

**Crystal structure of a new zigzag chain Cu(II) complex with terephthalato and 1,10-phenanthroline ligands,  $[\text{Cu}(\text{C}_8\text{H}_4\text{O}_4)(\text{C}_{12}\text{H}_8\text{N}_2)(\text{H}_2\text{O})]_n$**

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**Abstract:** X-Ray crystal structure analysis of the complex  $[\text{Cu}(\text{tpht})(\text{phen})(\text{H}_2\text{O})]_n$ , where tpht is the dianion of terephthalic acid and phen is 1,10-phenanthroline, showed that two crystallographically different, but chemically identical tpht ions with monodentately coordinated COO groups exist; both tpht ions act as bridging ligands forming zigzag chains. The Cu(II) ions are in a deformed trigonal bipyramidal environment consisting of two N atoms from phen, two O atoms from different tpht ligands and one O atom from coordinated H<sub>2</sub>O molecule. The crystal data are as follows:  $\text{C}_{20}\text{H}_{14}\text{CuN}_2\text{O}_5$ ,  $M_r = 425.87$ , triclinic system, space group  $P\bar{1}$ ,  $a = 9.007(5)$ ,  $b = 10.557(5)$ ,  $c = 11.554(5)$  Å,  $\alpha = 114.343(5)$ ,  $\beta = 92.942(5)$ ,  $\gamma = 114.516(5)$ °,  $V = 877.3(7)$  Å<sup>3</sup>,  $Z = 2$ ,  $F(000) = 434$ ,  $\rho_x = 1.612$  g cm<sup>-3</sup>,  $\mu = 1.281$  mm<sup>-1</sup>,  $R_1 = 0.0280$  for 4363 reflections with  $I > 2\sigma(I)$ ,  $wR_2 = 0.0785$  for 5104 independent reflections and 254 refined parameters. Some of data were compared with isostructural Co(II) and Zn(II) complexes having the same ligands.

**Keywords:** transition metal complexes, copper(II), terephthalate ions, 1,10-phenanthroline, crystal structure.

#### INTRODUCTION

The dianion of terephthalic (1,4-benzenedicarboxylic) acid, H<sub>2</sub>tpht, is a potential bis-bidentate and bridging ligand. In a large number of structurally characterised ternary transition metal complexes, tpht acts as a bis-monodentate ligand.<sup>1–8</sup> Moreover, bis-bidentate<sup>1,5,9</sup> and combined<sup>2,10–12</sup> modes of coordination are encountered. Numerous tpht complexes are binuclear or polymeric except quite rare discrete complexes.<sup>10</sup> Interest in tpht complexes is related to molecular magnetism, which is an attractive field in modern inorganic chemistry and materials science. The tpht dianion has been accepted to be the appropriate bridging unit for designing interesting poly-

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meric magnetic systems with a separation of 11 – 12 Å between two paramagnetic centers. Most articles concerning ternary complexes with tpht ligands are concentrated on Cu(II) complexes and their magnetic properties together with an orbital interpretation of the magnetic exchange mechanism.<sup>2–7,11,13</sup>

This paper presents a continuation of our studies on ternary transition metal complexes with tpht ions and some aromatic diamines.<sup>1,10</sup> The crystal structure of a new polymeric Cu(II)-tpht complex, *catena*-poly[[aqua(1,10-phenanthroline- $\kappa^2N,N'$ )copper(II)]- $\mu$ -benzene-1,4-dicarboxylato- $\kappa^2O^1:O^4$ ], containing 1,10-phenanthroline (phen) as an aromatic diamine ligand is reported. This compound is isostructural to the previously described Co<sup>1</sup> and Zn<sup>2</sup> complexes. Such a series of well-characterised transition metal complexes is not common, so the described complex enables a detailed comparison of the coordination polyhedra of 3 different central atoms in an identical environment.

