds (KBr pellet) were taken on a FT-IR spectrometer. UV–Vis absorption spectra were obtained on a Shimadzu UV-2100 UV–Vis recording spectrophotometer.

Results and discussion

Figure 1 shows a perspective view of the molecule and the atom labelling for $Cu_2(PDTB)(ClO_4)_4 \cdot 8H_2O$. Table 2 gives atomic coordinates and equivalent isotropic displacement coefficients. Bond lengths and bond angles are given in Tables 3 and 4, respectively Figure 1 shows that each of the two coppers is bonded to O6 of a ClO_4^- ion and to oxygen atoms (O9, O10) of two water molecules. Although the bond length Cu–O6 (in ClO_4^-), 3.019 Å, is rather long, distinct bonding interactions are present, rather than electrostatic interactions or crystallographic packing effects. The modest size of the atomic displacement parameters of O6 compared to the other ClO_4^- oxygen atoms (O5, O7, O8) and the nicely octahedral placement also point to a definite but weak interaction. There are examples of bridging perchlorate ions involving one or two oxygen atoms in the literature [9, 10]. In fact, a Cu–O(ClO_3) distance of 3.22 Å has been reported by McKee and Tandon [11]. Since the mean displacement of atoms from plane is 0.135 Å, the units Benz–Cu–(N)–Benz in

TABLE 4. Bond angles (°)

O(9)–Cu–O(10)	87.0(3)	O(9)–Cu–N(2)	95.9(3)
O(10)–Cu–N(2)	92.3(3)	O(9)–Cu–N(5)	98.6(3)
O(10)–Cu–N(5)	100.0(3)	N(2)–Cu–N(5)	161.5(3)
O(9)–Cu–N(4)	162.8(3)	O(10)–Cu–N(4)	109.9(3)
N(2)–Cu–N(4)	80.9(3)	N(5)–Cu–N(4)	81.9(3)
O(9)–Cu–O(6)	81.5	O(10)–Cu–O(6)	167.7
N(2)–Cu–O(6)	93.3	N(5)–Cu–O(6)	77.5
N(4)–Cu–O(6)	81.9	O(1)–Cl(1)–O(2)	112.5(8)
O(1)–Cl(1)–O(3)	100.2(7)	O(2)–Cl(1)–O(3)	107.9(8)
O(1)–Cl(1)–O(4)	111.6(11)	O(2)–Cl(1)–O(4)	114.4(8)
O(3)–Cl(1)–O(4)	109.2(11)	O(5)–Cl(2)–O(6)	108.7(15)
O(5)–Cl(2)–O(7)	87.5(20)	O(6)–Cl(2)–O(7)	103.8(13)
O(5)–Cl(2)–O(8)	104.9(21)	O(6)–Cl(2)–O(8)	101.1(10)
O(7)–Cl(2)–O(8)	146.8(17)	N(4)–C(3)–C(11)	105.0(8)
Cu–N(2)–C(11)	114.9(6)	Cu–N(2)–C(12)	139.3(7)
C(11)–N(2)–C(12)	105.8(8)	C(11)–N(3)–C(17)	108.1(9)
N(4)–C(4)–C(21)	107.0(7)	Cu–N(5)–C(21)	114.4(6)
Cu–N(5)–C(22)	137.9(6)	C(21)–N(5)–C(22)	107.3(7)
C(21)–N(6)–C(27)	108.1(8)	C(2)–C(1)–C(2A)	105.5(9)
C(1)–C(2)–N(4)	114.5(7)	Cu–N(4)–C(3)	104.5(4)
Cu–N(4)–C(4)	109.2(5)	C(3)–N(4)–C(4)	110.9(7)
Cu–N(4)–C(2)	111.5(5)	C(3)–N(4)–C(2)	108.8(6)
C(4)–N(4)–C(2)	111.8(6)	C(3)–C(11)–N(2)	119.3(8)
C(3)–C(11)–N(3)	127.4(10)	N(2)–C(11)–N(3)	113.3(9)
N(2)–C(12)–C(13)	132.0(11)	N(2)–C(12)–C(17)	108.5(10)
C(13)–C(12)–C(17)	119.5(11)	C(12)–C(13)–C(14)	117.1(12)
C(13)–C(14)–C(15)	123.4(14)	C(14)–C(15)–C(16)	120.2(15)
C(15)–C(16)–C(17)	116.9(13)	N(3)–C(17)–C(12)	104.3(9)
N(3)–C(17)–C(16)	132.9(12)	C(12)–C(17)–C(16)	122.8(13)
C(4)–C(21)–N(5)	121.2(8)	C(4)–C(21)–N(6)	126.9(8)
N(5)–C(21)–N(6)	111.8(8)	N(5)–C(22)–C(23)	133.2(9)
N(5)–C(22)–C(27)	106.4(8)	C(23)–C(22)–C(27)	120.4(9)
C(22)–C(23)–C(24)	119.5(12)	C(23)–C(24)–C(25)	117.7(14)
C(24)–C(25)–C(26)	125.7(11)	C(25)–C(26)–C(27)	114.7(13)
N(6)–C(27)–C(22)	106.4(8)	N(6)–C(27)–C(26)	131.6(11)
C(22)–C(27)–C(26)	122.0(11)		

