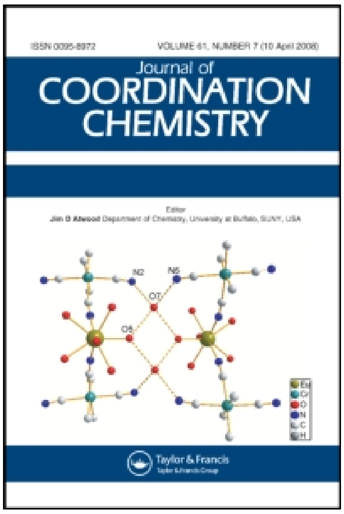

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

MAGNETO-STRUCTURAL CORRELATION IN (μ-ALKOXO/HYDROXOXμ-CARBOXYLATO)-DICOPPER(II) SYSTEMS: SYNTHESIS, X-RAY STRUCTURE AND MAGNETIC PROPERTIES OF AQUO(μ-HYDROXO) (μ-ARYLCARBOXYLATO)BIS(N,N,N',N'-TETRAMETHYLETHANE-l,2-DIAMINE)DICOPPER(II)DIPERCHLORATE

Kannappan Geetha[a]; Munirathinam Nethaji[a]; Nagasampagi Y. Vasanthacharya[a]; Akhil R. Chakravarty[a]
[a] Department of Inorganic and Physical Chemistry, bSolid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore, India

To cite this Article Geetha, Kannappan , Nethaji, Munirathinam , Vasanthacharya, Nagasampagi Y. and Chakravarty, Akhil R.(1999) 'MAGNETO-STRUCTURAL CORRELATION IN (μ-ALKOXO/HYDROXOXμ-CARBOXYLATO)-DICOPPER(II) SYSTEMS: SYNTHESIS, X-RAY STRUCTURE AND MAGNETIC PROPERTIES OF AQUO(μ-HYDROXO) (μ-ARYLCARBOXYLATO)BIS(N,N,N',N'-TETRAMETHYLETHANE-l,2-DIAMINE)DICOPPER(II)DIPERCHLORATE', Journal of Coordination Chemistry, 47: 1, 77 — 89

To link to this Article: DOI: 10.1080/00958979908024543

URL: http://dx.doi.org/10.1080/00958979908024543

J. Coord. Chem., 1999, Vol. 47, pp. 77–89
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Gordon and Breach Science
Publishers imprint.
Printed in Malaysia.

MAGNETO-STRUCTURAL CORRELATION IN (μ-ALKOXO/HYDROXO)(μ-CARBOXYLATO)-DICOPPER(II) SYSTEMS: SYNTHESIS, X-RAY STRUCTURE AND MAGNETIC PROPERTIES OF AQUO(μ-HYDROXO) (μ-ARYLCARBOXYLATO)BIS(N,N,N',N'-TETRAMETHYLETHANE-1,2-DIAMINE)DICOPPER(II) DIPERCHLORATE

KANNAPPAN GEETHA[a], MUNIRATHINAM NETHAJI[a],
NAGASAMPAGI Y. VASANTHACHARYA[b]
and AKHIL R. CHAKRAVARTY[a,*]

[a]*Department of Inorganic and Physical Chemistry,* [b]*Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012, India*

(Received 6 January 1998)

Asymmetrically dibridged dicopper(II) complexes, $[Cu_2(OH)(O_2CC_6H_4\text{-}p\text{-}Me)(tmen)_2(H_2O)](ClO_4)_2$ (**1**) and $[Cu_2(OH)(O_2CC_6H_4\text{-}p\text{-}OMe)(tmen)_2(H_2O)](ClO_4)_2$ (**2**) (tmen = N,N,N',N'-tetramethylethane-1,2-diamine), were prepared and structurally characterized. Complex **1** crystallizes in the monoclinic space group $P2_1/a$ with $a = 17.718(2)$, $b = 9.869(1)$, $c = 19.677(2)$ Å, $\beta = 115.16(1)°$, $V = 3114.3(6)$ Å^3 and $Z = 4$. The structure was refined to $R(wR^2) = 0.067(0.178)$. Complex **2** crystallizes in the monoclinic space group $P2_1/a$ with $a = 17.695(3)$, $b = 9.574(4)$, $c = 20.104(2)$ Å, $\beta = 114.18(1)°$, $V = 3107(1)$ Å^3 and $Z = 4$. The final residuals are $R(wR^2) = 0.067(0.182)$. The complexes have a $[Cu_2(\mu\text{-}OH)(\mu\text{-}O_2CAr)]^{2+}$ core with tmen ligands occupying the terminal sites of the core. In addition, one copper is axially bound to a water molecule. The Cu $\cdots$ Cu distances and the Cu–OH–Cu angles in the core are 3.394(1) Å, 124.4(2)° for **1** and 3.374(1) Å, 123.3(3)° for **2**. The complexes show axial X-band EPR spectral features in methanol glass at 77 K giving $g_\perp = 2.02$, $g_\| = 2.3$ ($A_\| = 165 \times 10^{-4}\,cm^{-1}$) and a visible band near ~630 nm in methanol. The complexes are weakly antiferromagnetic. A theoretical fit of the magnetic susceptibility data in the temperature range 40–295 K gives $-J = 10\,cm^{-1}$, $g = 2.05$ for **1** and $-J = 10\,cm^{-1}$, $g = 2.0$ for **2**. Plots of $-2J$ *versus* the Cu–OH–Cu angle (ϕ) in this class of asymmetrically dibridged dicopper(II) complexes having $d_{x^2-y^2}-d_{x^2-y^2}$ magnetic orbitals show a linear magneto-structural correlation: $-2J(cm^{-1}) = 11.48\phi(deg) - 1373$.

---

[*] Corresponding author.

