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# Synthesis and characterization of Co(II), Ni(II), Zn(II) and Cu(II) complexes with a new tetraazamacrocyclic Schiff base ligand containing a piperazine moiety: X-ray crystal structure determination of the Co(II) complex

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# ABSTRACT

Two macrocyclic Schiff base ligands, L<sup>1</sup> [1+1] and L<sup>2</sup> [2+2], have been obtained in a one-pot cyclocondensation of 1,4-bis(2-formylphenyl)piperazine and 1,3-diaminopropane. Unfortunately, because of the low solubility of both ligands, their separation was unsuccessful. In the direct reaction of these mixed ligands (L<sup>1</sup> and L<sup>2</sup>) and the appropriate metal ions only [CoL<sup>1</sup>(NO<sub>3</sub>)]ClO<sub>4</sub>, [NiL<sup>1</sup>](ClO<sub>4</sub>)<sub>2</sub>, [CuL<sup>1</sup>](ClO<sub>4</sub>)<sub>2</sub> and [ZnL<sup>1</sup>(NO<sub>3</sub>)]-ClO<sub>4</sub> complexes have been isolated. All the complexes were characterized by elemental analyses, IR, FAB-MS, conductivity measurements and in the case of the [ZnL<sup>1</sup>(NO<sub>3</sub>)]ClO<sub>4</sub> complex with NMR spectroscopy.

The crystal structure of the Co(II) complex has also been determined and the  $[CoL(NO_3)]^+$  cation contains the Co(II) ion sited in the middle of the macrocyclic cavity *endo*-macrocyclicly coordinated in a distorted octahedral geometry with a N<sub>4</sub>O<sub>2</sub> core, arising from coordination by the four donor nitrogen atoms from the macrocyclic framework and by two oxygen atoms from a bidentate nitrate ion. Neither positive-ion FAB mass spectrometry nor the X-ray crystal structure shows an indication relevant to the [2+2] macrocyclic products.

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# 1. Introduction

Schiff base complexes have remained an important and popular area of research due to their simple synthesis, versatility and diverse range of applications [1]. Macrocyclic Schiff bases have been widely studied due to their selective chelation to certain metal ions depending on the number, type and position of their donor atoms, the ionic radius of the metal ion and the coordinating properties of any counter ions [2–4]. Tetraazamacrocyclic ligands and their metal complexes have attracted interest among coordination chemists [5]. In particular, transition metal complexes of tetradentate Schiff base ligands are good candidates for application in catalysis [6–9] and as biomimetic enzyme models [10–12].

Piperazine is a well known building block for novel supramolecular structures due to the presence of two weakly held terminal amino protons [13]. Of the two readily interconvertible conformations of piperazine, the chair form is thermodynamically more stable since it is 17.2 KJ/mol higher than the boat form [14]. However, the boat form gives mononuclear complexes whereas the chair form gives binuclear complexes with no exogenous bridging for trans-N,N' coordination [15,16].

We have been interested for some time in the design and synthesis of a range of amines, polyamine and Schiff base macrocyclic and macroacyclic complexes [17–20]. We recently have reported some novel Mn(II), Cd(II), Zn(II), Pb(II) and Ag(I) macrocyclic and macroacyclic Schiff base and non-Schiff base complexes containing a piperazine moiety [21–25]. As an extension of this idea, in the present work two macrocyclic Schiff base ligands, L<sup>1</sup> [1+1] and L<sup>2</sup> [2+2], have been obtained in a one-pot synthesis starting from 1,4-bis(2-formylphenyl)piperazine and 1,3-diaminopropane (Scheme 1). We also report a study of the complexation capability of L<sup>1</sup> towards Co(II), Ni(II), Cu(II) and Zn(II) transition metal ions. All attempts to isolate L<sup>2</sup> complexes were unsuccessful.

# 2. Experimental

# 2.1. Starting materials

1,4-Bis(2-formylphenyl)piperazine was synthesized according to a modified literature procedure [26]. Piperazine, 2-fluorobenzaldehyde,

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**Scheme 1.** The synthesis of  $L^1$  and  $L^2$ .

