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Reactivity of benzil bis(4-methyl-3-thiosemicarbazone) with cadmium nitrate. Crystal structure of $[Cd(LMe_2H_4)(NO_3)_2][Cd(LMe_2H_4)(NO_3)(H_2O)]NO_3 \cdot H_2O$

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ABSTRACT

The reaction between cadmium nitrate dihydrate and benzil bis(4-methyl-3-thiosemicarbazone), LMe_2H_4, depends on the working conditions. In methanol the reaction gives the novel complex $[Cd(LMe_2H_4)(NO_3)_2][Cd(LMe_2H_4)(NO_3)(H_2O)]NO_3 \cdot H_2O$ (**1**). Its crystal structure shows the presence of two cadmium atoms with different coordination numbers, seven and eight, and the ligands acting as N_2S_2 neutral molecules. One cadmium has the coordination sphere completed by a bidentate nitrato group and a water molecule, whereas the other one is bonded to two bidentate nitrato groups. Both molecules are joined to one nitrate ion and to an additional water molecule by hydrogen bonds. In the presence of lithium hydroxide, the reaction leads to a binuclear complex with the ligand doubly deprotonated $[Cd(LMe_2H_2)]_2$ (**2**). The complexes were characterized by elemental analysis, mass spectrometry, ^{13}C and ^{113}Cd CP/MAS NMR and, in the case of complex **1**, by X-ray diffraction.

1. Introduction

In recent years, the heavy element cadmium has received increased attention due to its impact on plants and toxicity to humans, as well as for the luminescent properties of its complexes [1–6]. Cadmium is an extremely toxic element that is naturally present in the environment and also as a result of human activities. Its toxicity derives from the fact that it is rapidly localized intracellularly, mainly in the liver, and then is bound to metallothionein forming a complex that is slowly transferred to the bloodstream to be deposited in the kidneys. Therefore, it is an interesting area of research to get compounds which are able to form stable complexes with cadmium, because they could be employed as detoxificating agents. For this purpose thiosemicarbazone ligands could be very appropriate as both the ligands and their complexes have shown a wide range of pharmacological properties [7–9]. In particular, cadmium and mercury complexes of the related ligand benzil bis(thiosemicarbazone) have antimicrobial and antifungal activity [10], so it could be expected that these cadmium derivatives also possess some activity and studies are underway.

The coordination number of six for Cd(II) ions is well documented [11–13], but seven-coordinate complexes are scarce [14–17], and they are rarely found together in one compound [18]. An eight-coordinate structure is usually formed with species having larger ion radius, such as lanthanides and third row transition metals, and it is relatively unusual for the Cd(II) ion [19]. As far as we know, there are only two complexes containing simultaneously both seven- and eight-coordinate cadmium(II), a cluster and a complex with the ligand acting as bridge [20,21]. On the other hand, there are only two seven-coordinate cadmium(II) complexes of thiosemicarbazones that have been structurally characterized, one with a tridentate ligand and another containing 2,6-diacetylpyridine bis(^2N-methylthiosemicarbazone) [17,21]. Benzil bis(4-methyl-3-thiosemicarbazone) LMe_2H_4 (see Scheme 1) has four donor atoms that can lead to a tetradentate coordination mode, so there are at least two sites available on the Cd(II) ion for the NO_3^- coordination. This ligand has shown versatile behaviour with $PbPh_2Cl_2$, depending on the pH it acts as a monodeprotonated or dideprotonated ligand, it also acts as a bridge through a sulfur atom [22].