the structure are quite co-planar, and the Cu atom is only 0.073 Å above the least-squares plane defined by O9, N2, N4 and N5. Since four water molecules (O11, O11a, O12, O12a) and two ClO_4^- are in the lattice, the structure of $Cu_2(PDTB)(ClO_4)_4 \cdot 8H_2O$ may be written as $[Cu_2(PDTB)(ClO_4)_2(OH_2)_4](ClO_4)_2(H_2O)_4$. A stereoscopic view of the unit cell is shown in Fig. 2.

In comparison to the corresponding $Cu_2(EDTB)(ClO_4)_4 \cdot 4H_2O$ compound, Birker *et al.* [1b] report that one or two water molecules are probably bonded to each copper atom, since "apparently the ClO_4^- ions are not coordinating". It is unfortunate that only electronic absorption and EPR spectra of this compound were obtained and not the X-ray crystal structure. These authors however do report the crystal structure of mononuclear $Cu(EDTB)(BF_4)(BF_3OC_2H_5) \cdot H_2O$, in which the copper ion is bonded to four imidazole nitrogen atoms and two amine atoms. Their X-ray data suggest a distorted tetrahedron as another way to describe the geometry of the copper bonded to the four imidazole nitrogen atoms, in which case the amine nitrogen atoms are considered to be non-coordinating [1b].

Figure 3 gives FT-IR spectra of $Cu_2(PDTB)(ClO_4)_4$ and $Cu_2(PDTB)(ClO_4)_3(N_3)$. The peaks at 2050 and 2104 cm^{-1} in Fig. 3(b) are ascribed to $\nu(N_3)_{asym}$. In comparison, the FT-IR spectrum of $Cu_2(EDTB)(ClO_4)_3(N_3)$ [12] shows $\nu(N_3)_{asym}$ to be at 2040 cm^{-1}.

Resonance Raman spectra of $Cu_2(PDTB)(ClO_4)_3(N_3)$ with wavelengths 4880 (top) and 4579 (bottom) Å are shown in Fig. 4. Table 5 gives the resonance Raman frequencies in several dicopper compounds and met azido Hc (*Busycon*). Samples of $Cu_2(EGTB)(ClO_4)_3(N_3)$ and $Cu_2(MEGTB)(ClO_4)_3(N_3)$ were given by Lou [12]. From Figs. 3 and 4 and Table 5, we conclude that the IR and Raman frequencies for the azide moiety in $Cu_2(PDTB)(ClO_4)_3(N_3)$ are in fairly good agreement with those for met azido hemocyanin. The azide peaks in the protein and in $[Cu_2(L\text{-}Et)(N_3)]^{2+}$ are single [13], whereas two peaks are found for the first three dicopper compounds in Table 5. The reason for the difference is not clear at present. We are trying to grow X-ray quality crystals for $Cu_2(PDTB)$-

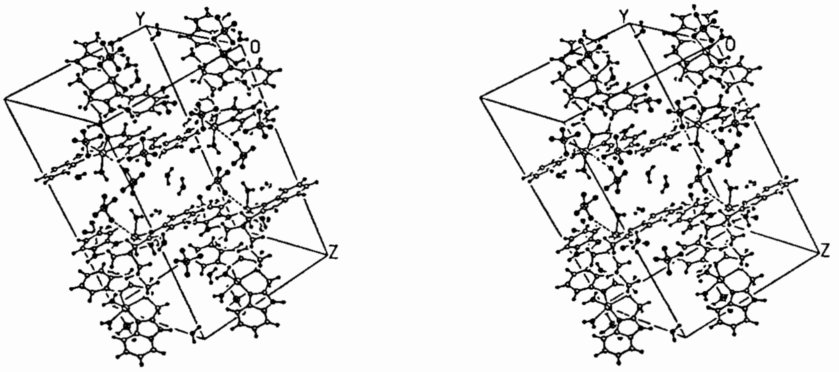

Fig. 2. A stereoscopic view of the unit cell of the title compound.