Keywords: Dicopper(II) complexes; hydroxo-carboxylato bridges; crystal structures; magnetochemistry

INTRODUCTION

Among binuclear copper(II) complexes, the tetracarboxylato species with a "paddle-wheel" structure show antiferromagnetic (AF) exchange coupling with a singlet ground state.[1] Symmetrically dibridged hydroxo or alkoxo complexes, however, show both singlet and triplet ground states depending upon the magnitude of the monoatomic bridge angle (ϕ) and the type of bridging atom.[2-4] The ϕ-angle dependence of the $2J$ value has been reported by Hatfield and Hodgson for a series of di-μ-hydroxo complexes.[2a,b] A combination of a *syn*, *syn*-bonded carboxylato and a monoatomic hydroxo/alkoxo bridge gives rise to a relatively new class of asymmetrically dibridged dicopper(II) complexes with a $[Cu_2(\mu\text{-OH/OR})(\mu\text{-}O_2CR)]^{2+}$ core.[5-15] The magneto-structural properties of these complexes are of interest as the magnitude of J is usually small, possibly due to the non-complimentary nature of the superexchange pathways.[5-9]

Although several alkoxo-carboxylato dibridged dicopper(II) complexes are reported in the literature, analogous hydroxo-carboxylato dibridged complexes are rare. The known complexes with a $[Cu_2(\mu\text{-OH})(\mu\text{-}O_2CR)]^{2+}$ core show the presence of an additional monoatomic bridge, which, despite being weak, alters significantly important structural parameters like the Cu $\cdots$ Cu distance and the Cu–OH–Cu angle.[12-15] A Cu–OH–Cu angle of < 110° in these "effectively tribridged" dicopper(II) cores makes the complexes ferromagnetic. A dicopper(II) species, $[Cu_2(OH)(O_2CPh)(Me_3\text{-}tacn)_2](ClO_4)_2$, with a $[Cu_2(\mu\text{-OH})(\mu\text{-}O_2CR)]^{2+}$ core and showing an antiferromagnetic interaction between the metal centres has recently been reported by Bürger *et al.* (Me_3tacn = trimethyl-1,4,7-triazacyclononane).[15] Prior to this report, we have shown that the metal centres in $[Cu_2(\mu\text{-OH})(\mu\text{-}O_2CMe)(tmen)_2](ClO_4)_2$ and $[Cu_2(\mu\text{-OH})(\mu\text{-}O_2CMe)(dmen)_2](ClO_4)_2$ are antiferromagnetically coupled (tmen = N,N,N',N'-tetramethylethane-1,2-diamine; and dmen = N,N-dimethylethane-1,2-diamine).[10] To explore the effect of the carboxylate bridge on the magnitude and sign of the exchange parameter J, we have now prepared and structurally characterized two new but related dicopper(II) complexes, $[Cu_2(OH)(O_2CC_6H_4\text{-}p\text{-}X)(tmen)_2\text{-}(H_2O)](ClO_4)_2$ (X = Me, **1**; OMe, **2**). Herein we report the syntheses, X-ray structures and magnetic properties of **1** and **2** along with a magneto-structural correlation observed in this class of asymmetrically dibridged dicopper(II) complexes having a $d_{x^2-y^2}-d_{x^2-y^2}$ ground state.

EXPERIMENTAL

Preparation of $[Cu_2(OH)(O_2CC_6H_4\text{-}p\text{-}X)(tmen)_2(H_2O)](ClO_4)_2$ (X = Me, 1; OMe, 2)

The complexes were prepared by a general procedure in which $[Cu_2(O_2CAr)_4(H_2O)_2]$ (0.5 mmol) was reacted with tmen (1 mmol) in 20 cm^3 of ethanol under magnetic stirring conditions for 10 min at 25°C. The mixture was filtered and the filtrate treated with an aqueous solution (10 cm^3) of $NaClO_4$ (2 mmol). Bluish-violet rhombic-shaped crystalline blocks of the complexes were obtained in ~75% yield on slow evaporation of the solution at ambient temperature; **1**: *Anal.* Calcd. for $C_{20}H_{42}N_4O_{12}Cl_2Cu_2$(%): C, 32.96; H, 5.77; N, 7.69. Found: C, 33.65; H, 5.92; N, 7.90; λ_{max}, nm (ϵ, $M^{-1}cm^{-1}$) in MeOH: 630 (180). EPR data: $g_\perp = 2.02$ and $g_\parallel = 2.3$ ($A_\parallel = 165 \times 10^{-4} cm^{-1}$) in MeOH glass at 77 K. Selected IR data (cm^{-1}) in KBr phase: 2925(w), 1595(s), 1558(s), 1471(m), 1407(s), 1288(w), 1093(vs, br) (ClO_4^-), 952(w), 853(w), 809(m), 769(m), 695(w), 625(w), 550(w), 479(w), 445(w) (vs, very strong; s, strong; m, medium; w, weak; br, broad). For **2**: *Anal.* Calcd. for $C_{20}H_{42}N_4O_{13}Cl_2Cu_2$(%): C, 32.25; H, 5.64; N, 7.53. Found: C, 31.63; H, 5.33; N, 7.29; λ_{max}, nm (ϵ, $M^{-1}cm^{-1}$) in MeOH: 629 (200). EPR data: $g_\perp = 2.02$ and $g_\parallel = 2.3$ ($A_\parallel = 165 \times 10^{-4} cm^{-1}$) in MeOH glass at 77 K. Selected IR data (cm^{-1}) in KBr phase: 2934(w), 2842(w), 1594(s), 1553(s), 1471(m), 1408(s), 1258(s), 1175(m), 1099(vs, br)(ClO_4^-), 952(w), 855(w), 809(w), 783(m), 702(w), 625(s), 544(w), 510(w), 406(w).

Caution! Perchlorate salts of complexes having organic ligands are potentially explosive and should be handled with great care.

Measurements

Elemental analyses were carried out with a Heraeus CHN-O Rapid instrument. Visible and EPR data were obtained using Hitachi U-3400 and Varian E-109 X-band spectrometers, respectively. Variable-temperature magnetic susceptibility data in the 40–295 K range were obtained for polycrystalline samples using a Faraday-type magnetometer equipped with a closed-cycle cryostat (Air Products) and a Cahn balance. $Hg[Co(NCS)_4]$ was used as calibrant. Experimental susceptibility data were corrected for diamagnetic contributions, temperature independent paramagnetism ($N_\alpha = 60 \times 10^{-6} cm^3 mol^{-1}$ per copper) and for possible dimeric ferromagnetic impurities.[16] The molar magnetic susceptibilties were fitted to a Bleaney–Bowers expression[17] by means of a least-squares-fitting computer programme. The molar susceptibility (per copper) expression is given below where ρ is the fraction of possible ferromagnetic dimeric impurity of composition [$Cu_2(OH)(O_2CAr)_2(tmen)_2](ClO_4)$. The values of J_1 and g_1, taken as $45\,cm^{-1}$ and 2.0, respectively, were similar to those reported for [$Cu_2(OH)(O_2CPh)_2(tmen)_2](ClO_4)$.[16] The best fit was obtained with a ρ value of 0.05. The susceptibility expression used for theoretical fitting was $\chi_M = (N\beta^2/3kT)[3g^2(1-\rho)\{3+\exp(-2J/kT)\}^{-1}+3g_1^2\rho\{3+\exp(-2J_1/kT)\}^{-1}]+N\alpha$. For magneto-structural correlation, the $-2J$ value of $55\,cm^{-1}$ reported[10] earlier by us for [$Cu_2(OH)(O_2CMe)(tmen)_2](ClO_4)_2$ was found to be actually $27.8\,cm^{-1}$ on refitting the susceptibility data using the Bleaney–Bowers expression. The infrared spectra of **1** and **2** were recorded on a BIO-RAD FTS-7 spectrometer.

