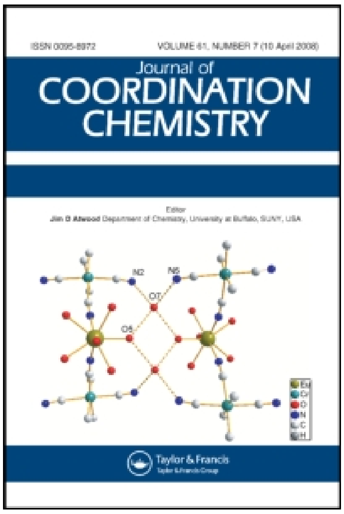

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Synthesis and Structure of A Carboxyl-Bridged Heteronuclear Copper-Terbium Complex: $[CuTb(CH_2C(CH_3)COO)_5(PHEN)(H_2O)]_2$

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SYNTHESIS AND STRUCTURE OF A CARBOXYL-BRIDGED HETERONUCLEAR COPPER–TERBIUM COMPLEX: $[CuTb(CH_2C(CH_3)COO)_5(PHEN)(H_2O)]_2$

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The title complex has prepared by the reaction of TbL_3, $Cu(NO_3)_2$ and phen in H_2O/EtOH (where L = α-methylacrylato; phen = 1,10-phenanthroline) and its structure determined by X-ray diffraction methods. The complex crystallizes in the triclinic space group $P\bar{1}$ with $Z = 1$, $a = 11.569(2)$, $b = 14.584(3)$, $c = 11.479(2)$ Å, $\alpha = 101.03(2)$, $\beta = 104.37(2)$, $\gamma = 74.01(1)°$, and the structure was refined to $R = 0.041$ for 6463 observed reflections. The structure contains a discrete tetranuclear CuTbTbCu molecule. Copper(II) and terbium(III) are bridged by three bidentate carboxyl groups with a Tb $\cdots$ Cu separation of 3.9059(9) Å. The Tb ion is eight coordinate and exhibits a distorted square antiprism. The Cu ion is five coordinate and has distorted pyramidal geometry.

Keywords: Copper; Terbium; Heteronuclear; Crystal structure

The synthesis of polynuclear mixed copper–lanthanide complexes has attracted attention for several reasons. The nature of magnetic exchange interactions between rare-earth and transition-metal ions is not only of theoretical interest, but also relevant to possible applications [1–4]. These kinds of compounds are also possible precursors for production of high-T_c superconductors [5]. Recently polynuclear metal complexes have also been reported as hosts for small molecules or ions [6,7]. Cu and Ln in most complexes are bridged by multidentate ligands [8,9], where it was

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intended that harder O-donors would favour binding to Ln^{3+} centres, while the softer N-donors would bind to the Cu^{2+} centres. In this paper we report the synthesis of the first complex in which Cu and Tb are bridged by α-unsaturated carboxylato groups.

EXPERIMENTAL

$TbL_3 \cdot H_2O$ (860 mg, 2.0 mmol, $HL = CH_2C(CH_3)COOH$) and $Cu(NO_3)_2 \cdot 3H_2O$ (240 mg, 1.0 mmol) were dissolved into 20 cm^3 of water and adjusted to pH 4.1 with HL (0.1 M). Some 4 cm^3 of an ethanol solution of 1,10-phenanthroline (200 mg, 1.0 mmol) are added to the mixture solution with stirring. After filtration, the filtrate was allowed to stand at room temperature and single crystals suitable for X-ray work were obtained after two weeks. *Anal.* calculated (%): C, 45.43; H, 4.17; N, 3.33. Found: C, 45.26; H, 4.21; N, 3.23. Infrared spectra of the complex were recorded in the range 4000–400 cm^{-1} using a powered sample spread on a KBr plate.

Crystal Structure Determination

A prismatic crystal of the title complex with approximate dimensions $0.30 \times 0.20 \times 0.20$ mm was mounted on a glass fibre. X-ray intensity data were collected on a Rigaku AFC7R diffractometer up to a 2θ value of 55.0° with graphite-monochromatized MoKα radiation ($\lambda = 0.71069$ Å) by the ω-2θ scan technique. A total of 8199 independent reflections was collected, of which 6463 reflections were considered as observed [$I > 3\sigma(I)$] and used for the structure determination. Usual Lp and adsorption corrections were applied.

The structure was solved by the Patterson method followed by Fourier syntheses. Structure refinement was carried out by full-matrix least-squares procedures using the TEXSAN program package [10]. H atoms were located in a difference Fourier map and their coordinates and thermal parameters were fixed during structure refinement. Anisotropic refinement including all the non-H atoms converged to agreement factors $R = 0.041$ and $R_w = 0.049$, where $w = 1/\sigma^2(F)$. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* [11].

