Indian Journal of Chemistry
Vol. 59A, March 2020, pp. 341-345

Notes

Preparation, structural and magnetic characterization of trinuclear and one-dimensional cyanide-bridged Co(III)-Cu(II) complexes

Wenlong Lan[a], Jingwen Shi[a], Zhen Zhou[a], Qingyun Liu[b] & Daopeng Zhang[a,]*

[a]College of Chemical and Chemical Engineering, Shandong University of Technology, Zibo 255049, PR China

[b]College of Chemical and Environmental Engineering, Shandong University of Science and Technology, Qingdao 266510, PR China

Email: dpzhang73@126.com

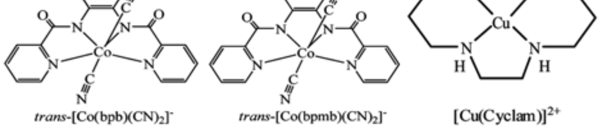
Received 27 July 2018; revised and accepted 10 February 2020

By employing two *trans*-dicyanocobolt(III) building blocks K[Co(bpb)(CN)$_2$] (bpb^{2-} = 1,2-bis(pyridine-2-carboxamido)benzenate), K[Co(bpmb)(CN)$_2$] (bpmb^{2-} = 1,2-bis(pyridine-2-carboxamido)-4-methyl-benzenate) and one 14-membered macrocycle Cu(II) compound as assembling segment, two cyanide-bridged Co^{III}-Cu^{II} complexes {{[Cu(cyclam)][Co(bpb)(CN)$_2$]}ClO$_4$}$_n$·nCH$_3$OH·nH$_2$O (**1**) and {[Cu(cyclam)][Co(bpmb)(CN)$_2$]$_2$}·4H$_2$O (**2**) (cyclam = 1,4,8,11-tetraazacyclotetradecane) have been successfully prepared and characterized by elemental analysis, IR spectroscopy and X-ray structure determination. Single X-ray diffraction analysis shows that complex **1** can be structurally characterized as one-dimensional cationic single chain consisting of alternating units of [Cu(cyclam)]$^{2+}$ and [Co(bpb)(CN)$_2$]$^-$ with free ClO$_4^-$ as balanced anion, while complex **2** presents cyanide-bridged neutral trinuclear bimetallic structure containing Co$_2$Cu core, giving clear information that the substitute group on the cyanide precursor has obvious influence on the structure type of the target compound. Investigation over magnetic properties of complex **1** reveals the weak antiferromagnetic coupling between the neighboring Cu(II) ions through the diamagnetic cyanide building block.

Keywords: Cyanide-bridged, Trinuclear and one-dimensional, Crystal structure, Magnetic property, Cu(III)-Cu(II) complex

During the past several decades, because of the efficient propagation of cyanide bridge for magnetic coupling between the paramagnetic centers, cyanide-bridged complexes with various structural types and over a wide range of dimensionalities including 0D polynuclear clusters, 1D chains, and 2D and 3D networks have been extensively studied in the field of molecular magnetism.[1-11] Many previous reported results have revealed that the designed synthesis of new cyanide-containing building blocks of polycyanometallates [M(L)(CN)$_m$]$^{n-}$ (M = Fe, Cr, Co, W, Mo, etc.; L represents blocking ligand) is a feasible strategy for the preparation of cyanide-bridged molecular magnetic materials. Because of the important role of the auxiliary ligand attached to the metal center in determining the number of charges, the arrangement of cyanide groups, and steric effect of the polycyanometallates [M(L)(CN)$_m$]$^{n-}$, the rational selection of the blocking ligand has become one of the most effective ways in controlling the molecular topological structure of the target cyanide-bridged magnetic systems.[12-22]