1,3-diaminopropane, solvents and metal salts were purchased from Merck and were used without further purification.

## 2.2. Physical measurements

Infrared spectra were collected on a BIO-RAD FTS-40A spectrophotometer (4000–400 cm<sup>-1</sup>). CHN analyses were carried out using a Perkin–Elmer, CHNS/O elemental analyzer model 2400. <sup>1</sup>H and <sup>13</sup>C NMR spectra were taken on a Bruker Avance 300 MHz spectrometer and a Bruker 400 MHz spectrometer. Electron impact (20 ev) mass spectra for the ligands were recorded on a Shimadzu, QP-1100EX spectrometer. FAB mass spectra were recorded using a Kratos-MS-50T spectrometer connected to a DS90 data system using 3-nitrobenzyl alcohol as the matrix. Conductance measurements were performed using a Hanna HI 8820 conductivity meter.

## 2.3. X-ray crystal structure determination

Vapour diffusion of diethyl ether into a solution of  $[CoL^1(NO_3)]$ -ClO<sub>4</sub> in acetonitrile, afforded brown prismatic crystals suitable for study by X-ray crystallography. Details of the X-ray experiments and crystal data are summarized in Table 1. Measurements were made on a STOE IPDS-2 two circle diffractometer at 296 K, using graphite monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å). The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least-squares and Fourier techniques using SHELXL-97 [27].

#### 2.4. Synthesis

# 2.4.1. Synthesis of 1,4-bis(2-formylphenyl)piperazine

Piperazine (0.43 g, 5 mmol) and potassium carbonate (1.4 g) were added to a *N*,*N*-dimethylformamide solution (80 mL). The mixture was stirred and heated to reflux for 1 h at 180 °C. 2-Fluorobenzaldehyde (1.24 g, 10 mmol) was also added and the mixture refluxed under the nitrogen atmosphere for 48 h. After cooling, the solution was extracted with chloroform. The solution volume was

then reduced to 10 mL and yellow crystals were obtained that were filtered off and then washed with absolute ethanol (Scheme 2). Yield: 2.0 g (70%). *Anal.* Calc. for  $C_{18}H_{18}N_2O_2$ : C, 73.45; H, 6.16; N, 9.52. Found: C, 73.65; H, 6.02; N, 9.73%. M.p. 175 °C. IR (Nujol mull, cm<sup>-1</sup>) 1682 v(C=O). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm)  $\delta_{H}$ : 3.31 (s, 8H); 7.16–7.85 (m, 8H); 10.38 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm)  $\delta_{c}$ : 53.92, 119.20, 123.03, 128.65, 128.84, 135.11, 155.32, 191.16. FAB-MS (*m*/*z*): 295.15 [M+1]<sup>+</sup>.

#### 2.4.2. Synthesis of ligands $(L^1 \text{ and } L^2)$

1,4-Bis(2-formylphenyl)piperazine (0.5 mmol, 0.147 g) in acetonitrile (20 mL) was added dropwise with stirring to a solution of 1,3-propanediamine (0.5 mmol, 0.037 g) in acetonitrile (50 mL). The mixture was stirred and heated to reflux for 24 h, during which time the macrocyclic Schiff base ligand precipitated as a white powder that was filtered off and dried in air. Yield: 0.12 g (75%). *Anal.* Calc. for C<sub>21</sub>H<sub>24</sub>N<sub>4</sub>: C, 75.9; H, 7.2; N, 16.8. Found: C, 75.6; H, 7.2; N, 16.3%. IR (Nujol mull, cm<sup>-1</sup>): 1634 v(C=N), 1596, 1483 v(C=C). EI-MS (m/z): 333 [L<sup>1</sup>+1]<sup>+</sup> and 664 [L<sup>2</sup>]<sup>+</sup>.