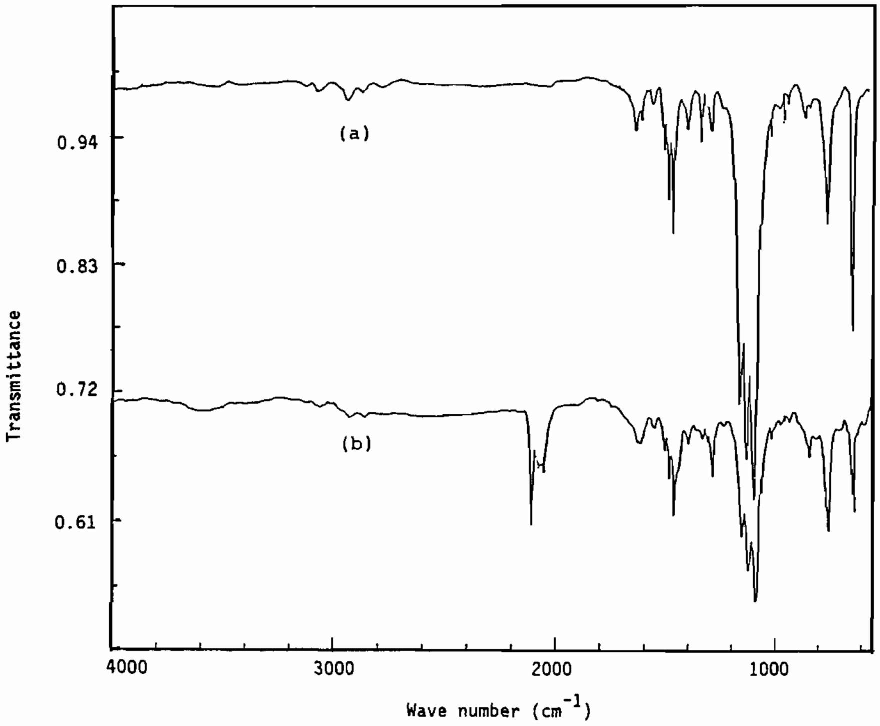

Fig. 3. FT-IR spectra of $Cu_2(PDTB)(ClO_4)_4$ (a) and $Cu_2(PDTB)(ClO_4)_3N_3$ (b).

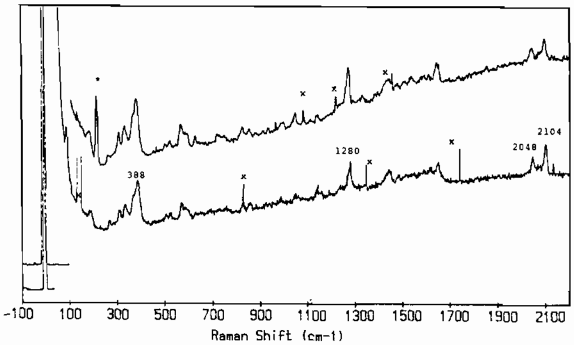

Fig. 4. Resonance Raman spectra of $Cu_2(PDTB)(ClO_4)_3N_3$. Spectral conditions: wavelength, 4880 (top) and 4579 (bottom) Å; power at sample, 150 mW; slit width, 8 cm^{-1}. The peak marked with * is due to a plasma line of the laser, × denotes noise. Samples were spun as solid (KBr pellet) at room temperature.

$(ClO_4)_3(N_3)$ and solve the crystal structure, in order to determine whether or not the three azide nitrogens bridge over the two coppers in a μ-1,3 bridging mode, as has been found for $[Cu_2(L\text{-}Et)(N_3)][BF_4]_2$ [14].

Addition of sodium azide to $Cu_2(PDTB)(ClO_4)_4$ gives rise to UV absorption peaks at 382 and 362 nm, and the absorbance at 382 nm increases with increase in azide concentration, as shown in Fig. 5. In comparison, addition of sodium azide to $Cu_2(EDTB)(ClO_4)_4$ also gives rise to an absorption peak at 380 nm (only a single peak). Since our crystal structure study shows the compound $Cu_2(PDTB)(ClO_4)_4\cdot 8H_2O$ to be $[Cu_2(PDTB)(ClO_4)_2(OH_2)_4](ClO_4)_2(H_2O)_4$, the reaction with azide may be written as

$$[Cu_2(PDTB)(ClO_4)_2](ClO_4)_2 + N_3^- \longrightarrow$$
$$[Cu_2(PDTB)(ClO_4)_2N_3](ClO_4) + ClO_4^-$$