With continuous interest in cyanide-bridged molecular magnetism field, we have developed a series of rigid *trans*-dicyanometallates as building blocks based-on large *quasi* planar tetradentate pyridinecarboxamide ligands to assemble cyanide-bridged mono- or heterobimetallic magnetic complexes.[23-30] Furthermore, the reported results have proved that these types of the cyano-containing precursors were excellent candidates for the preparation of low-dimensional cyanide-bridged magnetic system. The relative large equatorial in-plane ligands can efficiently decrease the dimensionality of the complex and also make the intermolecular supramolecular magnetic interaction become negligible, therefore sometime favoring of producing interesting magnetic properties. Along our continuous effort in this field, we investigated the reactions of these types of *trans*-dicyanocobolt(III) precursors with the macrocycle copper compound (Scheme 1) and obtained cyanide-bridged 1D and trinuclear Co-Cu complexes with the formula {{[Cu(cyclam)][Co(bpb)(CN)$_2$]}ClO$_4$}$_n$·nCH$_3$OH·nH$_2$O (**1**) and {[Cu(cyclam)][Co(bpmb)(CN)$_2$] $_2$}·4H$_2$O (**2**). This paper provides some information that the structure of the target complex can be tuned through rational selection of the substitute group on the cyanide precursor. The synthesis, crystal structures and magnetic properties for these two complexes will be described in this paper.



The starting materials used to prepare complexes **1** and **2**.

Scheme 1

Experimental

General procedures and materials

The two reactions were carried out under an air atmosphere and all chemicals and solvents used were reagent grade without further purification. The two cyanide building blocks K[Co(bpb)(CN)$_2$] and K[Co(bpmb)(CN)$_2$] were synthesized according to the method described in literature.[31]

Preparation of Complexes 1 and 2

The preparation methods for the two complexes are with the similar three layers diffusion method. K[Co(bpb)(CN)$_2$] (46.3 mg, 0.10 mmol) or K[Co(bpmb)(CN)$_2$] (47.7 mg, 0.10 mmol) dissolved in H_2O/CH_3OH (1:1, v:v) 5 mL was laid in the bottom of a tube, and a mixture solvent of H_2O, CH_3OH and CH_3CN with a ratio of 1:1:1 was carefully added. Then, a solution of [Cu(cyclam)][ClO$_4$]$_2$ (46.3 mg, 0.10 mmol) formed in-situ by mixing equivalent mole of cyclam and [Cu(ClO$_4$)$_2$]·6H$_2$O in CH_3CN was carefully added to the top of the mixture solvent layer above formed. About two weeks later, red block-like single crystals suitable for X-ray diffraction were obtained, collected by filtration and dried in air.

Complex **1**: Yield: 50.5 mg, 60%. Anal. Calcd. for $C_{31}H_{42}ClCoCuN_{10}O_8$: C, 44.29; H, 5.04; N, 16.66. Found: C, 44.41; H, 5.16; N, 16.49. Main IR bands (cm^{-1}): 2122 (s, $\nu_{C\equiv N}$), 1625, (vs, $\nu_{C\equiv N}$), 1100 (vs, $\nu_{Cl=O}$).

Complex **2**: Yield: 40.4 mg, 66.3%. Anal. Calcd. for $C_{52}H_{60}Co_2CuN_{16}O_8$: C, 51.25; H, 4.96; N, 18.39. Found: C, 51.39; H, 4.71; N, 18.25. Main IR bands (cm^{-1}): 2120, 2160 (s, $\nu_{C\equiv N}$), 1625 (vs, $\nu_{C\equiv N}$).

X-ray data collection and structure refinement. Crystal data of complexes 1 and 2 were collected by using single crystals with suitable dimensions on a Oxford Diffraction Gemini E diffractometer with Mo Kα radiation (λ = 0.71073 Å) at the room temperature, and the collected frames were integrated by using the preliminary cell-orientation matrix. The structures of these two complexes were solved by direct method and expanded using Fourier difference techniques with the SHELXTL-97 program package.[32] Anisotropic thermal parameters were used for the non-hydrogen atoms and isotropic parameters for the hydrogen atoms. Hydrogen atoms were assigned isotropic displacement coefficients U(H) =1.2U(C) or 1.5U(C) and their coordinates were allowed to ride on their respective carbon atoms or nitrogen atoms using SHELXL97 except of the solvent H atoms. For the latter, they were refined isotropically with fixed U values and the DFIX command was used to rationalize the bond parameter. (CCDC 1573591-1573592 for these two complexes contain the supplementary crystallographic data for this paper, from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.) Details of the crystal parameters, data collection, and refinement of complexes **1** and **2** are summarized in Table 1.

Physical measurements

Elemental analyses of carbon, hydrogen, and nitrogen were carried out with an Elementary Vario El. The infrared spectroscopy on KBr pellets was performed on a Magna-IR 750 spectrophotometer in the 4000–400 cm^{-1} region. Variable-temperature magnetic susceptibility and field dependence magnetization measurements were performed on a Quantum Design MPMS SQUID magnetometer. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms (Pascal's tables).