X-ray Crystallography

The crystal structures of **1** and **2** were obtained using general procedures described elsewhere.[18] The intensity data, collected on an Enraf-Nonius CAD4 diffractometer using MoKα radiation, were corrected for Lorentz, polarization and absorption[19] effects. There were 5470 unique data for **1**, giving 3760 reflections with $I > 2\sigma(I)$ and 5441 unique reflections for **2**, giving 3967 with $I > 2\sigma(I)$ used for structure solution and refinement. The structures were solved and refined by the SHELX program[20] using scattering factors taken from Ref. [21]. All non-hydrogen atoms except the disordered ones were refined anisotropically. The hydrogen atoms attached to carbon atoms in the cationic complex were generated and assigned isotropic thermal parameters, riding on their parent carbon atoms.

In both the structures, two carbon atoms of one tmen ligand were found to be positionally disordered. Two peaks for each carbon atom were refined with a site occupancy factor (s.o.f.) of 0.5 each. Several perchlorate oxygen atoms were found to be positionally disordered. Two peaks for each of the disordered oxygen atom were refined with a s.o.f. value of 0.5 each. Selected crystallographic data are given in Table I. Atomic positional parameters of **1** and **2** with estimated standard deviations are given in Tables II and III.

RESULTS AND DISCUSSION

Complexes **1** and **2** are obtained in high yield from a core conversion reaction of copper(II) arylcarboxylates in the presence of a bidentate diamine

TABLE I Crystallographic data for $[Cu_2(OH)(O_2CC_6H_4\text{-}p\text{-}Me)(tmen)_2(H_2O)](ClO_4)_2$ (**1**) and $[Cu_2(OH)(O_2CC_6H_4\text{-}p\text{-}OMe)(tmen)_2\,(H_2O)](ClO_4)_2$ (**2**)

Complex	**1**	**2**
Formula	$C_{20}H_{42}N_4O_{12}Cl_2Cu_2$	$C_{20}H_{42}N_4O_{13}Cl_2Cu_2$
Formula weight	728.54	744.56
Crystal colour	bluish-violet	bluish-violet
Crystal dimensions/mm	0.4 × 0.3 × 0.1	0.4 × 0.4 × 0.1
Crystal system	monoclinic	monoclinic
Space group	$P2_1/a$	$P2_1/a$
a/Å	17.718(2)	17.695(3)
b/Å	9.869(1)	9.574(4)
c/Å	19.677(2)	20.104(2)
β/deg	115.16(1)	114.18(1)
V/Å^3	3114.3(6)	3107(1)
d_{calc}/g cm^{-3}	1.554	1.592
Z	4	4
Temperature/K	294	294
μ (MoKα)/cm^{-1}	15.98	16.01
Transmission coefficient	0.97–1.02	0.97–1.07
Scan method	ω-2θ	ω-2θ
Range of reflections	$-20 \leq h \leq 18$	$-20 \leq h \leq 19$
	$0 \leq k \leq 11$	$0 \leq k \leq 11$
	$0 \leq l \leq 23$	$0 \leq l \leq 23$
2θ range/deg	$2 \leq \theta \leq 50$	$2 \leq \theta \leq 50$
No. of reflections		
Unique	5470	5441
Observed	3760 ($I > 2\sigma(I)$)	3967 ($I > 2\sigma(I)$)
Parameters refined	363	369
Goodness-of-fit	0.994	1.026
$R = \sum \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \lvert F_o\rvert$	0.067	0.067
$wR^2 = [\sum w(F_o^2 - F_c^2)/\sum w(F_o^2)^2]^{1/2}$	0.178	0.182
$w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$	$a = 0.1187$	$a = 0.1178$
where $P = [\max(F_o^2, 0) + 2F_c^2]/3$	$b = 16.79$	$b = 11.87$

ligand, tmen. The 1 : 2 electrolytic complexes display a broad visible d–d band near 630 nm. The complexes show an axial EPR spectrum in methanol glass at 77 K.

ORTEP[22] views of the cationic complexes in **1** and **2** are shown in Figures 1 and 2, respectively. Selected bond distances and angles are given in Table IV. The complexes have a $[Cu_2(\mu\text{-}OH)(\mu\text{-}O_2CAr)]^{2+}$ core and the terminal chelating tmen ligands. While one copper atom with an axially bound aqua ligand shows an elongated square pyramidal O_3N_2 coordination geometry, the other copper centre is essentially square-planar (O_2N_2 coordination). Cu(1)$\cdots$Cu(2) distances and Cu–OH–Cu angles in **1** and **2** are 3.394(1) Å, 124.4(2)° and 3.374(1) Å, 123.3(3)°, respectively. The angles are similar to those observed in related dibridged dicopper(II) complexes but much greater than those reported in "essentially tribridged" species (Table V).