# 2.5. Synthesis of the metal complexes

#### 2.5.1. $[ZnL^{1}(NO_{3})]ClO_{4}$

An ethanolic solution (20 mL) of  $Zn(NO_3)_2$ -6H<sub>2</sub>O (0.074 g, 0.25 mmol) was added dropwise with a stirring to a hot solution of the mixed ligands (L<sup>1</sup> and L<sup>2</sup>) (0.083 g, 0.25 mmol) in ethanol (50 mL). The mixture was refluxed for 6 h. The solution was reduced to 20–30 mL, then sodium perchlorate was added and the precipitate that formed was filtered off and dried in air. Yellow crystals were obtained by slow diffusion of Et<sub>2</sub>O vapour into a MeCN solution of the above solid. Yield: 0.095 g (68%). *Anal.* Calc. for C<sub>21</sub>H<sub>24</sub>ClZnN<sub>5</sub>O<sub>7</sub>: C, 45.1; H, 4.3; N, 12.5. Found: C, 45.7; H, 4.4; N, 11.9%. IR (Nujol mull, cm<sup>-1</sup>): 1634, 1650  $\nu$ (C=N), 1597, 1493  $\nu$ (C=C), 1088  $\nu$ (ClO<sub>4</sub>). <sup>1</sup>H NMR (DMSO, ppm)  $\delta_{H}$ : 2.18 (s, 2H), 3.44–3.58 (m, 8H), 4.03 (s, 4H), 7.57–7.86 (m, 8H), 8.79 (s, 2H). <sup>13</sup>C NMR (DMSO, ppm)  $\delta_{C}$ : 27.99, 60.37, 123.73, 125.33, 128.00, 135.01, 137.95, 148.71, 171.87. FAB-MS (*m*/*z*): 497

#### Table 1

Crystal data and structure refinement for [CoL<sup>1</sup>(NO<sub>3</sub>)]ClO<sub>4</sub>.

Complex	[CoL <sup>1</sup> (NO <sub>3</sub> )]ClO <sub>4</sub>
Empirical formula	$C_{21}H_{24}ClCoN_5O_7$
Formula weight	552.83
T (K)	296
Wavelength (Å)	0.71073
Crystal system, space group	monoclinic, P21/c
a (Å)	7.982(3)
b (Å)	15.717(7)
c (Å)	18.105(6)
α (°)	90
$\beta$ (°)	90.89
γ (°)	90
Volume (Å <sup>3</sup> )	2271.28(15)
Z, Calculated density (Mg/m <sup>3</sup> )	4, 1.617
F(0 0 0)	1140
Crystal size (mm <sup>3</sup> )	$0.44 \times 0.36 \times 0.22$
Absorption coefficient (mm <sup>-1</sup> )	0.928
Limiting indices	$-10 \leqslant h \leqslant 10, -19 \leqslant k \leqslant 18, -22 \leqslant l \leqslant 22$
Maximum and minimum transmission	0.7222 and 0.8808
$\theta$ Range for data collection (°)	1.72–26.50
Refinement method	full-matrix least-squares on $F^2$
Data/restraints/parameters	4695/0/316
Goodness-of-fit (GOF) on $F^2$	1.048
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0657, wR_2 = 0.1760$
R indices (all data)	$R_1 = 0.0527, wR_2 = 0.1680$
Largest difference in peak and hole ( $e A^{-3}$ )	1.500 and -0.685

 $[ZnL^{1}+2]ClO_{4}^{+}$ , 400  $[ZnL^{1}]^{+}$ .  $\Lambda_{m}/\Omega^{-1} \text{ cm}^{2} \text{ mol}^{-1}$  (in CH<sub>3</sub>CN): 122 (1:1).

# 2.5.2. [CoL<sup>1</sup>(NO<sub>3</sub>)]ClO<sub>4</sub>

Similarly, a mixture of the ligands  $L^1$  and  $L^2$  (0.083 g, 0.25 mmol) and Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.073 g, 0.25 mmol) was refluxed for 6 h. Brown crystals suitable for X-ray diffraction were obtained by slow diffusion of Et<sub>2</sub>O into an acetonitrile solution of the above solid. Yield: 0.096 g (70%). *Anal.* Calc. for C<sub>21</sub>H<sub>24</sub>ClCoN<sub>5</sub>O<sub>7</sub>: C, 45.6; H, 4.4; N, 12.7. Found: C, 46.1; H, 4.5; N, 12.3%. IR (Nujol mull, cm<sup>-1</sup>): 1629 v(C=N), 1595, 1493 v(C=C), 1093 v(ClO<sub>4</sub>). FAB-MS (*m*/*z*): 490 [CoL<sup>1</sup>]ClO<sub>4</sub><sup>+</sup>, 392 [CoL<sup>1</sup>+1]<sup>+</sup>, 333 [L<sup>1</sup>+1]<sup>+</sup>.  $\Lambda_m/\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup> (in CH<sub>3</sub>CN): 125 (1:1).

