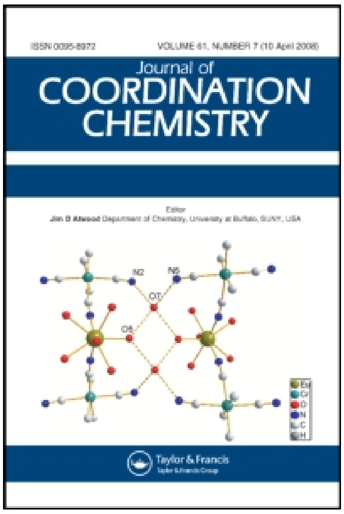

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DINUCLEAR COPPER(II) COMPLEXES WITH 3-FURANCARBOXYLIC ACID AND 2-THIOPHENCARBOXYLIC ACID

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The structures of Cu(II) 3-furancarboxylate and Cu(II) 2-thiophenate denoted hereafter as Cu-3F and Cu-2T, respectively, were determined. The structures are dinuclear, bridged by bidentate ligands. The coordination about copper is square pyramidal. The pKa of the respective acids is a factor influencing changes in Cu-Cu distances. The differences in hydrogen bond patterns and packing are described.

Keywords: 3-furancarboxylic acid; 2-thiophencarboxylic acid; copper complex; X-ray structure analysis

INTRODUCTION

Structural studies of copper complexes with carboxylic acids show a wide spectrum of coordination schemes: from discrete monomeric through dinuclear or tetranuclear, to polymeric.[1-4] The tendency to form dinuclear species was found to be connected with the pKa of the acid and the σ-donor strength of the axial ligands.[1,5] An important factor in the molecular structure is also the steric effect of bulky anions. Higher pKa of the parent acid favors formation of the mononuclear species, since the σ-electron donor strength of anion is not sufficient to reduce the positive charge on the copper atoms and does not allow

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dimerization of the molecule. To explain the Cu-Cu interactions within the dimer, two models have been proposed: either direct antiferromagnetic coupling or superexchange *via* the carboxylate group.[6,7] Since the copper 2-furoate was found to be a dimer (pKa of 2-furancarboxylic acid is 3.15) with a direct Cu-Cu bond,[8] it was of interest to investigate, whether such a configuration is present in copper complexes with ligands of similar size and shape, but different σ-electron density on the carboxylate oxygen atoms. The pKa of the acid is used as a measure of this electron density. 3-Furancarboxylic (pKa = 4.0) and 2-thiophencarboxylic (pKa 3.5) acids have therefore been chosen for this study.

EXPERIMENTAL

Both title compounds were obtained in aqueous solution by reaction of copper carbonate with 3-furancarboxylic acid and 2-thiophencarboxylic acid (Aldrich), respectively. The hot-filtered solutions were left for a week at room temperature. The dark blue, rectangular crystals obtained by solvent evaporation were used for the X-ray measurements. Data were collected with a KUMA KM-4 automated diffractometer. Cell constants were determined by the least square treatment for 25 reflections with $40° < 2\theta < 50°$. The intensities of three standard reflections showed no significant changes during data collection. Both structures were solved by the Patterson method using the SHELXS-86 program[9] and refined by application of the SHELXL-93 program.[10] Based on systematic absences hkl: $h + k + l = 2n$, $00l$: $l = 4n$; $hk0$: $k = 2n$, the space group $I4_1/a$ was chosen for Cu-3F. In the case of Cu-2T only the main absences hkl: $h + k + l = 2n$ were found (possible space groups: $I4$, $I\bar{4}$, $I4/m$). The intensity statistics indicated a noncentrosymmetric space group. Since the CFOM was the best for $I\bar{4}$, this group was proposed and subsequently confirmed by the refinement procedure. In both cases the initial Patterson and $\Delta\rho$ map clearly revealed the position of copper and all remaining nonhydrogen atoms. All hydrogens were included in geometrically calculated positions with d(C-H) = 0.93 Å, d(O-H) = 0.98 Å and nonbonding distance d(H,H) = 1.585 Å and refined isotropically with thermal displacement coefficients being 1.5 times larger than the respective parameters of the atoms to which they were bonded. All non-hydrogen atoms were refined with their anisotropic displacement parameters. Both structures are disordered in their hetero-ring parts. In Cu-3F both disordered positions of the O21-C25 ring are slightly twisted along the C_{ring}-$C_{carboxyl}$ direction, whereas in Cu-2T the disordered parts are rotated almost by a full 180°, so that the molecule becomes nearly twofold symmetrical. This explains, why the Cu-2T structure could also be solved in the $I4$ space group. The lack of real symmetry of the molecule and the better CFOM for $I\bar{4}$; symmetry were the reasons for the choice of the space group for this structure. In both cases the rings were restrained to conserve the reasonable geometry during refinement. The second ring (O11-C15) in Cu-3F is ordered. An absorption correction following the DIFABS procedure[11] was applied for both structures and the refinement procedure was repeated on corrected F^2 data. Minimum and maximum absorption corrections as well as the other data concerning the crystal structures and refinement procedures before and after absorption correction are collected in Table I.