TABLE II Positional coordinates and equivalent isotropic thermal parameters (Å^2) for the non-hydrogen atoms in $[Cu_2(OH)(O_2CC_6H_4\text{-}p\text{-}Me)(tmen)_2(H_2O)](ClO_4)_2$ (**1**)

Atom	x/a	y/b	z/c	U eq[a]
Cu(1)	0.5490(1)	−0.0605(1)	0.3172(1)	0.044(1)
Cu(2)	0.6150(1)	0.1524(1)	0.2181(1)	0.040(1)
O(1)	0.6182(3)	0.0824(5)	0.3109(2)	0.043(1)
O(11)	0.4511(3)	−0.0097(6)	0.2274(3)	0.048(1)
O(21)	0.4961(3)	0.1208(6)	0.1598(3)	0.054(1)
O(2)	0.5742(6)	0.3784(8)	0.2430(5)	0.097(2)
N(11)	0.4755(5)	−0.2028(8)	0.3339(4)	0.061(2)
N(12)	0.6425(5)	−0.1381(8)	0.4144(4)	0.068(2)
N(21)	0.6211(4)	0.1985(7)	0.1192(3)	0.044(1)
N(22)	0.7398(4)	0.1971(8)	0.2669(4)	0.054(2)
C(1)	0.4392(7)	−0.2959(10)	0.2691(6)	0.087(3)
C(2)	0.4068(7)	−0.1352(14)	0.3448(7)	0.098(4)
C(3A)	0.5207(14)	−0.2637(24)	0.4103(12)	0.069(5)[b]
C(3B)	0.5370(12)	−0.3104(22)	0.3930(11)	0.063(5)[b]
C(4A)	0.5965(11)	−0.2097(20)	0.4563(10)	0.059(4)[b]
C(4B)	0.6074(16)	−0.2736(28)	0.4286(15)	0.089(7)[b]
C(5)	0.6844(8)	−0.0343(14)	0.4714(6)	0.103(4)
C(6)	0.7038(8)	−0.2096(15)	0.3952(7)	0.108(4)
C(7)	0.7654(7)	0.2897(13)	0.3331(5)	0.084(3)
C(8)	0.7873(6)	0.0696(12)	0.2899(8)	0.100(4)
C(9)	0.7573(5)	0.2736(11)	0.2096(5)	0.066(3)
C(10)	0.7105(5)	0.2084(11)	0.1356(5)	0.061(2)
C(11)	0.5819(6)	0.0919(10)	0.0616(5)	0.062(2)
C(12)	0.5769(6)	0.3271(9)	0.0882(5)	0.062(2)
C(13)	0.4418(4)	0.0540(7)	0.1692(4)	0.037(2)
C(14)	0.3573(4)	0.0484(7)	0.1038(4)	0.036(1)
C(15)	0.3411(4)	0.1196(7)	0.0389(4)	0.041(2)
C(16)	0.2651(4)	0.1095(8)	−0.0231(4)	0.045(2)
C(17)	0.2021(4)	0.0276(8)	−0.0218(4)	0.045(2)
C(18)	0.2178(4)	−0.0418(7)	0.0446(4)	0.043(2)
C(19)	0.2944(4)	−0.0332(7)	0.1057(4)	0.039(2)
C(20)	0.1201(5)	0.0145(11)	−0.0892(5)	0.069(3)
Cl(1)	0.6264(2)	−0.2626(2)	0.1824(1)	0.063(1)
O(12)	0.5771(9)	−0.2750(16)	0.1015(8)	0.076(3)[b]
O(13)	0.6056(9)	−0.1503(15)	0.2164(8)	0.062(4)[b]
O(14)	0.7079(11)	−0.2272(18)	0.1844(9)	0.078(5)[b]
O(15)	0.6402(14)	−0.3856(23)	0.2266(12)	0.099(6)[b]
O(16)	0.5669(25)	−0.3099(42)	0.1171(23)	0.144(17)[b]
O(17)	0.5692(13)	−0.2399(24)	0.2151(12)	0.144(7)[b]
O(18)	0.6595(20)	−0.1327(33)	0.1924(17)	0.216(11)[b]
O(19)	0.6844(18)	−0.3637(30)	0.2111(16)	0.179(9)[b]
Cl(2)	0.5366(2)	0.2926(3)	0.4130(2)	0.092(1)
O(22)	0.5093(7)	0.1591(10)	0.4121(8)	0.150(5)
O(23)	0.6183(6)	0.2906(12)	0.4168(6)	0.129(4)
O(24)	0.4892(7)	0.3457(18)	0.3370(9)	0.193(7)
O(25)	0.4897(12)	0.3714(20)	0.4373(11)	0.098(6)[b]
O(26)	0.5670(14)	0.3797(24)	0.4811(13)	0.169(7)[b]

[a] $U\text{eq} = 1/3[\sum_i \sum_j U_{ij} a_i{*} a_j{*} a_i a_j]$.

[b] Refined isotropically with 0.5 site occupancy.

TABLE III Positional coordinates and equivalent isotropic thermal parameters (Å^2) for the non-hydrogen atoms in $[\mathrm{Cu_2(OH)(O_2CC_6H_4\text{-}}p\mathrm{\text{-}OMe)(tmen)_2(H_2O)](ClO_4)_2}$ (**2**)