Results and Discussion

Synthesis and general characterization

The *trans*-dicyanidemetallates based-on pyridine-carboxamide ligand containing planar N_4 coordination

Table 1 — Crystallographic data and structure refinement summary for the compounds **1** and **2**

Empirical formula	$C_{31}H_{42}ClCoCuN_{10}O_8$	$C_{52}H_{60}Co_2CuN_{16}O_8$
Formula weight	840.67	1218.56
Temperature (K)	293	293
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	P2(1)/n	P2(1)/c
a/Å	9.9283(8)	15.668(5)
b/Å	20.6632(15)	13.557(4)
c/Å	17.7696(13)	12.914(4)
α/deg	90	90
β/deg	96.9830(10)	91.545(6)
γ/deg	90	90
F(000)	1740	1262
Z	4	2
Completeness	100%	97.9%
θ/deg	1.97–25.01	1.30–25.01
Reflections/ collected/unique	17862/ 6381/ 5021	12791/ 4740/ 3748
Data/restraints/ parameters	6381/ 0/ 470	4740/ 1/ 359
Goodness-of-fit on F^2	1.020	1.112
Final R indices [I>2sigma(I)]	0.0449	0.0825
R indices (all data)	0.1388	0.2269
Largest diff. peak and hole (e/Å^3)	0.840 and –0.459	1.357 and –0.599

units, K[M(L)(CN)$_2$] (M = Fe, Cr, Co; L represents pyridinecarboxamide ligand), have been proven suitable building block to synthesize low-dimensional cyanide-bridged heterometallic magnetic complexes with many paramagnetic compounds as assemble segments, including Schiff-base Mn(III) compounds, macrocycle manganese(II) and nickel(II) compounds. The reactions of the two *trans*-dicyanocobolt(III) precursors with the macrocyclic copper compound [Cu(cyclam)][ClO$_4$]$_2$ were studied, and two cyanide-bridged Co-Cu complexes with different structural types were obtained, indicating that the substitute group on the cyanide precursor have obvious influence on the structure of the target complex.

Both of the two complexes have been characterized by IR spectra. In IR spectra of complex **1**, one broad peak due to the bridging cyanide groups in the range of 2115–2120 cm^{-1} was observed. This indicates the existence of only bridging cyanide ligands in these compounds. The IR spectra of complex **2** shows two sharp peaks at about 2120 and 2160 cm^{-1}, which indicates the presence of bridging and non-bridging cyanide groups in this complex.

Crystal structures of complexes 1 and 2

Some selected bond distances and bond angles for complexes **1** and **2** are collected in Table 2. The asymmetric unit and the cationic one-dimensional chain for complex **1** are given in Fig. 1. For complex **2**, its neutral trinuclear structure and the cell packing diagram are depicted in Fig. 2.

Table 2 — Selected bond lengths (Å) and angles (°) for complexes **1** and **2**

	1	**2**
Bond length (Å)		
Cu1-N1	2.450(3)	2.491(3)
Cu1-N2	2.611(2)	
Cu1-N9	2.014(3)	
Cu1-N10	1.991(3)	
Cu1-N7	2.030(4)	2.025(5)
Cu1-N8	2.022(3)	2.028(6)
Co1-C1	1.925(4)	1.936(7)
Co1-C2	1.929(4)	1.927(8)
Co1-N3	1.882(3)	1.892(6)
Co1-N4	1.890(3)	1.881(6)
Co1-N5	1.978(3)	1.984(6)
Co1-N6	1.971(3)	1.989(6)
Bond angles (º)		
C1-N1-Cu1	163.0(3)	140.2(0)
C2-N2-Cu2	145.0(6)	
N1-C1-Co1	178.1(3)	176.1(6)
N2-C2-Co1	176.2(3)	179.5(8)

These two complexes, which contain four and two independent units in the unit cell, crystallize in monoclinic cell setting P2$_1$/*n* and P2$_1$/*c* space group, respectively, as shown in Table 1. The cyanide precursor anion acting as bidentate liagnd in complex **1** connects two independent macrocyclic copper units through its two *trans* cyanide groups, therefore forming one dimensional cationic single chain structure comprised of repeating [-NC-Co(bpb)-CN-Cu(cyclam)-]$^+$ units (Fig. 1) with the positive charge