## EXPERIMENTAL

### Preparation of the complex

With the exception of phen, which was of purum quality, the other reagents were of analytical grade and were used without further purification. As the microcrystalline product of the title complex described in a previous paper<sup>10</sup> is insoluble in all common solvents, single crystals were prepared by a modification of the slow diffusion method. Typically, a dilute dimethyl sulfoxide (DMSO) solution ( $\approx 0.03 \text{ mol dm}^{-3}$ ), containing equimolar quantities of Cu(II) nitrate, phen and H<sub>2</sub>tpht, was prepared in a small test tube. A dilute aqueous solution of Na<sub>2</sub>tpht was then layered carefully and very slowly in order to minimize mixing of the solutions. After approximately two weeks, single crystals of suitable size were formed near the boundary of the solutions. The obtained complex is blue and stable in air. In its IR spectrum there are two characteristic bands,  $\nu_{\text{as}}(\text{COO})$  and  $\nu_{\text{s}}(\text{COO})$ , at 1575 and 1375 cm<sup>-1</sup>, respectively.<sup>14</sup>

### X-ray analysis

A blue, plate-like single crystal (dimensions: 0.56 × 0.38 × 0.16 mm) of the title complex was chosen for data collection on a Bruker AXS four-circle diffractometer equipped with a CCD 1K area detector and a flat graphite monochromator (MoK $\alpha$  radiation,  $\lambda = 0.710369 \text{ \AA}$ ). The crystal-to-detector distance and collimator size were 38.5 and 0.8 mm, respectively. A Gaussian face-indexed absorption correction was applied ( $T_{\text{min}} = 0.5979$ ,  $T_{\text{max}} = 0.8263$ ). The structure was solved by direct methods (SHELXS97)<sup>15</sup> and refined on  $F^2$  by full-matrix least-squares (SHELXL97).<sup>15</sup> All non-hydrogen atoms were refined anisotropically. The hydrogen atoms (excluding those from the H<sub>2</sub>O molecule) were placed at calculated positions and refined using the riding model [C–H = 0.93 Å,  $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ ]. The positions of the water H atoms (H1O1 and H2O1) were calculated by the program HYDROGEN<sup>16</sup> before the final cycle of refinement. Only common  $U_{\text{iso}}$  was refined in this case.

TABLE I. Crystal data, data collection and refinement details

Chemical formula	C <sub>20</sub> H <sub>14</sub> CuN <sub>2</sub> O <sub>5</sub>
$M_r$	425.87
Crystal system, space group	Triclinic, $P\bar{1}$
$a$ (Å)	9.007(5)
$b$ (Å)	10.557(5)
$c$ (Å)	11.554(5)

TABLE I. Continued

Chemical formula	C <sub>20</sub> H <sub>14</sub> CuN <sub>2</sub> O <sub>5</sub>
$\alpha$ (°)	114.343(5)
$\beta$ (°)	92.942(5)
$\gamma$ (°)	114.516(5)
$V$ (Å <sup>3</sup> )	877.3(7)
$Z$	2
$F(000)$	434
$\mu$ (mm <sup>-1</sup> )	1.281
$\rho_x$ (g cm <sup>-3</sup> )	1.612
Measurement temperature (K)	298(1)
Total no. of frames	2800
Time per frame (s)	10
Step (°)	0.25
Range for data collection, $\theta$ (°)	3.81–30.51
Limiting indices ( $h, k, l$ ranges)	-12→12, -15→15, -16→16
Measured reflections	11351
Independent reflections	5104 [ $R_{\text{int}} = 0.0248$ ]
Observed reflection [ $I > 2\sigma(I)$ ]	4363
Refined parameters	254
$R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0280, wR_2 = 0.0785^+$
$R$ indices (all data)	$R_1 = 0.0343, wR_2 = 0.0809^+$
Goodness of fit, $S$	1.082
$(\Delta\rho)_{\text{max}}$ (e Å <sup>-3</sup> )	0.398
$(\Delta\rho)_{\text{min}}$ (e Å <sup>-3</sup> )	-0.340
$(\Delta\sigma)_{\text{max}}$	0.001

$$^+w = 1/[\sigma^2(F_o^2) + (0.0476P)^2], \text{ where } P = (F_o^2 + 2F_c^2)/3$$

Further details of the structure analysis are given in Table I. Selected geometric parameters are listed in Table II. The full list of bond distances and angles together with atomic coordinates and their displacement parameters has been deposited at the Cambridge Crystallographic Data Centre (see Supplementary materials).