Following our systematic study on the coordination chemistry of thiosemicarbazone ligands with toxic metals [22], here we report the synthesis and structural characterization of two new cadmium coordination compounds derived from benzil bis(4-methyl-3-thiosemicarbazone). Complex **1** is obtained in methanol and it contains two different types of Cd(II) ions. The Cd(1) atom is seven-coordinate by two nitrogen and two sulfur atoms from the ligand and three oxygen from a bidentate nitrato ligand and one water molecule, but in the Cd(2) coordination sphere the water molecule is replaced by an additional bidentate nitrato group. Both units are linked to a nitrate ion and a water molecule by hydrogen bonds. Complex **2** is synthesised in the presence of lithium hydroxide, so the ligand is doubly deprotonated and the cadmium(II) atom could be penta-coordinate in a binuclear structure. To the best of our knowledge, here we report the first thiosemicarbazone

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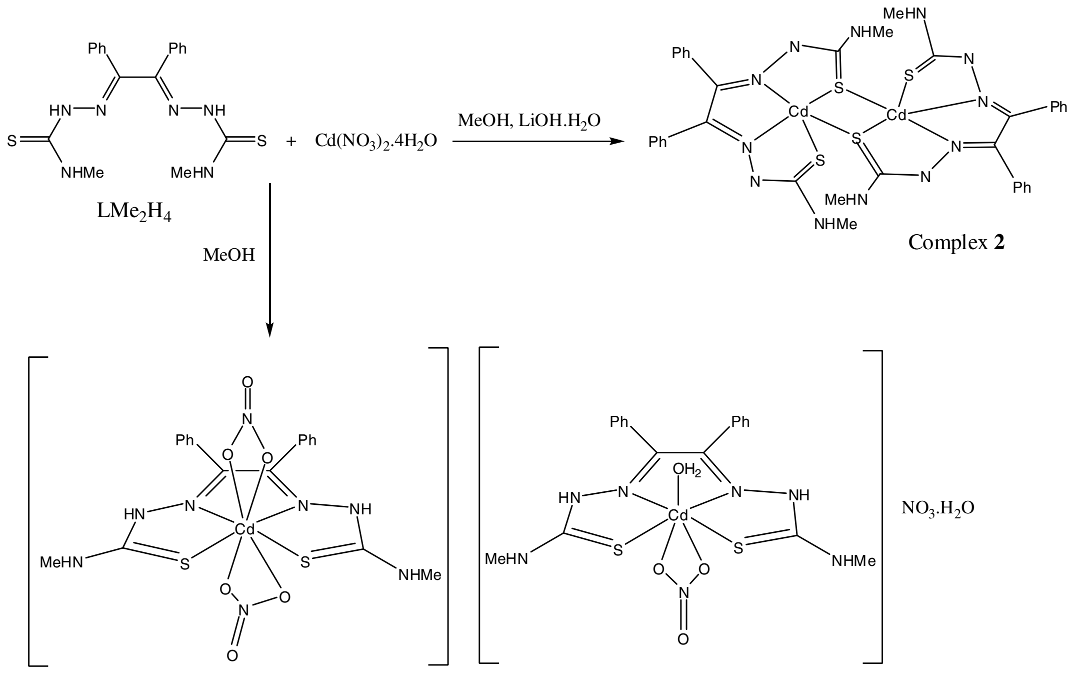

Complex **1**

Scheme 1. A drawing showing the working conditions and the complexes obtained.

complex with eight-coordinate Cd(II). Moreover, it also is the first compound in which two cadmium ions are present with seven and eight coordination spheres in two independent units.

2. Experimental

2.1. Materials and methods

4-Methyl-3-thiosemicarbazide, 1,2-diphenylethanedione and cadmium nitrate tetrahydrate were used as received. Microanalyses were carried out using a Perkin–Elmer 2400 II CHNS/O Elemental Analyser. IR spectra in the 4000–400 cm^{-1} range were recorded as KBr pellets on a Jasco FT/IR-410 spectrophotometer. Fast atom bombardment mass spectra were recorded on a VG Auto Spec instrument using Cs as the fast atom and *m*-nitrobenzylalcohol (*m*NBA) as the matrix. ^{13}C NMR spectra were recorded on a Bruker AMX-300 spectrometer using methanol-d_4 and DMSO-d_6 as solvents and TMS as an internal reference. ^{113}Cd NMR spectra were recorded in the same spectrometer using methanol-d_4 or DMSO-d_6 as solvents and using absolutes as references, the chemical shifts are reported relative to $Cd(ClO_4)_2$ 0.1 M. ^{13}C CP/MAS NMR spectra were recorded at 298 K in a Bruker AV400WB spectrometer equipped with a 4 mm MAS-NMR probe (magic-angle spinning) and obtained using a cross-polarization pulse sequence. For the recorded spectra a contact time of 4 ms was used and recycle delays of 4 s were used. Chemical shifts are reported relative to TMS, using the CH group of adamantano as a secondary reference (29.5 ppm). ^{113}Cd CP/MAS NMR spectra were also recorded in the same spectrometer and the chemical shifts are reported relative to $Cd(ClO_4)_2$ 0.1 M, using $Cd(NO_3)_2 \cdot 4H_2O$ as secondary reference (−100 ppm).