# 2.5.3. [CuL<sup>1</sup>](ClO<sub>4</sub>)<sub>2</sub>·0.3C<sub>2</sub>H<sub>5</sub>OH

An ethanolic solution (20 mL) of Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.092 g, 0.25 mmol) was added dropwise with stirring to a hot solution of the mixed ligands (L<sup>1</sup> and L<sup>2</sup>) (0.083 g, 0.25 mmol) in ethanol (50 mL). This mixture was stirred and heated to reflux for 6 h. The solution was reduced and a blue precipitate was formed. This was filtered off and air dried. Blue crystals were obtained by slow diffusion of Et<sub>2</sub>O vapour into a MeCN solution of the above solid. Yield: 0.088 g (58%). *Anal.* Calc. for. C<sub>21</sub>H<sub>24</sub>Cl<sub>2</sub>CuN<sub>4</sub>O<sub>8</sub>·0.3C<sub>2</sub>H<sub>5</sub>OH: C, 42.6; H, 4.9; N, 9.2. Found: C, 43.5; H, 4.4; N, 9.6%. IR (Nujol mull, cm<sup>-1</sup>): 1635, 1653 v(C=N), 1595, 1497 v(C=C), 1098 v(ClO<sub>4</sub>). FAB-MS (*m/z*): 494 [CuL<sup>1</sup>+1]ClO<sub>4</sub><sup>+</sup>, 396 [CuL<sup>1</sup>+1]<sup>+</sup>, 333 [L<sup>1</sup>+1]<sup>+</sup>.  $\Lambda_m/\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup> (in CH<sub>3</sub>CN): 262 (2:1).

# 2.5.4. [NiL<sup>1</sup>](ClO<sub>4</sub>)<sub>2</sub>

Similarly, a mixture of the ligands  $L^1$  and  $L^2$  (0.083 g, 0.25 mmol) and Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.091 g, 0.25 mmol) yielded a product as red crystals. Yield: 0.09 g (61%). *Anal.* Calc. for. C<sub>21</sub>H<sub>24</sub>Cl<sub>2</sub>NiN<sub>4</sub>O<sub>8</sub>: C, 42.7; H, 4.1; N, 9.5. Found: C, 43.5; H, 4.2; N, 9.7%. IR (Nujol mull, cm<sup>-1</sup>): 1647 v(C=N), 1597, 1463 v(C=C), 1075 v(ClO<sub>4</sub>). FAB-MS (m/z): 489 [NiL<sup>1</sup>]ClO<sub>4</sub><sup>+</sup>.  $\Lambda_m/\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup> (in CH<sub>3</sub>CN): 254 (2:1).

# 3. Results and discussion

The ligands  $L^1$  and  $L^2$  were obtained in a one-pot synthesis according to Scheme 1, and they were characterized by IR, elemental analyses and mass spectroscopy. Unfortunately, because of the low solubility of both ligands in common solvents, we were unable to separate these two products. The infrared spectra shows a strong absorption band at 1634 cm<sup>-1</sup> assigned to a C=N stretching vibration, indicating the formation of the Schiff base linkages. Furthermore, the absence of C=O and N-H stretching vibrations in the spectra of the ligands indicate the occurrence of Schiff base condensation. The mass spectrum shows peaks at m/z 333 and m/z 664 corresponding to the L<sup>1</sup> and L<sup>2</sup> macrocyclic ligands, respectively.