DISCUSSION

Crystals of both title compounds contain dinuclear units (see Figure 1 and 2) with four bidentate anions forming *syn-syn* bridges between the two copper atoms. A pair of anions forms an approximate plane together with the Cu-Cu unit. The maximum shifts from each mean plane do not exceed 0.017 Å for Cu-2T and 0.021 Å for Cu-3F. Two such planes intersecting along the Cu-Cu line form the dihedral angle 84.81(16)° for Cu-3F. In the case of Cu-2T, both Cu and the water oxygen atom occupy the special position 0, 0, z on the twofold axis [0 0 1] in the $I\bar{4}$ space group, resulting in a dihedral angle of almost exactly 90°. The coordination about the Cu cation is approximately square pyramidal with four oxygen atoms from four symmetry related anions in the base plane (with maximum deviation 0.027(6) for Cu-2T and 0.026(5) Å for Cu-3F, respectively) and the water oxygen atom above it. The copper atom is slightly above this plane: (0.180(2) in Cu-2T and 0.210(4) Å in Cu-3F, respectively). The observed variation of the Cu-Cu bond distance (see Table II and Table III) is not affected by the σ-donor strength of the different axial ligands, but seems to depend only on the pKa of the acid. Taking into account three copper complexes differing in pKa, a tendency to increase the Cu-Cu distance when decreasing the pKa of the acid, whose anions bridge the metal, is observed. In the isomeric carboxylates: Cu(II) 2-furancarboxylate (Cu-2F)[8] and Cu-3F (pKa of respective acids is 3.15 and 4.0) this distance decreases from 2.638(1)[8] Å to 2.612(2) Å. In the Cu-2T (pKa of 2-thiophencarboxylic acid is 3.5) the Cu-Cu distance is 2.607(2) Å. All discussed distances, are in good agreement with those observed in many other dinuclear copper carboxylates,[1-5] and are only slightly longer than the shortest interatomic distance in metallic copper (d(Cu-Cu) = 2.556 Å[12]). For carboxylates formed by weaker carboxylic acids (pKa > 4) the mononuclear compounds are preferred.[1] The Cu-O-C-O-Cu bridging lengths as well as the Cu-O distances (see Table II and Table III) are in good agreement with those found in Cu-2F and

TABLE I Crystal data and structure refinement parameters for Cu-3F and Cu-2T.

	Cu(II) 3-furancarboxylate	Cu(II) 2-thiophenate
Empirical formula	$C_{20}H_{16}Cu_2O_{14}$	$C_{20}H_{16}Cu_2O_{10}S_4$
Formula weight	607.41	667.62
Temperature	293(2) K	293(2) K
Wavelength	1.54178 Å	1.54178 Å
Crystal system	tetragonal	tetragonal
Space group	$I4_1/a$	$I\bar{4}$
Unit cell dimensions	$a = b = 16.508(2)$ Å, $c = 17.499(3)$ Å $\alpha = \beta = \gamma = 90°$	$a = b = 10.570(1)$ Å $c = 10.510(2)$ Å $\alpha = \beta = \gamma = 90°$
Volume	4768.7(12) $Å^3$	1174.2(3) $Å^3$
Z	8	2
Density (calculated)	1.692 Mg m^{-3}	1.888 Mg m^{-3}
Absorption coefficient	2.853 mm^{-1}	6.075 mm^{-1}
$F(000)$	2448	668
Crystal size	0.2 × 0.2 × 0.3 mm	0.3 × 0.2 × 0.3 mm
Theta range for data collection	3.68 to 76.47°	5.94 to 64.87°.
Index ranges	0<=h<=17, 0<=k<=20, 0<=l<=21	− 12<=h<=0, 0<=k<=12, − 12<=l<=2
Reflections collected	878	521
Independent reflections	813 [R_{int} = 0.1447]	503 [R_{int} = 0.0728]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data /restraints /parameters	813/33/163	503/39/97
Goodness-of-fit on F^2	1.099	1.050
Final R indices	$R_1 = 0.0447$, $wR_2 = 0.1080$	$R_1 = 0.0448$, $wR_2 = 0.1153$
R indices (after abs. corr.)	$R_1 = 0.0390$, $wR_2 = 0.0913$	$R_1 = 0.0400$, $wR_2 = 0.1043$
Extinction coefficient	0.00042(7)	0.0009(2)
Largest diff. peak and hole	0.477 and − 0.291 e$Å^{-3}$	0.789 and − 0.663 e$Å^{-3}$
Absorption parameters	$t_{min} = 0.748$, $t_{max} \approx 1.450$	$t_{min} = 0.752$, $t_{max} = 1.173$