2.2. Synthesis of benzil bis(4-methyl-3-thiosemicarbazone), LMe_2H_4

This molecule was synthesised as reported earlier [23]. Selected spectroscopic data: ^{13}C NMR (DMSO-d_6, 300 MHz, 25 °C): δ/ppm 178.6 (CS), 140.4 (CN), 133.2, 130.3, 129.1, 126.8 (Ph), 31.5 (CH_3). ^{13}C CP/MAS NMR (300 MHz, 25 °C): δ/ppm 177.2 (CS), 139.8 (CN), 130.6, 128.1, 124.7 (Ph), 32.1 (CH_3). FTIR (KBr, cm^{-1}): 3420, 3386, 3342, 3330, 3210, 3151 (s) [ν(NH)], 1608 (w) [ν(CN)], 1581 (s) [$\delta(NH_2)$] and 848 (w) [ν(CS)].

2.3. Synthesis of $[Cd(LMe_2H_4)(NO_3)_2][Cd(LMe_2H_4)(NO_3)(H_2O)]NO_3 \cdot H_2O$ (**1**)

Cadmium nitrate tetrahydrate (0.12 g, 0.39 mmol) dissolved in methanol (15 mL) was added to a LMe_2H_4 (0.15, 0.39 mmol) solution in methanol (15 mL). The mixture was stirred under reflux for 6 h. The solution was concentrated whereby a solid precipitated, which was filtered off, washed with methanol and dried in vacuo. M.p.: 187 °C. The compound was isolated as a yellow solid (0.16 g, 64%). Suitable crystals for X-ray analysis were obtained by slow evaporation of the mother liquor. M.p.: 187 °C. *Anal.* Calc. for $C_{36}H_{42}N_{16}O_{14}S_4Cd_2$ (1275.9): C, 33.88; H, 3.32; N, 17.57; S, 10.03. Found: C, 33.75; H, 3.44; N, 17.16; S, 10.19%. ^{13}C NMR (300 MHz, methanol-d_4): δ/ppm 181.0 (CS), 148.8 (CN), 131.9, 130.9, 130.7, 130.3, 130.1, 129.8, 129.5, 129.2, 128.1, 128.0 (Ph), 32.1 (CH_3). ^{113}Cd NMR (300 MHz, methanol-d_4): δ/ppm 167.3 ^{13}C CP/MAS NMR (300 MHz): δ/ppm 180.2 (CS), 148.1, 147.0 (CN), 134.1, 131.9, 130.8, 129.0, 128.1, 127.1 125.8 (Ph), 35.3, 31.4 (CH_3). ^{113}Cd CP/MAS NMR (300 MHz): δ/ppm 186.3, 144.3. MS (FAB$^+$): *m/z* 496.8 ($[Cd(LMe_2H_3)]^+$, 100%). FTIR (KBr, cm^{-1}) 3446, 3344, 3222 (m) [ν(NH)], 1617 (w) [ν(CN)], 1574 (s) [δ(NCS)], 1384 (s) [ν(NO)], 819 (w) [ν(CS)].