Atom	x/a	y/b	z/c	Ueq[a]
Cu(1)	0.4507(1)	0.0589(1)	0.1768(1)	0.046(1)
Cu(2)	0.3887(1)	−0.1457(1)	0.2816(1)	0.044(1)
O(1)	0.3848(3)	−0.0897(6)	0.1888(3)	0.056(1)
O(2)	0.4164(13)	−0.4005(24)	0.2452(12)	0.343(9)
O(11)	0.5491(3)	0.0164(5)	0.2648(3)	0.051(1)
O(21)	0.5065(3)	−0.1141(6)	0.3355(3)	0.056(1)
N(11)	0.5210(4)	0.1972(7)	0.1504(3)	0.064(2)
N(12)	0.3540(5)	0.1357(9)	0.0846(4)	0.076(2)
N(21)	0.3860(3)	−0.2040(6)	0.3788(3)	0.046(1)
N(22)	0.2688(4)	−0.2178(8)	0.2344(4)	0.065(2)
O(3)	0.8740(3)	0.0243(7)	0.5557(3)	0.071(2)
C(1)	0.5538(7)	0.3083(10)	0.2057(6)	0.088(3)
C(2)	0.5933(7)	0.1266(13)	0.1449(7)	0.097(4)
C(3A)	0.4776(11)	0.2392(19)	0.0733(10)	0.060(4)[b]
C(3B)	0.4568(13)	0.2880(23)	0.0879(11)	0.071(5)[b]
C(4A)	0.3874(11)	0.2756(20)	0.0668(10)	0.063(4)[b]
C(4B)	0.3925(15)	0.2014(28)	0.0399(13)	0.093(7)[b]
C(5)	0.3142(8)	0.0256(15)	0.0308(6)	0.117(5)
C(6)	0.2906(7)	0.1999(14)	0.1046(7)	0.109(4)
C(7)	0.2528(10)	−0.3133(15)	0.1736(6)	0.130(6)
C(8)	0.2135(6)	−0.0949(14)	0.2089(8)	0.126(5)
C(9)	0.2535(5)	−0.2939(10)	0.2921(5)	0.066(2)
C(10)	0.2959(5)	−0.2231(9)	0.3625(5)	0.062(2)
C(11)	0.4228(6)	−0.0999(10)	0.4374(4)	0.066(2)
C(12)	0.4309(5)	−0.3372(9)	0.4034(5)	0.067(2)
C(13)	0.5596(4)	−0.0432(7)	0.3240(3)	0.041(2)
C(14)	0.6430(4)	−0.0291(7)	0.3860(3)	0.037(1)
C(15)	0.6617(4)	−0.0991(8)	0.4505(4)	0.046(2)
C(16)	0.7379(4)	−0.0842(8)	0.5090(4)	0.052(2)
C(17)	0.7970(4)	0.0019(8)	0.5027(4)	0.045(2)
C(18)	0.7802(4)	0.0723(7)	0.4381(4)	0.046(2)
C(19)	0.7033(4)	0.0570(7)	0.3800(4)	0.041(1)
C(20)	0.8966(5)	−0.0512(13)	0.6232(5)	0.093(4)
Cl(1)	0.3737(2)	0.2417(2)	0.3104(1)	0.077(1)
O(12)	0.4251(12)	0.2443(21)	0.3893(10)	0.088(6)[b]
O(13)	0.4283(12)	0.2926(22)	0.3754(11)	0.104(6)[b]
O(14)	0.3109(13)	0.3380(22)	0.2815(11)	0.104(6)[b]
O(15)	0.3464(14)	0.3658(23)	0.2733(11)	0.139(6)[b]
O(16)	0.4305(9)	0.2365(17)	0.2687(8)	0.070(4)[b]
O(17)	0.3886(7)	0.1325(13)	0.2764(6)	0.089(3)[b]
O(18)	0.3401(10)	0.1031(18)	0.3008(9)	0.078(4)[b]
O(19)	0.2950(12)	0.1973(22)	0.3196(10)	0.141(6)[b]
Cl(2)	0.5326(2)	0.3019(3)	−0.0892(2)	0.092(1)
O(22)	0.4694(9)	0.3858(15)	−0.0782(8)	0.075(4)[b]
O(23)	0.5094(21)	0.4040(35)	−0.0599(17)	0.189(13)[b]
O(24)	0.4924(12)	0.3316(19)	−0.1700(10)	0.115(5)[b]
O(25)	0.5534(20)	0.3538(31)	−0.1396(16)	0.172(10)[b]
O(26)	0.6151(12)	0.3121(20)	−0.0888(11)	0.123(5)[b]
O(27)	0.5993(15)	0.3270(26)	−0.0191(13)	0.157(7)[b]
O(28)	0.4991(9)	0.1609(15)	−0.1037(9)	0.081(4)[b]
O(29)	0.5263(13)	0.1646(22)	−0.0705(12)	0.122(6)[b]

[a] $U\mathrm{eq} = 1/3[\sum_i \sum_j U_{ij} a_i{*} a_j{*} a_i a_j]$.

[b] Refined isotropically with 0.5 site occupancy.

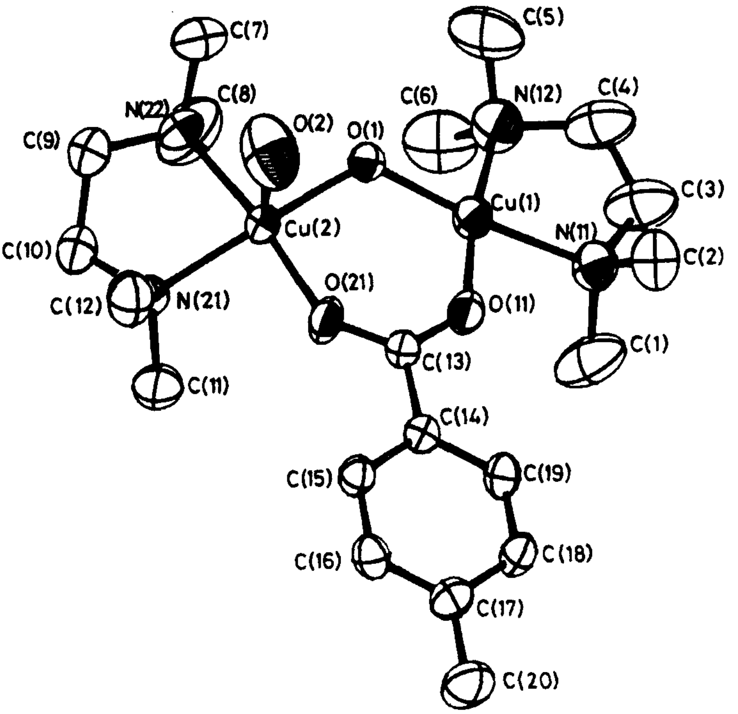

FIGURE 1 An ORTEP view of the cationic complex in $[Cu_2(OH)(O_2CC_6H_4\text{-}p\text{-}Me)(tmen)_2(H_2O)](ClO_4)_2$ (**1**) showing 50% probability thermal ellipsoids and the atom labelling scheme.

Magnetic susceptibilities of the powdered samples of **1** and **2** have been measured in the temperature range 40–295 K. A theoretical fit of the observed data gave $-J = 10\,\mathrm{cm}^{-1}$, $g = 2.05$ for **1** and $-J = 10\,\mathrm{cm}^{-1}$, $g = 2.0$ for **2** (Figure 3). The dicopper(II) centres in **1** and **2** are antiferromagnetically coupled resulting in a singlet ground state. The low-magnitude of J considering the large Cu–OH–Cu angle of ~ 124° is due to the counter-complimentary nature of the spin-coupling interaction through the monoatomic bridging hydroxo and the *syn–syn* bridging carboxylato ligands.