Metal complexes have been isolated from the direct reaction of the mixed macrocyclic Schiff base ligands ( $L^1$  and  $L^2$ ) and Co(II), Ni(II), Cu(II) and Zn(II) metal ions. All the isolated  $L^1$  complexes were characterized by elemental analyses, IR, conductivity measurements and FAB-MS, and also by NMR spectroscopy for the [ZnL<sup>1</sup>(NO<sub>3</sub>)]ClO<sub>4</sub> complex. The elemental analyses data are



Scheme 2. The procedure of 1,4-bis(2-formylphenyl)piperazine synthesis.



**Fig. 1.** Structure of the  $[Zn(L^1)NO_3]^+$  cation, along with the NMR numbering.

consistent with the proposed molecular formula that showed the ratio of metal:ligand is 1:1 in these complexes. FAB mass spectroscopic data for all complexes indicate that the compounds are the result of [1+1] condensation reactions.

All the complexes exhibit a v(C=N) vibration in the range 1629– 1653 cm<sup>-1</sup>, corresponding to the imine C=N, and also bands at *ca*. 1597 and 1493 cm<sup>-1</sup>, associated with v(C=C) vibrations from the aromatic rings, are present in the spectra [28]. No bands for free carbonyls or primary diamines are observed, which indicates that complete condensation has occurred. All the complexes exhibit a strong unsplit absorption band centered at 1075–1098 cm<sup>-1</sup> and a medium band at 621 cm<sup>-1</sup>, characteristic of non-coordinated perchlorate [29,30].

The <sup>1</sup>H NMR spectrum of the  $[ZnL^1(NO_3)]ClO_4$  complex in DMSO solvent confirms its proposed structure. The NMR numbering of the atoms is shown in Fig. 1.

The <sup>1</sup>H NMR spectrum of this complex shows a signal due to the <sup>1</sup>H imine resonance at *ca.* 8.79 ppm, a signal due to the  $H_a$  resonance at *ca.* 2.18 ppm and a signal due to the  $H_b$  resonance at *ca.* 4.04 ppm. The absorption signals of aromatic protons appear in the region 7.57–7.86 ppm and the signals in the range 3.45–3.56

are related to piperazine protons. The  $^{13}$ C NMR spectrum shows a peak at 171.87 ppm, corresponding to the imine carbon atoms. In the region corresponding to the signals of aromatic ring carbons (123.73–148.71), sixteen peaks are observed as expected. Two peaks at 27.99 and 60.37 ppm are related to C<sub>a</sub> and C<sub>b</sub> carbon atoms, respectively, and a single peak related to the piperazine ring carbons appears at 51.57 ppm.

The molar conductance values of  $10^{-3}$  M solutions for the Co(II) and Zn(II) complexes, were measured in acetonitrile are in the range characteristic of 1:1 electrolytes in this solvent [31]. It is concluded that one perchlorate anion is out of the coordination sphere as a counter ion. For the Ni(II) and Cu(II) complexes the values, measured under the same conditions, are in the range characteristic of 2:1 electrolytes, indicating that two perchlorate anions are out of the coordination sphere, acting as a counter ions.

#### 3.1. X-ray crystal structure analysis

Crystals of the formula  $[CoL^1(NO_3)]ClO_4$  suitable for X-ray diffraction were obtained. Details of the crystal structure determination for compound  $[CoL^1(NO_3)]ClO_4$  are given in Table 1.

The crystal structure contains the  $[CoL^1(NO_3)]^+$  cation together with a isolated perchlorate ion. The atomic numbering scheme adopted for the  $[CoL^1(NO_3)]^+$  cation together with selected bond distances and angles, are shown in Fig. 2 and Table 2, respectively.

The  $[CoL^1(NO_3)]^+$  cation contains the Co(II) ion sited in the middle of the macrocyclic cavity *endo*-macrocyclicly coordinated in a distorted octahedral geometry with a N<sub>4</sub>O<sub>2</sub> core, arising from coordination by the four donor nitrogen atoms from the macrocyclic framework and by two oxygen atoms from a bidentate nitrate ion. As usually happens, the main distortion of the octahedral geometry is due to the small bite angle of the bidentate nitrate group, 57.23(13)°.