## RESULTS AND DISCUSSION

The described compound is isostructural to the previously reported complexes with the general formula  $[M(\text{tpht})(\text{phen})(\text{H}_2\text{O})]_n$ ,  $M = \text{Co}^1$  and  $\text{Zn}^2$ . The structure of  $[\text{Co}(\text{tpht})(\text{phen})(\text{H}_2\text{O})]_n$  has also been solved using low-temperature data,<sup>2</sup> but in the further text only the structures solved at room temperature will be compared. In addition, the structure of the similar  $[\text{Cu}(\text{tpht})(\text{phen})]_n$  complex containing the same ligands is also known.<sup>2</sup>

In the title compound,  $[\text{Cu}(\text{tpht})(\text{phen})(\text{H}_2\text{O})]_n$ , two crystallographically dif-

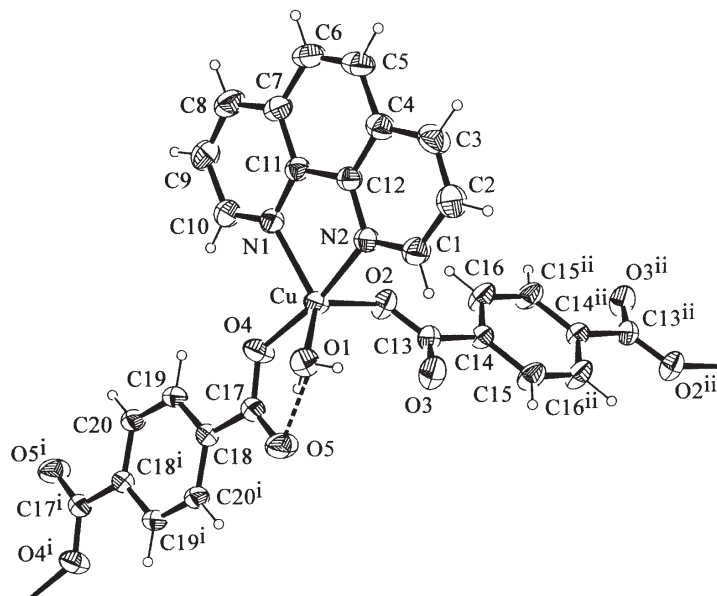


Fig. 1. Part of the polymeric chain with the atomic labelling scheme for non-hydrogen atoms. The intramolecular O1–H1O1...O5 hydrogen bond is represented by a dashed line. Displacement ellipsoids are plotted at the 50 % probability level and the H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i)  $2-x, -y, 1-z$ ; (ii)  $-x, -1-y, -z$ .]

ferent, but chemically identical tpht ions exist (Fig. 1). Since the crystallographic inversion centre coincides with the centres of both aromatic rings, only half of each tpht ion belongs to the asymmetric unit. The dihedral angle between two tpht aromatic rings is  $80.6(1)^\circ$  and dihedral angle between COO groups coordinated to the same Cu atom is  $83.1(2)^\circ$ . The overall tpht ions do not deviate very much from planarity, with an acute dihedral angle between the C14–C16 aromatic ring and the adjacent COO group of  $5.1(2)^\circ$  and corresponding angle for the C18–C20 ring of  $2.0(2)^\circ$ . In some recently described tpht complexes<sup>1,2,4,10</sup> these angles are also relatively small, ranging between  $3.5$  and  $22.3^\circ$ . The carboxylate groups show nearly trigonal geometry with the expected values of the C–O bond distances and O–C–O intracarboxylate bond angles (Table II).

TABLE II. Comparison of selected bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) for the series of  $[\text{M}(\text{tpht})(\text{phen})(\text{H}_2\text{O})_n]_n$  complexes with  $\text{M} = \text{Cu}, \text{Co}$  and  $\text{Zn}$

	Cu	Co	Zn
	In coordination polyhedron		
M–O1	2.027(1)	2.061(2)	2.053(3)
M–O2	2.109(1)	2.044(2)	2.003(2)
M–O4	1.927(1)	2.013(2)	2.023(2)
M–N1	2.093(1)	2.102(2)	2.109(3)