Crystal Data

$C_{64}H_{70}O_{22}N_4Cu_2Tb_2$, $Mr = 1692.22$, triclinic, $P\bar{1}$, $a = 11.569(2)$, $b = 14.584(3)$, $c = 11.479(2)$ Å, $\alpha = 101.03(2)$, $\beta = 104.37(2)$, $\gamma = 74.01(1)°$, $V = 1787.8(6)$ Å^3, $Z = 1$, $F(000) = 846.00$, $D_c = 1.572$ g/cm^3, $\mu(\mathrm{MoK}\alpha) = 2.61$ cm^{-1}, $(\Delta/\sigma)_{\max} = 0.01$, $(\Delta\rho)_{\max} = 1.49$ e/Å^3 and $(\Delta\rho)_{\min} = -1.33$ e/Å^3.

RESULTS AND DISCUSSION

Crystal Structure

The molecular structure of the title complex is illustrated in Fig. 1 with the atom numbering scheme. Final atomic coordinates and equivalent isotropic thermal parameters for all non-H atoms are presented in Table I . Selected bond distances and angles are listed in Table II . X-ray analysis revealed that the complex consists of a discrete tetranuclear CuTbTbCu unit bridging by a α-methylacryl groups. The Cu ion and Tb ion are bridged by three carboxyl groups. The Tb ion and Tb* ion are linked by two carboxyl groups. Each Tb ion is eight-coordinated by seven O atoms from six carboxyl groups and one O atom from a water molecule forming a distorted square antiprism. O(11), O(7), O(10), O(8)* atoms and O(2), O(9), O(4), O(6) atoms form two faces of the square antiprism, respectively, with the dihedral angle between the mean planes being 6.0°. Each Cu ion is five-coordinated by three O atoms from three carboxyl groups and two N atoms from a phenanthroline ligand to form a slightly distorted pyramid. N(1), O(1), O(5) and O(3) atoms form the square face of the pyramid.

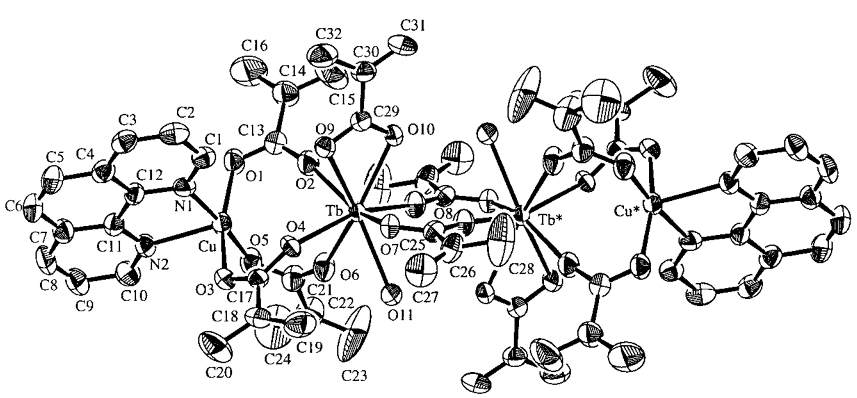

FIGURE 1 A prospective view of the complex showing the atom numbering scheme.

TABLE I Atomic coordinates and equivalent isotropic thermal parameters (10^2 Å^2) for non-H atoms