The iminic groups provide the shortest bond to the Co(II) atom [Co(1)-N(3) 2.088(3) Å, Co(1)-N(4) 2.052(3) Å] as usually happens



Fig. 2. The crystal structure of [CoL<sup>1</sup>(NO<sub>3</sub>)]ClO<sub>4</sub>.

#### Table 2

Selected bond lengths (Å) and bond angles (°) for [CoL<sup>1</sup>(NO<sub>3</sub>)]ClO<sub>4</sub>.

Bond lengths (Å)	
Co(1)-N(1)	2.186(3)
Co(1)-N(2)	2.167(3)
Co(1)-N(3)	2.088(3)
Co(1)-N(4)	2.052(3)
Co(1)-O(1)	2.170(3)
Co(1)-O(2	2.189(4)
Bond angles (°)	
N(4)-Co(1)-N(3)	89.63(12)
N(4)-Co(1)-N(2)	91.92(12)
N(3)-Co(1)-N(2)	121.09(11)
N(4)-Co(1)-N(1)	152.94(12)
N(3)-Co(1)-N(1)	83.69(11)
N(2)-Co(1)-N(1)	69.71(11)
N(4)-Co(1)-O(1)	104.42(16)
N(3)-Co(1)-O(1	86.80(12)
N(4)-Co(1)-O(2)	103.19(15)
N(3)-Co(1)-O(2)	143.67(13)
N(2)-Co(1)-O(2)	92.69(12)
N(1)-Co(1)-O(2)	97.55(14)
O(1)-Co(1)-N(1)	101.36(15)
N(2)-Co(1)-O(1)	148.07(12)
O(1)-Co(1)-O(2)	57.23(13)

with this kind of ligand. The Co(II)-N<sub>am</sub> distances are similar to the Co(II)–O ones and have an average value of 2.18 Å.

The ligand shows a nearly plane conformation with a dihedral angle between the planes containing the aromatic groups of 19.84°. Face-to-face  $\pi,\pi$ -stacking interactions have been observed between the aromatic groups of adjacent molecules. The C(1)-C(6) aromatic unit of one molecule interacts with the C(9)-C(13)ring of the molecule in the position -x + 1, +y - 1/2, -z + 1/2. These rings are tilted by 10.64°, with an interplanar distance between them of *ca*. 3.5 Å. There is no possibility for hydrogen bond formation. The perchlorate group shows no interactions with the metal center.

In the equatorial plane, the Co(1)-N(1), Co(1)-N(2), Co(1)-N(4)and Co(1)-O(1) bond lengths (2.186(3), 2.167(3), 2.052 (3) and 2.170(3) Å, respectively) are close to the corresponding distances observed in other Schiff base Co(II) complexes [32,33]. The N(1)-Co(1)-N(2) angle of the six-membered ring is smaller than  $90^{\circ}$  $[N(2)-Co(1)-N(1) = 69.71(11)^{\circ}]$  and there are three larger angles  $[N(4)-Co(1)-N(2) = 91.92(12)^{\circ},$  $N(4)-Co(1)-O(1) = 104.42(16)^{\circ}$ ,  $O(1)-Co(1)-N(1) = 101.36(15)^{\circ}$ ]. The O(1)-Co(1)-N(2)angle 148.07(12)°, deviates considerably from linearity by  $32.93^{\circ}$  due to the smaller chelate bite of the nitrate group. The average value of the Co–N bond length is 2.12 Å, which is similar to that found in other macrocyclic nitrate complexes of octahedral Co(II) [34].

# 4. Conclusion

In spite of steric hindrance due to the structural restriction of piperazine, four new Co(II), Ni(II), Cu(II) and Zn(II) macrocyclic Schiff base complexes were obtained by the direct reaction of the appropriate metal ions, and the reaction mixture derived from cyclocondensation of 1,4-bis(2-formylphenyl)piperazine and 1,3diaminopropane. The crystal structure of the Co(II) complex was determined and it indicates that the Co(II) ion is coordinated by four nitrogen atoms of the tetradentate ligand and two oxygen atoms of the bidentate nitrate group to form a distorted octahedral geometry.

#### 5. Supplementary data

CCDC 735336 contains the supplementary crystallographic data for <yyy>. These data can be obtained free of charge via http:// www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ. UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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