To obtain a meaningful magneto-structural correlation, complexes with the copper(II) centres having $d_{x^2-y^2} - d_{x^2-y^2}$ magnetic orbitals are listed in Table V. The magnitude and sign of J are found to be primarily dependent on the Cu–OH–Cu angle (ϕ). A plot of $-2J$ *versus* ϕ shows a reasonably good linear dependence of the $-2J$ value with the ϕ angle (Figure 4). The empirical relationship obtained from this least-squares fit is $-2J = 11.48\phi - 1373$ for the dibridged core (Figure 4b). The $-2J$ values of the

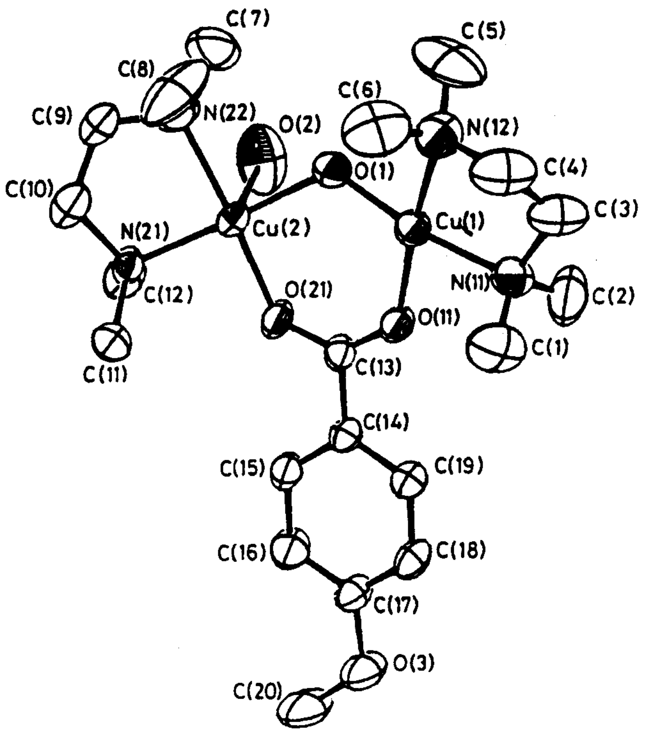

FIGURE 2 An ORTEP view of the complex cation in $[Cu_2(OH)(O_2CC_6H_4\text{-}p\text{-}OMe)(tmen)_2(H_2O)](ClO_4)_2$ (2) showing 50% probability thermal ellipsoids and the atom numbering scheme.

TABLE IV Selected bond distances (Å) and bond angles (°) in $[Cu_2(OH)(O_2CC_6H_4\text{-}p\text{-}Me)(tmen)_2(H_2O)](ClO_4)_2$ (1) and $[Cu_2(OH)(O_2CC_6H_4\text{-}p\text{-}OMe)(tmen)_2(H_2O)](ClO_4)_2$ (2)

Complex	1	2		1	2
Bond distances (Å)					
Cu(1)···Cu(2)	3.394(1)	3.374(1)	Cu(2)–O(21)	1.948(5)	1.940(5)
Cu(1)–O(1)	1.907(5)	1.917(5)	Cu(2)–N(21)	2.046(6)	2.052(6)
Cu(1)–O(11)	1.943(5)	1.951(5)	Cu(2)–N(22)	2.050(6)	2.056(6)
Cu(1)–N(11)	2.035(7)	2.030(7)	O(11)–C(13)	1.254(8)	1.263(8)
Cu(1)–N(12)	2.072(7)	2.075(7)	O(21)–C(13)	1.244(8)	1.254(8)
Cu(2)–O(1)	1.930(5)	1.917(5)	C(13)–C(14)	1.503(9)	1.497(8)
Bond angles (°)					
Cu(1)–O(1)–Cu(2)	124.4(2)	123.3(3)	O(1)–Cu(2)–N(22)	92.4(2)	91.5(2)
O(1)–Cu(1)–O(11)	95.7(2)	95.4(2)	O(21)–Cu(2)–N(21)	87.5(2)	87.2(2)
O(1)–Cu(1)–N(11)	173.9(3)	170.6(3)	O(21)–Cu(2)–N(22)	172.4(2)	168.5(3)
O(1)–Cu(1)–N(12)	92.8(3)	93.1(3)	N(21)–Cu(2)–N(22)	85.1(2)	85.7(2)
O(11)–Cu(1)–N(11)	86.6(2)	87.6(2)	C(13)–O(11)–Cu(1)	132.9(4)	132.9(4)
O(11)–Cu(1)–N(12)	171.5(3)	170.9(3)	C(13)–O(21)–Cu(2)	135.1(5)	134.2(4)
N(11)–Cu(1)–N(12)	85.0(3)	84.5(3)	O(21)–C(13)–O(11)	126.2(6)	125.8(6)
O(1)–Cu(2)–O(21)	95.2(2)	95.8(2)	O(21)–C(13)–C(14)	116.4(6)	116.9(6)
O(1)–Cu(2)–N(21)	170.8(2)	176.8(2)	O(11)–C(13)–C(14)	117.4(6)	117.3(5)

TABLE V A comparison of magneto-structural data for (μ-hydroxo/alkoxo)(μ-carboxylato)dicopper(II) complexes[a] having $d_{x^2-y^2}$–$d_{x^2-y^2}$ magnetic orbitals