TABLE II. Continued

	Cu	Co	Zn
In coordination polyhedron			
M–N2	2.012(1)	2.142(2)	2.178(3)
M...O3	2.912(2)	2.653(2)	2.831(3)
N1–M–N2	80.75(6)	77.89(9)	77.57(11)
N1–M–O1	133.76(5)	124.44(8)	127.27(12)
N1–M–O2	97.18(5)	94.22(8)	101.47(11)
N1–M–O4	90.47(6)	92.54(9)	91.60(11)
N2–M–O1	93.46(6)	89.5(1)	91.09(13)
N2–M–O2	91.70(7)	90.04(8)	94.70(11)
N2–M–O4	170.37(5)	167.33(8)	165.14(11)
O1–M–O2	128.96(5)	140.21(8)	130.95(11)
O1–M–O4	89.75(6)	89.2(1)	87.42(12)
O2–M–O4	93.33(6)	99.03(8)	97.44(11)
In COO groups			
O2–C13	1.254(2)	1.261(3)	1.264(4)
O3–C13	1.246(2)	1.251(3)	1.241(4)
O4–C17	1.276(2)	1.275(3)	1.268(4)
O5–C17	1.239(2)	1.256(3)	1.253(4)
C13–C14	1.512(2)	1.501(3)	1.507(5)
C17–C18	1.499(2)	1.493(4)	1.494(5)
O2–C13–O3	123.9(1)	121.7(3)	122.8(3)
O2–C13–C14	116.8(1)	117.2(3)	116.9(3)
O3–C13–C14	119.3(1)	121.1(3)	120.3(3)
O4–C17–O5	125.1(1)	124.4(3)	124.2(3)
O4–C17–C18	115.8(1)	116.9(3)	117.3(3)
O5–C17–C18	119.1(1)	118.8(3)	118.4(3)

Phen acts as a usual chelate ligand with typical Cu–N distances and a characteristic N–Cu–N chelating angle (Table II). The tpht ions are coordinated in a bis-monodentate manner with Cu–O distances of 1.927(1) and 2.109(1) Å. Thus, each tpht is a bridging ligand linking two metal centres and each metal centre connects two tpht ligands to form a one-dimensional zigzag chain structure, with neighbouring phen ligands *trans* to each other (Fig. 2). One of the reasons for the existence of zigzag chains is probably the above-mentioned value of the dihedral angle between two tpht aromatic rings. It is also interesting to notice that the plane of the phen ligand is almost parallel to the C18–C20 aromatic ring [11.0(1)°] and almost perpendicular to the other C14–C16 ring [84.2(1)°].

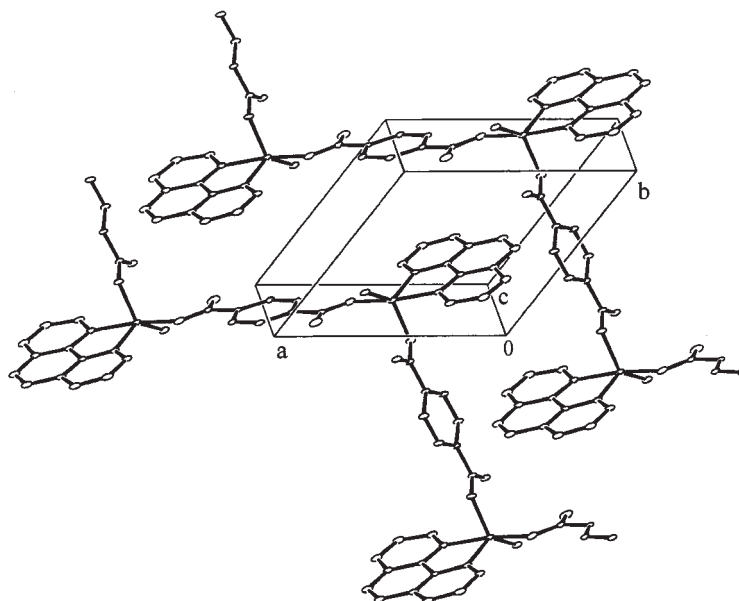


Fig. 2. Crystal packing diagram. H atoms are omitted for clarity.