Atom	*x/a*	*y/b*	*z/c*	*B(eq)*
Tb	0.05924(2)	−0.14524(2)	0.07474(2)	3.088(5)
Cu	0.24142(6)	−0.33696(5)	0.29138(6)	3.73(1)
O(1)	0.3789(4)	−0.3517(3)	0.2081(4)	4.6(1)
O(2)	0.2538(4)	−0.2446(3)	0.0947(4)	5.0(1)
O(3)	0.0730(4)	−0.3104(3)	0.3274(3)	4.19(9)
O(4)	−0.0076(3)	−0.2474(3)	0.1563(3)	3.68(8)
O(5)	0.2783(4)	−0.2266(3)	0.4008(3)	5.1(1)
O(6)	0.1443(4)	−0.1186(3)	0.2929(3)	5.4(1)
O(7)	−0.1468(3)	−0.1193(3)	−0.0366(3)	4.00(8)
O(8)	−0.1428(4)	0.0194(3)	−0.0803(4)	4.4(1)
O(9)	0.0523(4)	−0.2865(3)	−0.0865(3)	4.22(9)
O(10)	0.0887(4)	−0.1593(2)	−0.1294(3)	4.07(9)
O(11)	−0.0718(4)	−0.0149(3)	0.1918(3)	4.6(1)
N(1)	0.2127(4)	−0.4605(3)	0.1933(4)	3.7(1)
N(2)	0.3144(4)	−0.4353(3)	0.4328(4)	4.0(1)
C(1)	0.1659(5)	−0.4725(4)	0.0753(5)	4.2(1)
C(2)	0.1458(6)	−0.5619(5)	0.0136(5)	4.8(1)
C(3)	0.1735(6)	−0.6383(4)	0.0765(6)	4.7(1)
C(4)	0.2258(6)	−0.6282(4)	0.1993(6)	4.5(1)
C(5)	0.2628(7)	−0.7051(4)	0.2715(7)	5.9(2)
C(6)	0.3155(7)	−0.6940(5)	0.3905(7)	6.1(2)
C(7)	0.3363(5)	−0.6021(4)	0.4499(6)	4.4(1)
C(8)	0.3928(6)	−0.5854(5)	0.5713(6)	5.4(2)
C(9)	0.4067(6)	−0.4960(5)	0.6218(6)	5.2(2)
C(10)	0.3648(6)	−0.4214(5)	0.5485(5)	4.8(1)
C(11)	0.2987(5)	−0.5242(4)	0.3828(5)	3.7(1)
C(12)	0.2447(5)	−0.5372(4)	0.2566(5)	3.7(1)
C(13)	0.3535(5)	−0.3033(4)	0.1213(5)	3.8(1)
C(14)	0.4461(6)	−0.3185(5)	0.0453(6)	5.5(2)
C(15)	0.4202(9)	−0.2647(9)	−0.050(1)	10.9(4)
C(16)	0.5558(9)	−0.3857(8)	0.074(1)	10.2(3)
C(17)	−0.0173(5)	−0.2729(3)	0.2512(4)	3.5(1)
C(18)	−0.1423(6)	−0.2589(5)	0.2742(5)	4.8(1)
C(19)	−0.2382(7)	−0.1987(6)	0.2099(7)	6.8(2)
C(20)	−0.1543(8)	−0.3089(8)	0.3661(8)	8.5(3)
C(21)	0.2203(6)	−0.1424(4)	0.3868(5)	4.8(1)
C(22)	0.2418(9)	−0.0637(6)	0.4896(7)	8.0(2)
C(23)	0.179(2)	0.0283(8)	0.477(1)	17.1(5)
C(24)	0.326(1)	−0.0904(8)	0.5940(9)	12.6(4)
C(25)	−0.2000(5)	−0.0427(4)	−0.0796(5)	3.6(1)
C(26)	−0.3343(6)	−0.0247(4)	−0.1315(6)	5.0(1)
C(27)	−0.4014(7)	−0.0753(7)	−0.1009(8)	7.4(2)
C(28)	−0.3880(9)	0.0459(7)	−0.213(1)	11.4(3)
C(29)	0.0738(5)	−0.2435(4)	−0.1607(5)	3.8(1)
C(30)	0.0876(6)	−0.2942(4)	−0.2842(5)	4.7(1)
C(31)	0.1058(8)	−0.2460(6)	−0.3629(6)	7.1(2)
C(32)	0.0778(8)	−0.3950(5)	−0.3124(7)	7.0(2)