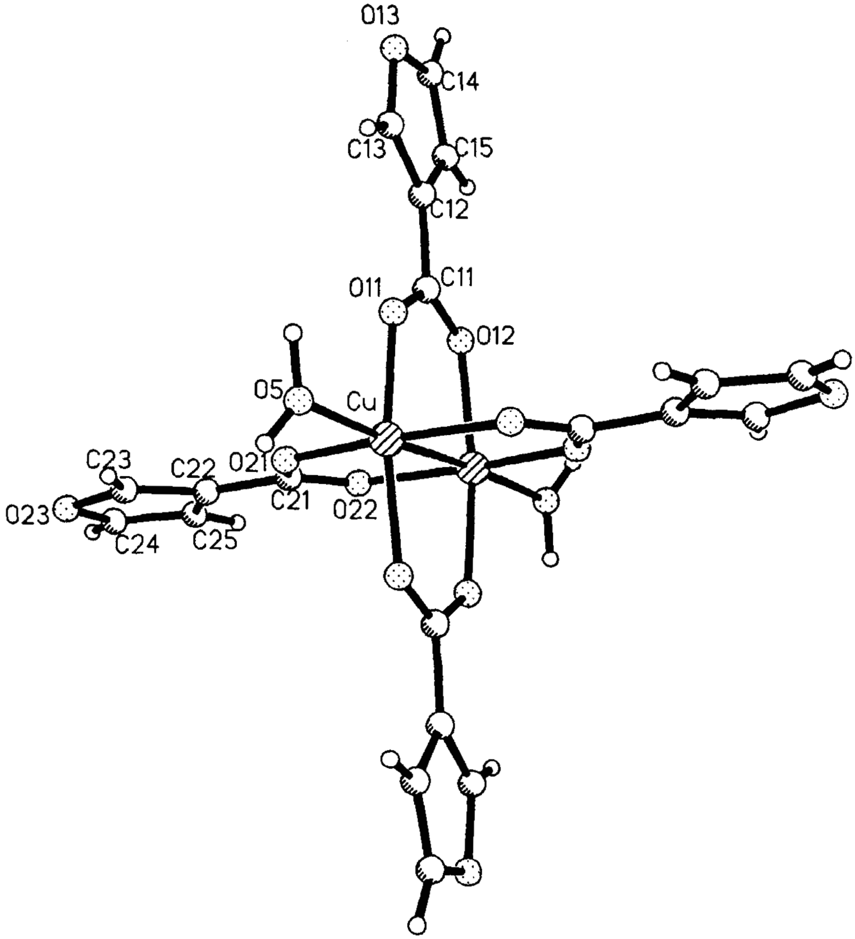

FIGURE 1 The view of Cu-Cu coordination and the numbering scheme for Cu-3F. Only one position of every disordered O21-C25 ring is shown.

other analogous complexes. The common feature of both title compounds is the absence of direct bonding between the oxygen (or sulphur) atoms of the hetero-ring and the copper cations. However, the hetero-atoms participate in networks of intermolecular H-bonding. In Cu-2T the sulphur atoms are involved in hydrogen bond networks as the acceptors of C_{ring}-H (Figure 3). The thiophene ring is rotationally disordered along the C1-C2 bond (with the occupancy factor 0.55), inducing the *pseudo*-centrosymmetry of the whole dimer. The thiophene ring in both disordered parts is, as could be expected, not ideally planar. The rms deviation from the best planes are 0.060 and 0.089 Å for parts I and II, respectively. The water molecule seems to be inactive in hydrogen bond formation. The water hydrogen atoms could not be localized, most probably due to high degree of disorder. In Cu 3-furoate all axial water molecules belonging to one dimer donate both hydrogens to O-H...O bonds with carboxylate oxygens of the adjacent dimers (Figure 4). The furan rings are slightly disordered. Sharing two planes (with an occupancy factor 0.510) inclined to each other by 17.1(9)°.