The entire phen ligand as well as all individual aromatic rings are reasonably planar with the maximum deviation of 0.039(2) Å, for N2 from the plane of the whole ligand, and of 0.008(2) Å, for C7 from the C4C5C6C7C11C12 ring. In most cases the bond distances and angles in the tpht and phen ligands are in good agreement (within  $\pm 3\sigma$  limits) with the corresponding values in the isostructural Co(II) and Zn(II) complexes.<sup>1,2</sup> This is not quite true for the COO groups (Table II), where, for example, the O5–C17 bond distance in the Cu(II) complex is significantly shorter than in the other two complexes. This could be a consequence of the very short and strong Cu–O4 bond that increases the O5–C17 bond order toward a double bond character.

The intrachain Cu...Cu distances are alternately 11.107 and 11.327 Å, whereas the shortest interchain Cu...Cu distance is 6.186 Å. These values are quite normal for tpht-bridged transition metal complexes, and therefore both intra- and interchain magnetic interactions might be expected. The orientation of the chains is parallel to [211]. Very similar intra- and interchain metal-metal distances are observed in isostructural complexes<sup>1,2</sup> and in [Cu(tpht)(phen)]<sub>n</sub>.<sup>2</sup> Similar zigzag chain structures are also found in some Cu(II)-tpht complexes containing ethylenediamine<sup>3</sup> or other aromatic diamine ligands.<sup>4,6</sup> General characteristic of all these complexes is that the metal centres are bridged by tpht ions coordinated in an amphoteric fashion.

The coordinated H<sub>2</sub>O molecule is a double H bond donor toward two O atoms (O3 and O5) from the COO groups, which belong to different tpht ions (Fig. 1 and Table III). One H bond (O1–H1O1...O5) is intramolecular and the other (O1–H2O1...O3) connects

adjacent chains. Both H bonds are relatively short and strong. Such a system of H bonds increases the stability of the crystal lattice and together with the non-electrolyte character of the complex explains its high insolubility. The H-bonding geometry is very similar for all three isostructural complexes.

TABLE III. Geometry of the hydrogen bonds

$D-H...A$	$d(D-H)/\text{\AA}$	$d(H...A)/\text{\AA}$	$d(D...A)/\text{\AA}$	$D-H...A/^\circ$
O1-H1O1...O5	0.733(2)	1.877(2)	2.605(3)	172.2(1)
O1-H2O1...O3 <sup>i</sup>	0.826(1)	1.833(2)	2.644(2)	166.60(9)

Symmetry code: (i) 1-x, -y, -z.

The coordination polyhedron of Cu(II) can be described as a deformed trigonal bipyramid. Atoms O1, O2 and N1 are in the equatorial plane, while N2 and O4 occupy the axial positions (Fig. 1 and Table II). Atoms O2, Cu and O4 do not deviate very much from a linear configuration, with an N2-Cu-O4 angle of 170.37(5)°. The Cu atom shows only slight deviation from the equatorial plane [0.0079(4) Å], where the O1 atom shows the maximum deviation [0.033(1) Å]. The axial distances (Cu-O4 and Cu-N2) are shorter than the equatorial ones (Table II). The long Cu...O3 contact of 2.912(2) Å, which is practically equal to the sum of the Cu and O van der Waals radii,<sup>17</sup> should also be noticed. The corresponding M...O3 contact in the Zn<sup>2</sup> and especially in the Co<sup>1</sup> complex are significantly shorter than in the Cu complex. This very probably could be related to the value of the O2-C13-O3 bond angle, which increases in the order: Co < Zn < Cu (Table II). These M...O3 contacts apparently influence the neighbouring bond angles in the coordination polyhedra. Thus, while the length of the M...O3 contact decreases in the order: Cu > Zn > Co, the angles O1-M-O2 and O2-M-O4 increase in the opposite direction: Cu < Zn < Co.

A further comparison of the coordination polyhedra of the series of isostructural complexes (Table II) displays significant variations of the metal to ligand bond distances and corresponding angles. In spite of this, the average M-L bond distances are nearly equal for the Co and Zn complex and only slightly smaller for the Cu complex (Table IV). The unit cell volumes, as well as most polyhedra distortion parameters listed in Table IV increase in the order: Cu < Co < Zn. This is in agreement with the ionic radii of the central atom. The only exception to this order is the volume sphericity parameter, indicating that the coordination sphere around Co is the most regular, while the sphere around Cu is very irregular. This is in accordance with the observed ranges of M-L distances listed in Table II. It is, however, interesting to notice that the volume of the Cu coordination polyhedron is very close to that of an ideal trigonal bipyramid, which is not the case for the Co complex. This is shown by the polyhedron distortion parameter given in the last column of Table IV.