and an apparent equilibrium constant may be written

$$K' = \frac{[Cu_2(PDTB)(ClO_4)_3N_3]}{[Cu_2(PDTB)(ClO_4)_3][N_3^-]}$$

The value of K' was calculated from the UV data in the following manner. The observed absorbance at 382 nm, A, is a weighted average of the absorbances of $Cu_2(PDTB)(ClO_4)_3N_3$, A_c, and of $Cu_2(PDTB)(ClO_4)_4$ (before adding azide), A_f. In the region where $[N_3^-] > [Cu_2(PDTB)(ClO_4)_3N_3]$, the following equation is written

$$\frac{1}{A-A_f} = \frac{1}{K'}\frac{1}{(A_c-A_f)}\frac{1}{[N_3^-]} + \frac{1}{(A_c-A_f)}$$

From the data of Fig. 5, a linear plot of $1/(A-A_f)$ versus $1/[N_3^-]$ is obtained, with $K' = 3.5 \times 10^3\ M^{-1}$.

TABLE 5. Resonance Raman frequencies in model compounds and met azido hemocyanin[a]

	$\nu(N_3)_{asym}$	$\nu(N_3)_{sym}$	$(Cu-N_3)_{asym}$	Reference
$Cu_2(PDTB)(N_3)(ClO_4)_3$	2048, 2104	1280	388	this work
$Cu_2(EGTB)(N_3)(ClO_4)_3$	2052, 2089sh	1278	376	this work
$Cu_2(MEGTB)(N_3)(ClO_4)_3$	2050, 2094	1290(w)	394	this work
$Cu_2(L\text{-}Et)(N_3)(BF_4)_2$	2025	1304	358	13
Met azido Hemocyanin	2042		397	13

[a] EGTB = 1,1,10,10-tetrakis-(2-benzimidazolylmethyl)-1,10,diaza-4,7-dioxadecane; MEGTB = 1,1,10,10-tetrakis-(1-methylbenzimidazol-2-ylmethyl)-1,10-diaza-4,7-dioxadecane; L-Et is the anion of *N,N,N′,N′*-tetrakis[2-(1-ethyl)-benzimidazolylmethyl]2-hydroxy-1,3-propanediamine.

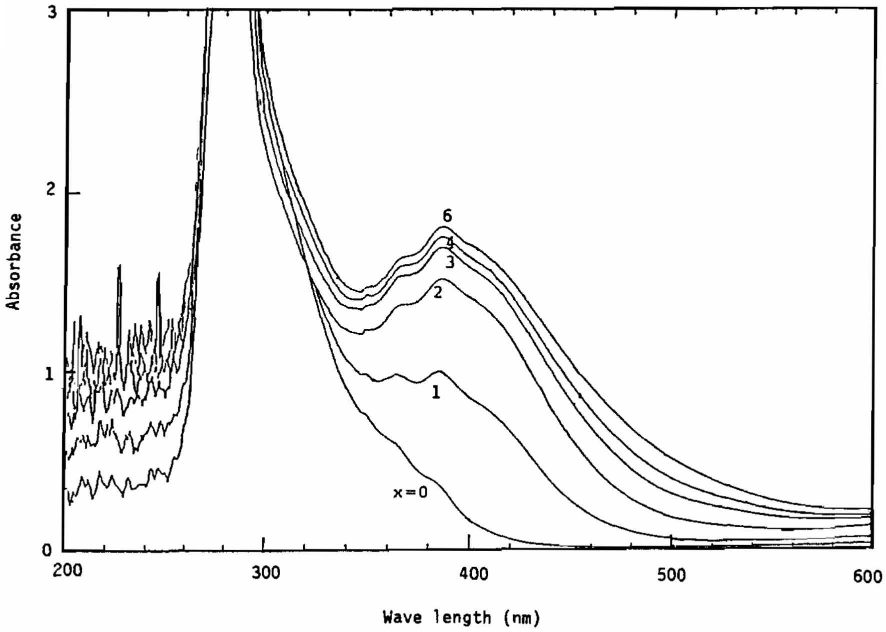

Fig. 5. Absorption spectra of 0.0005 M $Cu_2(PDTB)(ClO_4)_4$ in $Me_2SO+xN_3^-$; x (ratio of N_3^-: Cu_2) = 0, 1, 2, 3, 4 and 6.

Supplementary material

Table 6 giving H-atom coordinates and isotropic displacement coefficients, and Table 7 listing anisotropic coefficients are available from the authors on request.

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