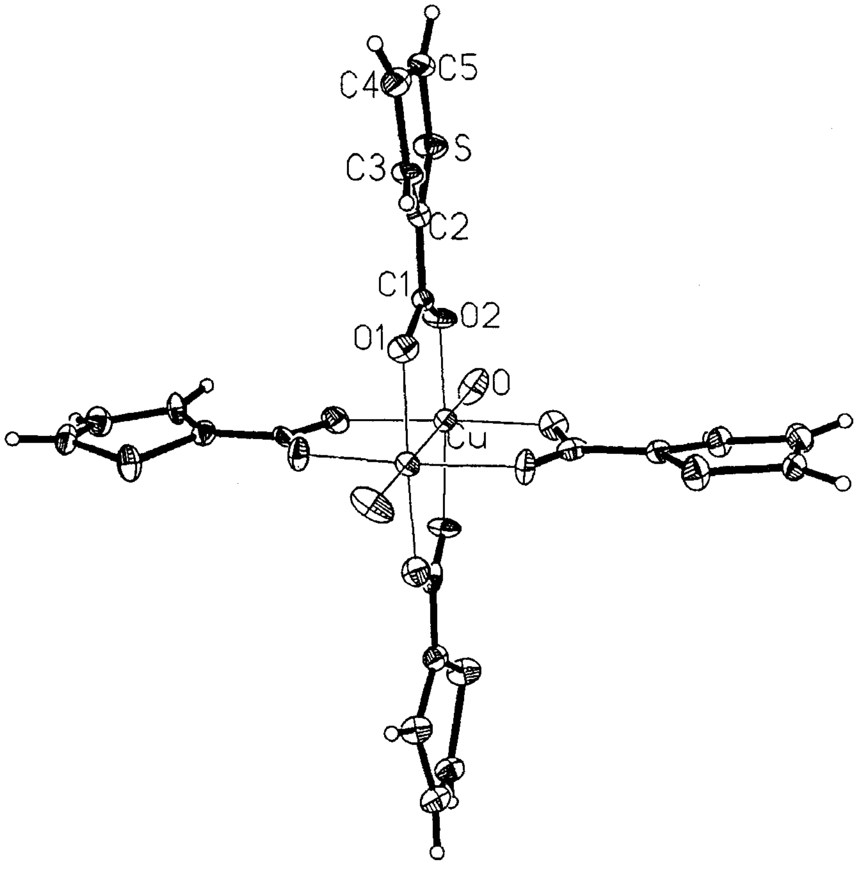

FIGURE 2 The view of Cu-Cu coordination and the numbering scheme for Cu-2T. Only one position of every disordered ring is shown. The water hydrogen atoms have not been localized and are not shown on the drawing. The coordination and the Cu-Cu bonds are shown as the thin lines.

TABLE II Bond lengths [Å] and angles [°] for Cu-3F

Cu-O23	1.932(5)	O23-Cu-O13	90.1(2)
Cu-O13	1.950(6)	O23-Cu-O22#1	168.7(2)
Cu-O22#1	1.960(5)	O13-Cu-O22#1	88.7(2)
Cu-O12#1	1.972(5)	O23-Cu-O12#1	90.7(2)
Cu-O	2.164(5)	O13-Cu-O12#1	168.7(2)
Cu-Cu#1	2.612(2)	O22#1-Cu-O12#1	88.4(2)
O13-C11	1.242(9)	O23-Cu-O	95.3(2)
O12-C11	1.272(9)	O13-Cu-O	92.5(2)
C11-C13	1.458(11)	O22#1-Cu-O	96.0(2)
C13-C12	1.358(11)	O12#1-Cu-O	98.7(2)
C13-C14	1.391(11)	O23-Cu-Cu#1	80.7(2)
C12-O11	1.376(11)	O13-Cu-Cu#1	82.5(2)
O11-C15	1.345(11)	O22#1-Cu-Cu#1	88.0(2)
C15-C14	1.307(11)	O12#1-Cu-Cu#1	86.4(2)
O23-C21	1.251(9)	C11-O13-Cu	125.8(5)
O22-C21	1.266(9)	C11-O12-Cu#1	119.4(5)
C21-C23	1.454(11)	C21-O22-Cu#1	117.9(5)
C23-C22	1.37(2)	O13-C11-O12	125.8(7)
C23-C24	1.42(2)	O13-C11-C13	116.3(7)
C22-O21	1.39(2)	O12-C11-C13	117.9(8)
O21-C25	1.32(2)	C12-C13-C14	105.0(8)
C25-C24	1.32(2)	C12-C13-C11	126.8(9)
		C14-C13-C11	128.2(8)
		C13-C12-O11	109.0(8)
		C15-O11-C12	106.8(8)
		C14-C15-O11	109.5(8)
		C15-C14-C13	109.7(9)
		C21-O23-Cu	128.3(5)
		O23-C21-O22	125.0(7)
		O23-C21-C23	117.4(7)
		O22-C21-C23	117.6(8)
		C22-C23-C24	101.7(10)
		C22-C23-C21	122.6(9)
		C24-C23-C21	129.6(9)
		C23-C22-O21	109.1(11)
		C25-O21-C22	107.2(11)
		O21-C25-C24	108.9(11)
		C25-C24-C23	109.7(11)