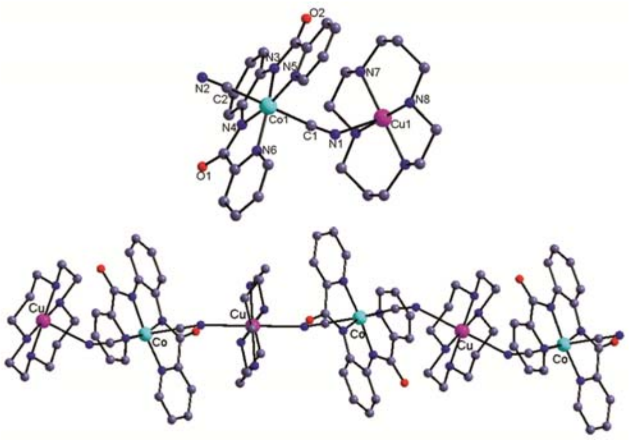


Fig. 1 — The asymmetry unit and one-dimensional cationic chain structure of complex **1**. (The balance ClO$_4^-$ anions, all the hydrogen atoms and solvent molecules have been omitted for clarity.)

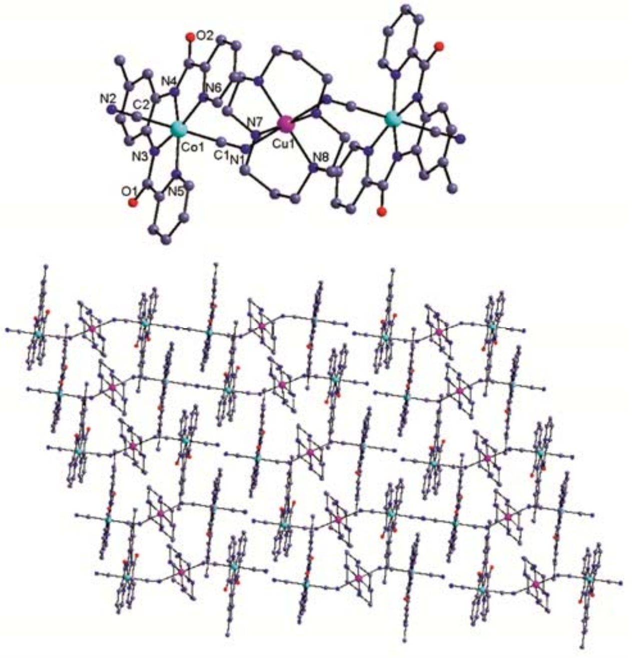


Fig. 2 — The neutral trinuclear structure and the cell packing along b axial for complex **2**. (All the hydrogen atoms and solvent molecules have been omitted for clarity.)

balanced by ClO_4^- anion. Different from that in complex **1**, two cyanide building block anions functioning as monodentate ligand in complex **2** coordinate to the central macrocyclic copper cation, so that forming a neutral sandwich-like complex containing trinuclear Co_2Cu core. The Co atoms in these two complexes are surrounded by four N atoms of cyanide-containing precursor locating in the equatorial plane and two C atoms of cyanide groups in *trans* position. The bond parameters around the Co atom with no obvious difference indicate that the coordination sphere of the Co atom is a lightly distorted octahedron.

The Cu(II) ion in both of the two complexes is six-coordinated by a N_6 unit with the four equatorial positions occupied four N atoms of the cyclam ligand and the other two axial ones from the N atoms of the bridging cyanide groups. The average Cu-N_{cyclam} bond lengths in complexes **1** and **2** are 2.015 and 2.027 Å, respectively, while the average distances between the Cu atom and the N atom of the cyanide-bridge are 2.450(3) and 2.491(3) Å, which are obviously longer than the Cu-N_{cyclam} bond length and clearly indicate the obviously axially distorted octahedron surrounding of the Cu(II) ion. The Cu-C≡N bond angles in these two complexes are 163.0(3)°, 145.0(6)° for complex **1** and 140.2(0)° for complex **2**, respectively, demonstrating that the conformation of three atoms is seriously deviated from a linear. The shortest intermolecular metal-metal distances are 9.928 and 10.327 Å in complexes **1** and **2**, respectively, which are almost twice to the separations between the cyanide-bridged intramolecular Co atom and the Cu atom with the values 5.441 and 5.215 Å.