2.4. Synthesis of $[Cd(LMe_2H_4)]_2$ (**2**)

The reaction was carried out as described previously, but in the presence of $LiOH \cdot H_2O$ (0.04 g, 0.79 mmol). Complex **2** was isolated as an orange solid (0.17 g, 88%), washed with methanol and dried in vacuo. M.p.: 247 °C. *Anal.* Calc. for $C_{36}H_{36}N_{12}S_4Cd_2$ (988.8): C, 43.68; H, 3.67; N, 16.98; S, 12.96. Found: C, 43.52; H, 3.65; N, 16.84; S, 12.87%. ^{113}Cd NMR (300 MHz, DCM + $CDCl_3$): δ/ppm 410.4. ^{13}C CP/MAS NMR (300 MHz): δ/ppm 178.7, 162.5, 158.7

Table 1
Crystal data and structure refinement for $[Cd(LMe_2H_4)(NO_3)_2][Cd(LMe_2H_4)(NO_3)(H_2O)]NO_3 \cdot H_2O$ (**1**)

Empirical formula	$C_{36}H_{42}Cd_2N_{16}O_{14}S_4$
Formula weight	1275.90
Temperature (K)	100(2)
Wavelength (Å)	1.54178
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	9.396(4)
b (Å)	12.069(5)
c (Å)	23.862(11)
α (°)	83.65(3)
β (°)	86.63(3)
γ (°)	68.10(2)
Volume (Å^3)	2495.0(19)
Z	2
D_{calc} (Mg/m^3)	1.698
Absorption coefficient (mm^{-1})	9.072
$F(000)$	1284
Crystal size (mm)	0.14 × 0.12 × 0.06
θ Range for data collection (°)	1.86–66.67
Index ranges	$-11 \leqslant h \leqslant 11$, $-14 \leqslant k \leqslant 14$, $-28 \leqslant l \leqslant 28$
Reflections collected	19983
Independent reflections [R_{int}]	8342 [0.0427]
Completeness to theta = 66.67° (%)	94.4
Absorption correction	semi-empirical from equivalents
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	8342/0/661
Goodness-of-fit on F^2	1.028
Final R indices $I > 2\sigma(I)$	$R_1 = 0.0371$, $wR_2 = 0.0960$
R indices (all data)	$R_1 = 0.0447$, $wR_2 = 0.1020$
Largest difference in peak and hole (e Å^{-3})	0.862 and −0.760

(CS), 146.0 (CN), 137.5, 135.5, 132.8, 130.4, 128.9, 127.0 (Ph), 29.9 (CH_3). ^{113}Cd CP/MAS NMR (300 MHz): δ/ppm 425.4. MS (FAB$^+$): m/z 990.8 ([M+1]$^+$, 31%), 496.9 ($[CdLMe_2H_3]^+$, 100%). FTIR (KBr, cm^{-1}) 3415, 3370 (s) [ν(NH)], 1618, 1600 (w) [ν(CN)], 1561 (s) [δ(NCS)], 836 (w) [ν(CS)].

2.5. X-ray crystallography

Data for **1** (see Table 1) were collected at 100 K with a Bruker SMART 6K CCD area-detector three-circle diffractometer with a MAC Science Co., Ltd. Rotating Anode (Cu Kα radiation, λ = 1.54178 Å) generator. The unit cell parameters were obtained by full-matrix least-squares refinements of 8342 independent reflections. The structures were solved by direct methods (SHELXS-97), completed with difference Fourier syntheses, and refined with full-matrix least squares using SHELXL-97 minimizing $\omega(F_o^2 - F_c^2)^2$. Weighted R factors (R_w) and all goodness-of-fit S are based on F^2; conventional R factors (R) are based on F, giving $R_1 = 0.0371$, $wR_2 = 0.0960$ using 19983 reflections with $I > 2\sigma(I)$ [24,25]. All non-hydrogen atoms were refined with anisotropic displacement parameters. All scattering factors and anomalous dispersions factors are contained in the SHELXTL 6.10 program library. All the hydrogen atoms were included in geometric positions except those of the water molecule, which were located by difference maps and refined isotropically.

3. Results and discussion

3.1. Synthesis

The reaction between LMe_2H_4 and cadmium nitrate depends on the presence of a basic medium (Scheme 1). The reaction carried out in methanol gives a crystalline solid (**1**), which analytical data agree with a 1:1 cadmium:ligand ratio, confirmed by its FAB mass spectrum (Fig. 1a), and the presence of two nitrate groups and one water molecule. However, the reaction in the presence of lithium hydroxide yields complex (**2**), which analytical data are in agreement with a 1:1 ratio and the absence of nitrate groups. The FAB mass spectrum (Fig. 1b) shows a peak at 494.9 corresponding to $[Cd(LMe_2H_3)]^+$ and another one at 990.8, relatively intense, corresponding to $[Cd_2(LMe_2H_2)_2+1]^+$, suggesting a binuclear structure for this complex.