Symmetry transformations used to generate equivalent atoms: #1 − x + 1, − y + 1, − z

TABLE III Selected bond lengths [Å] and angles [°] for Cu-2T.

Cu1-O2	1.957(3)	O2-Cu1-O2#1	167.9(2)
Cu1-O2#1	1.957(3)	O2-Cu1-O1#2	87.6(2)
Cu1-O1#2	1.981(3)	O2-Cu1-O1#3	91.5(2)
Cu1-O1	1.981(3)	O1#2-Cu1-O1#3	171.1(2)
Cu1-O	2.195(4)	O2-Cu1-O	96.1(2)
Cu1-Cu1#3	2.607(2)	O1#2-Cu1-O	94.4(1)
O1-C1	1.341(9)	O2-Cu1-Cu1#2	84.0(2)
O2-C1	1.174(9)	O1#2-Cu1-Cu1#2	85.6(1)
C1-C2	1.470(5)	O-Cu1-Cu1#2	180.0
C2-C3	1.364(4)	C1-O1-Cu1#2	118.4(3)
C2-S	1.701(3)	C1-O2-Cu1	125.3(4)
C3-C4	1.425(4)	O2-C1-O1	126.6(5)
C4-C5	1.361(4)	O2-C1-C2	120.7(6)
C5-S	1.712(4)	O1-C1-C2	112.6(6)
		C3-C2-C1	130.8(4)
		C3-C2-S	110.9(2)
		C1-C2-S	118.3(4)
		C2-C3-C4	116.2(3)
		C5-C4-C3	104.6(4)
		C4-C5-S	117.1(3)
		C2-S-C5	89.1(2)

Symmetry transformations used to generate equivalent atoms: #1 − x + 2, − y + 2,z #2 y, − x + 2, − z + 2 #3 − y + 2, x, − z + 2

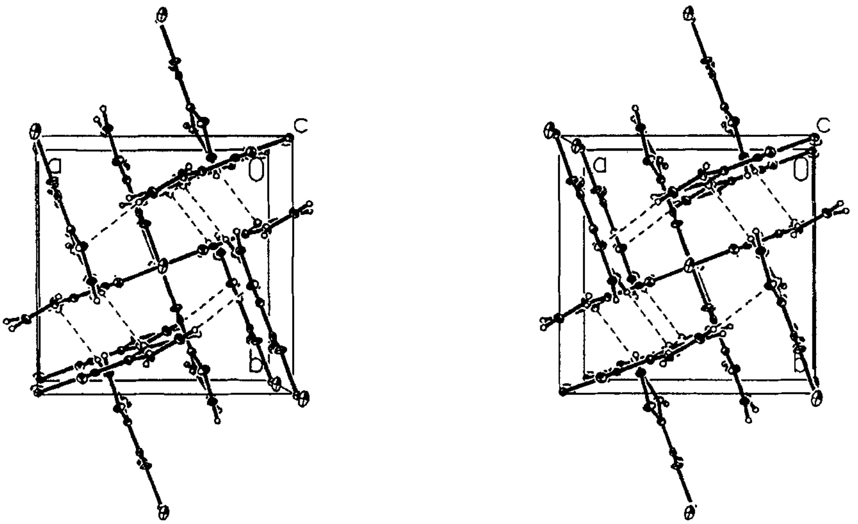

FIGURE 3 The stereoview of the unit cell along the *c*-axis of the lattice content for Cu-2T. Only one position of the disordered part of the structure is shown. The C4-H4...S hydrogen bonds are shown as the dashed lines.