Magnetic property of complexp

As described above, the complex **1** contains cyanometallate-bridged paramagnetic Cu(II) ions, while the complex **2** is only mononuclear Cu(II) ion from the view of the molecular magnetism. Therefore, the temperature (T) dependence of magnetic susceptibility (χ_m) only for complex **1**, which was measured in the temperature range of 2–300 K in the applied field of 2000 Oe, is given in Fig. 3. The $\chi_m T$ value at room temperature is about 0.4 emu K mol^{-1}, slightly higher than the spin only value of 0.375 emu K mol^{-1} for the isolated Cu(II) (S = 1/2). With the temperature decreasing, the $\chi_m T$ value is almost constant until the temperature lowering to about 50 K. From this point, the $\chi_m T$ value starts to decrease with a high speed and reaches its lowest peak at about 0.28 emu K mol^{-1}. The magnetic susceptibility of complex **1** conforms well to Curie-Weiss law in the whole temperature and gives the negative Weiss constant $\theta = -1.72$ K and Curie constant C = 0.41 emu K mol^{-1}, which primarily indicates the antiferromagnetic magnetic coupling between the two Cu(II) centers bridged by diamagnetic cyanide building block. The magnetic susceptibility for complex **1** has been simulated by using MAGPACK program[33] with the experimental $\chi_m T$ value of 2–300 K. The best-fit parameters obtained are $J = -0.59(2)$ cm^{-1}, g = 2.02(3), $R = \sum(\chi_{obsd}T - \chi_{calcd}T)^2/\sum(\chi_{obsd}T)^2 = 2.68 \times 10^{-5}$, which can further confirm the weak antiferromagnetic interaction between the two adjacent Cu(II) ions.

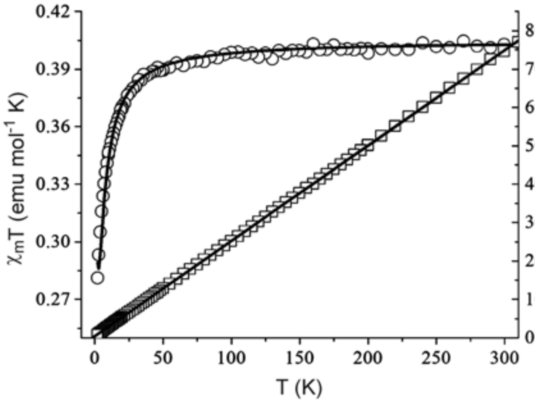


Fig. 3 — Temperature dependences of χ_mT and χ_m^{-1} (the solid line represents the best fit based on the parameters discussed in the text) for complex **1**.

Conclusions

In summary, with one macrocyclic copper compound as assemble segment and *trans*-dicyanidecobolt(III)-containing as building blocks, two heterobimetallic cyanide-bridged Co(III)-Cu(II) complexes with one-dimensional single cationic chain and sandwich-like neutral trinuclear structure have been synthesized, structurally characterized and magnetically studied. The result here indicates that the substitute group on the cyanide precursor has obvious influence on the structure type of the target complex formed. Investigation over the magnetic property of the one-dimensional complex reveals weak antiferromagnetic interaction between the Cu(II) ions bridged by the long diamagnetic cyanometallate building block.

Acknowledgement

This work was supported by the Natural Science Foundation of China (21171107 and 21671121).

References

1 Entley W R & Girolami G S, *Science*, 268 (1995) 397.

2 Goodwin A L, Kennedy B J & Kepert C J, *J Am Chem Soc*, 131 (2009) 6334.

3 Nihei M, Sekine Y, Suganami N, Nakazawa K, Nakao A, Nakao H, Murakami Y & Oshio H, *J Am Chem Soc*, 133 (2011) 3592.

4 Trzop E, Zhang D P, Piñiro-Lopez L, Valverde-Muñoz F J, Muñoz M C, Palatinus L, Guerin L, Cailleau H, Real J A & Collet E, *Angew Chem Int Ed*, 55 (2016) 8675.