Complex	Cu···Cu (Å)	Cu–O–Cu (°)	$-2J$ (cm^{-1})	*Ref.*
Core: $\{Cu_2(\mu\text{-}OH)(\mu\text{-}O_2CR)(\mu\text{-}Y)^{n+}\}[Y = H_2O, MeOH, n = 2; Y = ClO_4^-, RCO_2^-, n = 1]$				
1 $[Cu_2(OH)(O_2CMe)(MeOH)(L^1)](ClO_4)_2 \cdot 1.5THF$	3.156(3)	109.3(4)	−2.6	[12]
2 $[Cu_2(OH)(O_2CMe)(H_2O)(bpy)_2](ClO_4)_2$	3.035(2)	103.8(2)	−38.6	[13]
3 $[Cu_2(OH)(O_2CMe)(H_2O)(phen)_2](NO_3)_2$	3.017(2)	103.4(2)	−111.0	[14]
4 $[Cu_2(OH)(O_2CEt)(H_2O)(phen)_2](NO_3)_2$	3.015(2)	103.6(2)	−109.0	[14]
5 $[Cu_2(OH)(O_2CPh)(Me_3tacn)_2)](ClO_4)_2$	3.445(av)	124(av)	132	[15]
6 $[Cu_2(OH/OMe)(O_2CPh)_2(tmen)_2](PF_6)$	3.230[1]	113.1[2]	−70.8	[16]
7 $[Cu_2(OH)(O_2CPh)_2(tmen)_2](PF_6)0.5NH_4PF_6$	3.250[3]	114.9[7]	−90.2	[16]
Core: $\{Cu_2(\mu\text{-}OR/OH)(\mu\text{-}O_2CR)^{2+}\}$				
8 $[Cu_2(O_2CMe)(apaca)] \cdot H_2O$	3.502(2)	133.3(3)	165	[9(a),(b)]
9 $[Cu_2(O_2CMe)(apaca)]$	3.237(1)	114.3(2)	−37.8	[5]
10 $[Cu_2(O_2CMe)(L^2)]$	3.495(3)	134.5(5)	170	[9(b)]
11 $[Cu_2(O_2CPh)(L^2)] \cdot H_2O$	3.482(2)	132.7(3)	160	[9(b)]
12 $[Cu_2(OH)(O_2CMe)(tmen)_2]\ (ClO_4)_2$	3.339(2)	120.1(2)	27.8	[10]
13 $[Cu_2(OH)(O_2CMe)(dmen)_2](ClO_4)_2$	3.382[5]	120.0[2]	20.2	[10]
14 $[Cu_2(OH)(O_2CC_6H_4\text{-}p\text{-}Me)(tmen)_2(H_2O)](ClO_4)_2$ (**1**)	3.394(1)	124.4(2)	20	This work
15 $[Cu_2(OH)(O_2CC_6H_4\text{-}p\text{-}OMe)(tmen)_2(H_2O)]\ (ClO_4)_2$ (**2**)	3.374(1)	123.3(3)	20	This work

[a] L^1 is a hexaimidazole dinucleating ligand; Me_3tacn, 1,4,7-trimethyl-1,4,7-triazacyclononane; H_3apaca, bis(acetylacetoneimine)-1,3-propan-2-ol; bpy, 2,2′-bipyridine; phen, 1,10-phenanthroline; H_3L^2, bis(salicylaldeimine)-1,3-propan-2-ol.

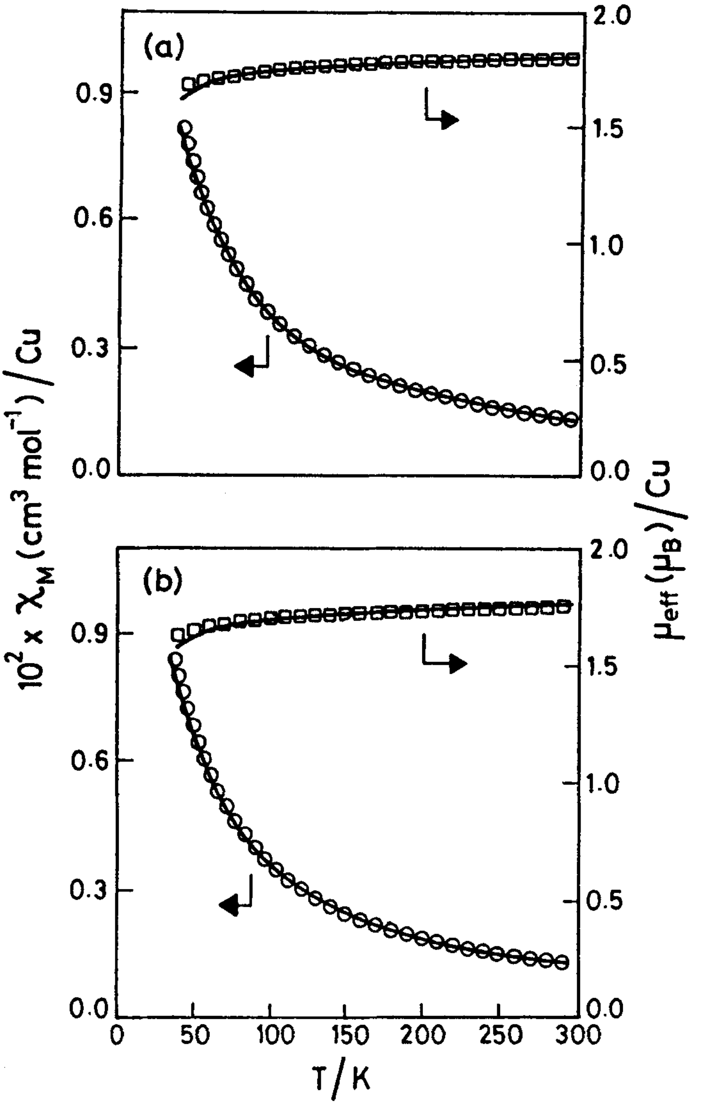

FIGURE 3 Plots of molar magnetic susceptibility per copper (χ_M/Cu) and the effective magnetic moment per copper (μ_{eff}/Cu) *versus* temperature for complexes **1** (a) and **2** (b). The theoretical fit of the magnetic data is shown by the solid line.

"essentially tribridged" dicopper(II) complexes, when plotted against ϕ, also show a similar linear correlation: $-2J = 10.77\phi - 1198$ (Figure 4a). The observed difference could be due to the presence of an additional monoatomic bridge (μ-Y) which affects the spin-coupling phenomena by

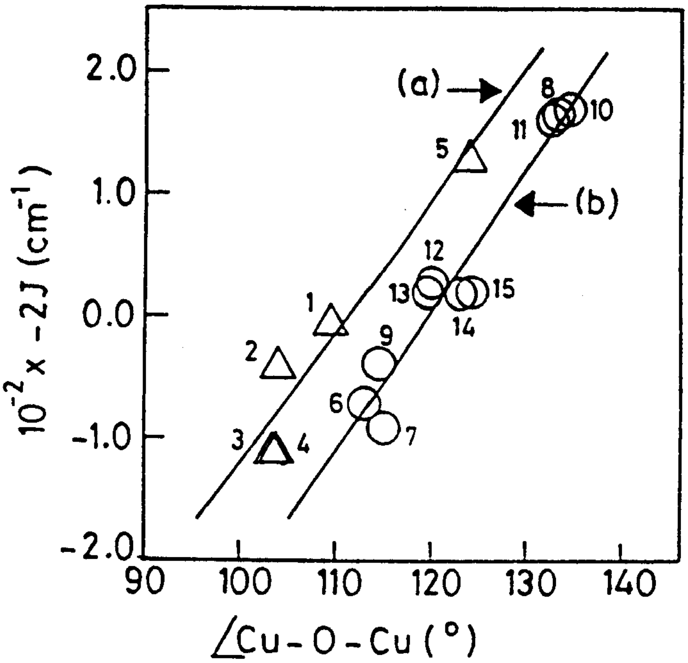

FIGURE 4 Linear plots of $-2J$ *versus* the Cu–OH–Cu angle (ϕ) for the "essentially tribridged" (a, △) and dibridged (b, ○) dicopper(II) complexes listed in Table V. The complex numbers shown in the plots correspond to the numbers given in Table V.