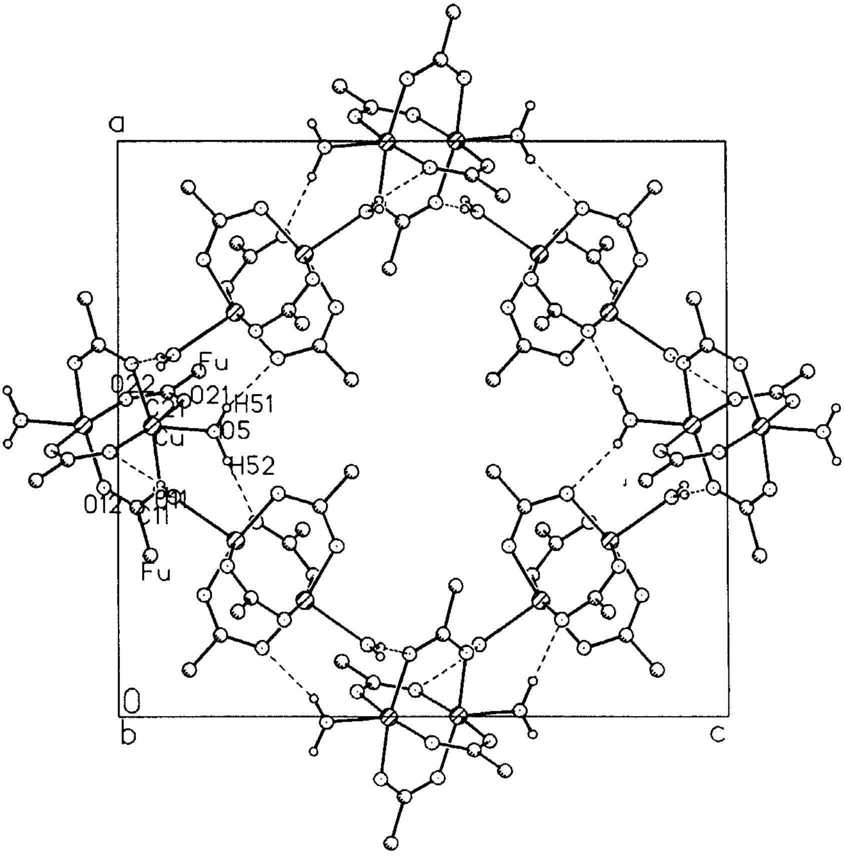

FIGURE 4 The view showing the hydrogen bonding scheme in Cu-3F structure. Four atoms of every ring and the hydrogen atoms bonded to them have been omitted for clarity. The hydrogen bonds are marked as the dashed lines.

References

1. M. Melník, *Coord. Chem. Rev.* **36**, 1 (1981).
2. D.M.L. Goodgame, C.J. Page, D.J. Williams and I.J. Stratford, *Polyhedron* **11**, 2507 (1992).
3. S.S. Sandhu, M.S. Hundal, G. Sood and S.S. Dhillon, *J. Chem. Soc., Dalton Trans* 1341 (1989).
4. T. Fujita, S. Ohba, M. Nagamatsu, T. Tokii, C.F. Jury, O.W. Steward and M. Kato, *Acta Cryst.* **C49**, 2095 (1993).
5. V.M. Rao, D.N. Sathyanarayana and H. Manohar, *J. Chem. Soc. Dalton Trans* 2167 (1983).
6. M. Melník, *Coord. Chem. Rev.* **42**, 259 (1982).
7. G.M. Brown, R. Chidambaram, *Acta Cryst.* **B29**, 2393 (1973).

8. F. Charbonnier, M. Petit-Ramel, R. Faure and H. Loiseleur, *Rev. Chim. Miner.* **21**, 601 (1984).
9. G.M. Sheldrick, *Acta Cryst.*, **A46**, 467 (1990).
10. G.M. Sheldrick, *Program for crystal structure refinement* (1993).
11. N. Walker, and D. Stuart, *Acta Cryst* **A39**, 158 (1983).
12. *Intern. Tables for X-Ray Cryst.*, Vol. III, p.278, The Kynoch Press, Birmingham (1962).