3.2. Spectroscopic studies

The shifts observed in the ν(CN) and ν(CS) bands in the IR spectra of both complexes are in accordance with the ligand being bonded to the cadmium through the imine nitrogen and the sulfur atoms, acting as a tetradentate chelate in both complexes. Moreover, the IR spectrum of **1** shows a sharp and strong band at 1385 cm^{-1} corresponding to ν(N–O) of the NO_3^- group. Several bands in the ν(N–H) and δ(N–H) regions are observed, which agrees with the ligand being in the neutral form. By contrast, the spectrum of **2** only shows two bands in the amine tension region and the absence of any band assignable to the nitrate group.

Complex **2** is sparingly soluble in all common solvents and its ^{1}H and ^{13}C NMR spectra are useless, indicating the decomposition. Therefore ^{13}C and ^{113}Cd CP/MAS of both complexes were measured for comparison. The ^{13}C CP/MAS NMR spectrum of **1** shows one signal corresponding to the thioamide carbon atom, two to the imine, three to the methine carbon and seven corresponding to the aromatic carbon atoms. By contrast, the spectrum of complex **2** shows three signals corresponding to the thioamide group, one to the imine and the methine carbons and six to the aromatic carbon atoms. These differences can be explained due to the presence of ligands with a different behaviour in each complexes: in complex **1** the two ligands act in the same way, but there are a slight differences in the bonds lengths and angles; in complex **2** at least one sulfur atom is bonded to two cadmiums, acting as a bridge as observed in the organolead(IV) derivative and in the binuclear cadmium complex obtained from benzil bis(thiosemicarbazone) [22,26].

It is well known that the ^{113}Cd chemical shift is very sensitive to changes in the coordination number of cadmium as well as to the nature of the bonding, so it is a useful tool to determine the environment of this metal in a complex. Replacement of sulfur by nitrogen and oxygen atoms tends to give greater shielding [27–30] and a decrease in the coordination number tends to give greater deshielding [31,32]. ^{113}Cd CP/MAS NMR spectrum of complex **1** shows two signals at 186.3 and 144.3 ppm, whereas complex **2** only shows a signal at 425.4 ppm. These data are consistent with two cadmium atoms with different environments in complex **1** and only one kind of geometry around the metal ion in complex **2**. The values of the chemical shifts agree with the presence of seven and eight-coordinate cadmium atoms, with several oxygen atoms in the coordination sphere of both Cd(II) centres in complex **1**, while a lower coordination number and the absence of oxygen atoms is suggested for complex **2** [11,13]. The ^{113}Cd NMR spectrum of **1** in methanol only exhibits one signal at 167.3 ppm, which is almost the average between the solid state signals, indicating partial substitution of the nitrato ligands and/or the water molecule by solvent molecules, giving the same coordination sphere. The ^{113}Cd NMR spectrum of complex **2** in DCM shows the signal has been slightly displaced to 410 ppm, which indicates that the coordination sphere remains in this solvent and it is in the range expected for S_3N_2 coordination.

3.3. Crystal structure of $[Cd(LMe_2H_4)(NO_3)_2][Cd(LMe_2H_4)(NO_3)(H_2O)]NO_3 \cdot H_2O$ (**1**)

The X-ray structural analysis of complex **1** revealed the presence of two units, each containing one cadmium atom and one li-