drastically reducing the Cu–OH–Cu angle in the $[Cu_2(\mu\text{-}OH)(\mu\text{-}O_2CR)(\mu\text{-}Y)]^{n+}$ core (Table V). Interestingly, the tribridged species having a $[Cu_2(\mu\text{-}OH)(\mu\text{-}O_2CPh)_2]^+$ core shows a magneto-structural correlation that is similar to those exhibited by the dibridged species. Observation of such linear correlations is of significance for understanding the magneto-structural properties in this emerging class of asymmetrically di- and tribriged dicopper(II) complexes.

Supplementary Material Available

Tables of interatomic parameters, thermal parameters, hydrogen atom coordinates, observed and calculated structure factors and magnetic susceptibility data for **1** and **2** are available on request from the authors.

Acknowledgments

This work was supported by the Department of Science and Technology, Government of India (SP/Sl/F-02/95). K.G. thanks the Council of Scientific and Industrial Research, New Delhi, for a senior research fellowship.

References

[1] (a) M. Kato and Y. Muto, *Coord. Chem. Rev.*, **92**, 45 (1988); (b) R.J. Doedens, *Prog. Inorg. Chem.*, **21**, 209 (1976); (c) M. Melnik, *Coord. Chem. Rev.*, **42**, 1981 (1982).

[2] (a) W.E. Hatfield, *Comments Inorg. Chem.*, **1**, 105 (1981); (b) D.J. Hodgson, *Prog. Inorg. Chem.*, **19**, 173 (1975); (c) O. Kahn, *Angew. Chem. Int. Ed. Engl.*, **24**, 834 (1985); (d) O. Kahn, *Comments Inorg. Chem.*, **3**, 105 (1984).

[3] P.J. Hey, J.C. Thibeault and R. Hoffmann, *J. Am. Chem. Soc.*, **97**, 4884 (1975).

[4] (a) I. Castro, J. Faus, M. Julve, C. Bois, I.A. Real and F. Lloret, *J. Chem. Soc., Dalton Trans.*, **47** (1992); (b) V.H. Crawford, H.W. Richardson, J.R. Wasson, D.J. Hodgson and W.E. Hatfield, *Inorg. Chem.*, **15**, 2107 (1976); (c) W.E. Marsch, K.C. Patel, W.E. Hatfield and D.J. Hodgson, *Inorg. Chem.*, **122**, 511 (1983).

[5] W. Mazurek, B.J. Kennedy, K.S. Murray, M.J. O'Connor, J.R. Rodgers, M.R. Snow, A.G. Wedd and P.R. Zwack, *Inorg. Chem.*, **24**, 3258 (1985).

[6] T.N. Sorrell, C.J. O'Connor, D.P. Anderson and J.H. Reibenspies, *J. Am. Chem. Soc.*, **107**, 4199 (1985).

[7] V. McKee, M. Zvagulis, J.V. Dagdigian, M.G. Patch and C.A. Reed, *J. Am. Chem. Soc.*, **106**, 4765 (1984).

[8] W.M. Davis and S.J. Lippard, *Inorg. Chem.*, **24**, 3688 (1985).

[9] (a) Y. Nishida, M. Takeuchi, K. Takahashi and S. Kida, *Chem. Lett.*, 1815 (1982); (b) Y. Nishida and S. Kida, *J. Chem. Soc., Dalton Trans.*, 2633 (1986); (c) Y. Nishida, M. Takeuchi, K. Takahashi and S. Kida, *Chem. Lett.*, 631 (1985); (d) T. Kawata, M. Yamanaka, S. Ohba, Y. Nishida, M. Nagamatsu, M. Tokii, M. Kato and O.W. Steward, *Bull. Chem. Soc. Jpn.*, **65**, 2739 (1992).

[10] S. Meenakumari, S.K. Tiwari and A.R. Chakravarty, *J. Chem. Soc., Dalton. Trans.*, 2175 (1993).

[11] (a) J.W. Satcher Jr., M.W. Droege, T.J.R. Weakley and R.T. Taylor, *Inorg. Chem.*, **34**, 3317 (1995); (b) X.M. Chen, X.L. Yu, Y.-X. Yao and X.-Y. Huang, *Polyhedron*, **16**, 259 (1996).

[12] W.B. Tolman, R.L. Rardin and S.J. Lippard, *J. Am. Chem. Soc.*, **111**, 4532 (1989).

[13] G. Christou, S.P. Perlepes, E. Libby, K. Folting, J.C. Huffman, R.J. Webb and D.N. Hendrickson, *Inorg. Chem.*, **29**, 3657 (1990).

[14] T. Tokii, N. Hamamura, M. Nakashima and Y. Muto, *Bull. Chem. Soc. Jpn.*, **65**, 1214 (1992).

[15] K.-S. Bürger, P. Chaudhuri and K. Wieghardt, *J. Chem. Soc., Dalton Trans.*, 247 (1996).

[16] K. Geetha, M. Nethaji, A.R. Chakravarty and N.Y. Vasanthacharya, *Inorg. Chem.*, **35**, 7666 (1996).

[17] B. Bleaney and K.D. Bowers, *Proc. R. Soc. London, A*, **214**, 451 (1952).

[18] B.K. Das and A.R. Chakravarty, *Inorg. Chem.*, **29**, 2078 (1990).

[19] A.C.T. North, D.C. Phillips and F.S. Mathews, *Acta Crystallogr.*, **A24**, 351 (1968).

[20] G.M. Sheldrick, "SHELXS-86 and SHELXL-93: Programs for X-ray Crystal Structure Solution and Refinement" (Universität Göttingen, Germany, 1986 and 1993).

[21] "International Tables X-ray Crystallography", Vol. IV (Kynoch Press, Birmingham, UK, 1974).

[22] C.K. Johnson, "ORTEP, Rep. ORNL-3794" (Oak Ridge National Laboratory, Tennessee, 1971).