5 Cornia A, Mannini M, Sainctavit P & Sessoli R, *Chem Soc Rev*, 40 (2011) 3076.

6 Zhang D P, Zhang L F, Chen Y T, Wang H L, Ni Z H, Wernsdorfer W & Jiang J Z, *Chem Commun*, 46 (2010) 3550.

7 Aguilà D, Prado Y, Koumousi E S, Mathonière C & Clérac R, *Chem Soc Rev*, 45 (2016) 203.

8 Inoue K, Imai H, Ghalsasi P S, Kikuchi K, Ohba M, Okawa H & Yakhmi J V, *Angew Chem Int Ed*, 40 (2001) 4242.

9 Kaye S S & Long J R, *J Am Chem Soc*, 127 (2005) 6506.

10 Beauvais L G & Long J R, *J Am Chem Soc*, 124, (2002) 12096.

11 Sorace L, Benelli C & Gatteschi D, *Chem Soc Rev*, 40 (2011) 3092.

12 Miyasaka H, Saitoh A & Abe S, *Coord Chem Rev*, 251 (2007) 2622.

13 Wang S, Ding X H, Zuo J L, You X Z & Huang W, *Coord Chem Rev*, 255 (2011) 1713.

14 Li Y H, He W R, Ding X H, Wang S, Cui L F & Huang W, *Coord Chem Rev*, 256 (2012) 2795.

15 Wang S, Ding X H, Li Y H & Huang W, *Coord Chem Rev*, 256 (2012) 439.

16 Lv Z, Wang X, Liu Z, Liao F, Gao S, Xiong R, Ma H, Zhang D & Zhu D, *Inorg Chem*, 45 (2006) 999.

17 Panja A, Guionneau P, Jeon I R, Holmes S M, Clérac R & Mathonière C, *Inorg Chem*, 51 (2012) 12350.

18 Liu C M, Xiong R G, Zhang D Q & Zhu D B, *J Am Chem Soc*, 132 (2010) 4044.

19 Zhu Y Y, Guo X, Cui C, Wang B W, Wang Z M & Gao S, *Chem Commun*, 47 (2011) 8049.

20 Toma L M, Lescouëzec R, Pasan J, Ruiz-Perez C, Vaissermann J, Cano J, Carrasco R, Wernsdorfer W, Lloret F & Julve M, *J Am Chem Soc*, 128 (2006) 4842.

21 Bartual-Murgui C, Salmon L, Akou A, Ortega-Villar N A, Shepherd H J, Muñoz M C, Molnár G, Real J A & Bousseksou A, *Chem Eur J*, 18 (2012) 507.

22 Jeon I R, Calancea S, Panja A, Piñero Cruz D M, Koumousi E S, Dechambenoit P, Coulon C, Wattiaux A, Rosa P, Mathonière C & Clérac R, *Chem Sci*, 4 (2013) 2463.

23 Ni Z H, Kou H Z, Zhang L F, Tangoulis V, Wernsdorfer W, Cui A L & Sato O, *Inorg Chem*, 46 (2007) 6029.

24 Kou H Z, Ni Z H, Liu C M, Zhang D Q & Cui A L, *New J Chem*, 33 (2009) 2296.

25 Ni Z H, Tao J, Wernsdorfer W, Cui A L & Kou H Z, *Dalton Trans*, (2009) 2788.

26 Zhang D P, Wang H L, Chen Y T, Ni Z H, Tian L J & Jiang J Z, *Inorg Chem*, 48 (2009) 5488.

27 Zhang D P, Zhao Z D, Wang P & Ni Z H, *Cryst Eng Comm*, 15 (2013) 2504.

28 Zhang D P, Si W J, Wang P, Chen X & Jiang J Z, *Inorg Chem*, 53 (2014) 3494.

29 Zhang H Y, Xue C C, Shi J W, Liu H, Dong Y H, Zhao Z D, Zhang D P & Jiang J Z, *Crystal Growth & Des,* 16 (2016) 5753.

30 Zhang D P & Zhang H Y, *Polyhedron*, 100 (2015) 36.

31 Ray M, Mukherjee R, Richardson J F & Buchanan R M, *J Chem Soc Dalton Trans*, (1993) 2451.

32 Sheldrick G M, (1997) SHELXTL97, Program for the Refinement of Crystal Structure, University of Göttingen, Germany.

33 Borrás-Almenar J J, Clemente-Juan J M, Coronado E & Tsukerblat B S, *J Comput Chem*, 22 (2001) 985.