TABLE II Selected bond distances (Å) and angles (°) for the complex

Tb-O(2)	2.301(4)	Cu-N(2)	2.225(4)
Tb-O(4)	2.285(3)	O(1)-C(13)	1.260(6)
Tb-O(6)	2.451(4)	O(2)-C(13)	1.240(6)
Tb-O(7)	2.374(4)	O(3)-C(17)	1.254(6)
Tb-O(8)*	2.282(4)	O(4)-C(17)	1.255(6)
Tb-O(9)	2.496(4)	O(5)-C(21)	1.246(7)
Tb-O(10)	2.414(3)	O(6)-C(21)	1.249(7)
Tb-O(11)	2.483(4)	O(7)-C(25)	1.246(6)
Cu-O(1)	1.994(4)	O(8)*-C(25)	1.262(6)
Cu-O(3)	2.010(4)	O(9)-C(29)	1.255(6)
Cu-O(5)	1.920(4)	O(10)-C(29)	1.259(6)
Cu-N(1)	1.998(4)		
O(2)-Tb-O(4)	91.5(1)	O(6)-Tb-O(11)	65.0(1)
O(2)-Tb-O(6)	76.7(2)	O(7)-Tb-O(10)	78.8(1)
O(2)-Tb-O(7)	146.3(1)	O(7)-Tb-O(11)	71.3(1)
O(2)-Tb-O(8)*	88.5(1)	O(8)-Tb-O(9)	127.2(1)
O(2)-Tb-O(9)	72.3(1)	O(8)-Tb-O(10)	76.3(1)
O(2)-Tb-O(10)	80.5(1)	O(8)-Tb-O(11)	79.3(1)
O(2)-Tb-O(11)	141.2(1)	O(9)-Tb-O(10)	52.6(1)
O(4)-Tb-O(6)	75.4(1)	O(9)-Tb-O(11)	142.7(1)
O(4)-Tb-O(7)	80.9(1)	O(10)-Tb-O(11)	130.4(1)
O(4)-Tb-O(8)*	155.2(1)	O(1)-Cu-O(3)	162.8(1)
O(4)-Tb-O(9)	76.1(1)	O(1)-Cu-O(5)	93.6(2)
O(4)-Tb-O(10)	128.2(1)	O(1)-Cu-N(1)	87.8(2)
O(4)-Tb-O(11)	85.3(1)	O(1)-Cu-N(2)	105.9(2)
O(6)-Tb-O(7)	131.4(1)	O(3)-Cu-O(5)	92.4(2)
O(6)-Tb-O(8)*	80.5(1)	O(3)-Cu-N(1)	88.1(2)
O(6)-Tb-O(9)	136.7(1)	O(3)-Cu-N(2)	89.7(2)
O(6)-Tb-O(10)	147.7(2)	O(5)-Cu-N(1)	173.4(2)
O(7)-Tb-O(8)*	111.8(1)	O(5)-Cu-N(2)	93.9(2)
O(7)-Tb-O(9)	74.0(1)	N(1)-Cu-N(2)	79.5(2)

*Symmetry code: $-x$, $-y$, $-z$.

The carboxyl ligand has various modes of coordination with a rare earth metal ion [12]. The title complex has two modes, chelating bidentate and bridging bidentate. Average bond lengths of $\text{Tb-O}_{\text{chelating}}$ and $\text{Tb-O}_{\text{bridging}}$ are 2.455, 2.339 Å, respectively. The former is longer than the latter because of ring strain (Tb, O9, C29, O10). Cu-O bond lengths are similar to (1.994, 2.010, 1.920 Å) and the average Cu-N bond length is 2.112 Å. The Tb ⋯ Tb* separation (4.6025 Å) in the complex is significantly longer than that (4.0456 Å) in $[\text{La}(\text{CH}_2\text{C}(\text{CH}_3)\text{COO})_3(\text{phen})(\text{HL})]_2$ [13] in which there are four bridging carboxyl groups between La and La*. The Cu ⋯ Tb separation is 3.9059 Å, exceeding the sum of the two ionic radii.

The notable feature of this structure is that it has two kinds of different carboxyl groups. In the carboxyl group formed by O(1), C(13) and O(2) atoms, the C(13)-O(1) distance of 1.240(6) Å is significantly shorter than the C(13)-O(2) distance of (1.260(6) Å) and suggests C(13) and O(2) are mainly double-bonded. However, the other carboxyl groups formed by C(17), O(3) and O(4) or C(21), O(5) and O(6), have nearly equal C-O bond distances. This suggests that the COO^- groups are highly conjugated, and may be helpful in transferring electrons with respect to magnetic interaction between Cu and Ln.

The complex contains coordinated water. The bond length Tb-O_{water} is 2.483 Å and is significantly longer than average bond lengths for Tb-$O_{carboxyl\ group}$ (2.372 Å). H-bonds between the carboxyl group and water were not found although the O(6)–O(11) distance is 2.652(6) Å and the O(7)–O(11) distance is 2.831(5) Å.

The carboxyl groups give rise to very strong IR absorptions, which can be used to distinguish between the different coordination modes by comparison of the band separation with that of the corresponding sodium compound [14]. Stretching vibrations were observed at 1558 cm^{-1} [ν_{asym}(COO)] and 1427 cm^{-1} [ν_{sym}(COO)], in agreement with values reported previously [13,15]. Separation (131 cm^{-1}) between ν_{asym}(COO) and ν_{sym}(COO) is smaller than the value of 146 cm^{-1} for the sodium salt and is indicative of bidentate coordination.

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Supplementary material

Full lists of crystallographic data are available from the author upon request.

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