Finally, a comparison of the title complex with [Cu(tpht)(phen)]<sub>n</sub> shows that the tpht and phen ligands have the same coordination mode but, due to the lack of a

TABLE IV. Comparison of some structural and polyhedron distortion parameters<sup>†</sup> for the series of isostructural  $[M(\text{tpht})(\text{phen})(\text{H}_2\text{O})]_n$  complexes.

Central atom	Ionic radius/Å*	Unit cell volume/Å <sup>3</sup>	Coordination polyhedron mean bond distance/Å	Polyhedron volume/Å <sup>3</sup>	Volume of circumscribed sphere/Å <sup>3</sup>	Volume eccentricity	Volume sphericity	Polyhedron distortion
Cu	0.65	877.3(7)	2.034	7.026	35.09	0.099	0.919	0.032
Co	0.67	890.6(3)	2.072	7.183	37.02	0.105	0.992	0.064
Zn	0.68	895.9(7)	2.073	7.372	37.12	0.143	0.969	0.040

<sup>†</sup>The polyhedron distortion parameters are defined by Balić-Žunić and Makovicky<sup>18</sup> and calculated by the program IVTON.<sup>19</sup>

\*For coordination number 5.<sup>20</sup>



coordinated H<sub>2</sub>O molecule, the environment of the Cu atom in [Cu(tpht)(phen)]<sub>n</sub> is distorted square planar.<sup>2</sup> The compound was obtained by a different synthetic route. This shows how the conformational flexibility of tpht and other aromatic polycarboxylate ions can bring about the formation of structurally very different complexes containing similar or even identical ligands. In particular, this is expected in the case of Cu(II) as the central atom.

*Supplementary materials.* Cambridge Crystallographic Data Centre, CCDC No. 218922 contains supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)). Crystallographic Information File (CIF) is also available from the authors upon request.

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## ИЗВОД

КРИСТАЛНА СТРУКТУРА НОВОГ ЛАНЧАСТОГ ЦИК-ЦАК Cu(II)  
КОМПЛЕКСА СА ТЕРЕФТАЛАТО И 1,10-ФЕНАНТРОЛИН ЛИГАНДИМА,  
[Cu(C<sub>8</sub>H<sub>4</sub>O<sub>4</sub>)(C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>)(H<sub>2</sub>O)]<sub>n</sub>

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Рендгенска структурна анализа комплекса [Cu(tpht)(phen)(H<sub>2</sub>O)]<sub>n</sub>, где је tpht анјон терефталне киселине и phen је 1,10-фенантролин, показала је да постоје два кристалографски независна, а хемијски идентична tpht-јона, са монодентатно координираним COO-групама; оба tpht-јона понашају се као мостовни лиганди формирајући цик-цак ланце. Cu(II)-јони су у деформисаном тригонално-бипирамидалном окружењу које чине два атома N из phen, два атома O из различитих tpht-лиганада и један атом O из координираног молекула H<sub>2</sub>O. Кристалографски подаци су следећи: C<sub>20</sub>H<sub>14</sub>CuN<sub>2</sub>O<sub>5</sub>, M<sub>r</sub> = 425,87, триклинични систем, просторна група P  $\bar{1}$ , a = 9,007(5), b = 10,557(5), c = 11,554(5) Å, α = 114,343(5), β = 92,942(5), γ = 114,516(5) °, V = 877,3(7) Å<sup>3</sup>, Z = 2, F(000) = 434, ρ<sub>x</sub> = 1,612 g cm<sup>-3</sup>, μ = 1,281 mm<sup>-1</sup>, R<sub>1</sub> = 0,0280 за 4363 рефлексја са I > 2σ(I), wR<sub>2</sub> = 0,0785 за 5104 независних рефлексја и 254 утачњавана параметра. Неки подаци су упоређени са изоструктурним Co(II) и Zn(II) комплексима са истим лигандима.

(Примљено 8. септембра, ревидирано 12. децембра 2003)

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