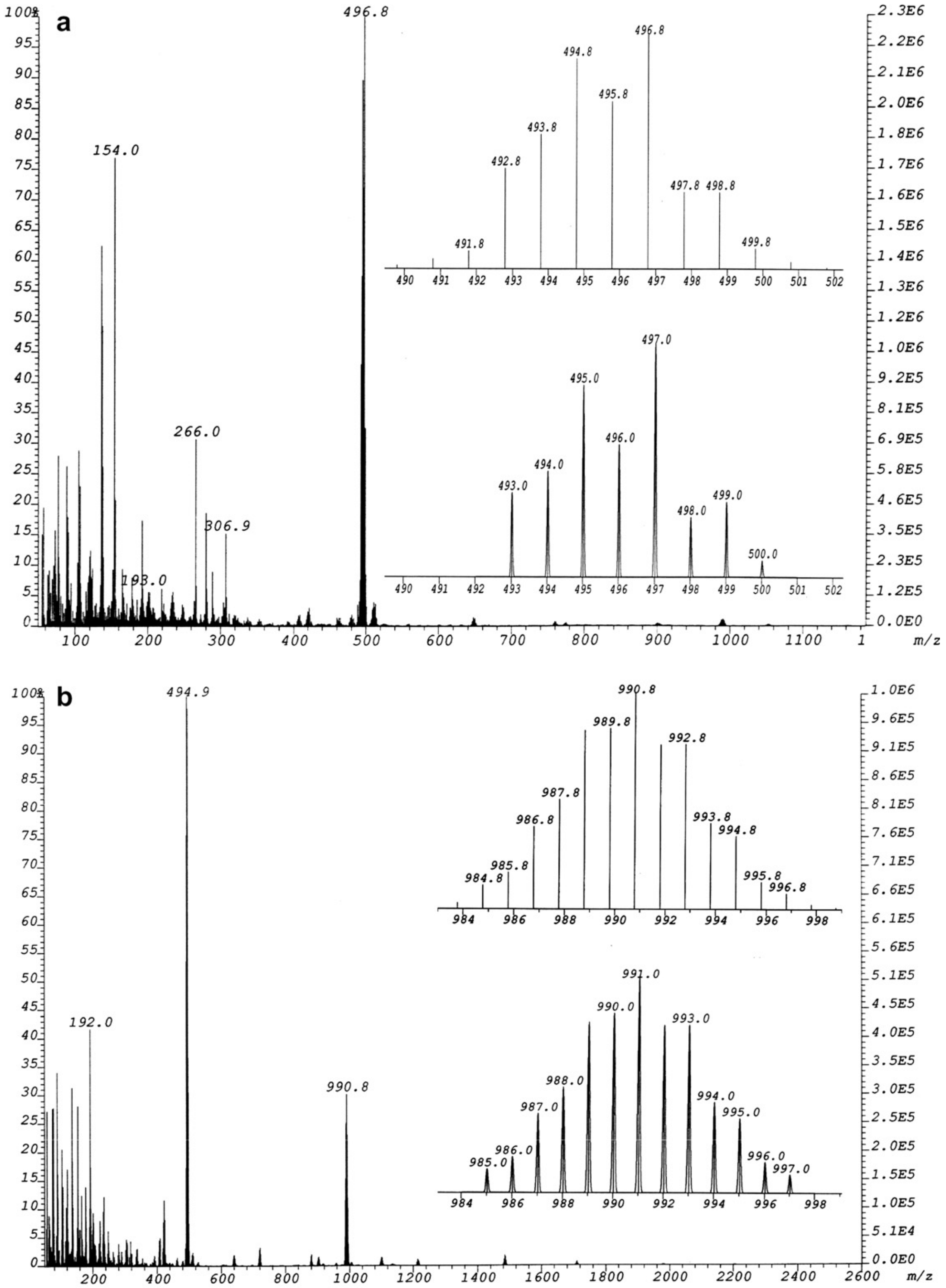

Fig. 1. (a) FAB mass spectrum of complex **1** (theoretical and experimental isotope distribution in the inset); (b) FAB mass spectrum of complex **2** (theoretical and experimental isotope distribution in the inset).

gand, with one nitrate group and a water molecule linking them (Fig. 2). The two Cd(II) ions have different coordination environments with the ligand acting, as it could be expected for this compound, as a N_2S_2 chelate and where the coordination spheres are completed by oxygen atoms. The $N_2S_2O_3$ coordination environment of the seven-coordinate Cd(1) (Fig. 3) is made up of the imine nitrogen and the sulfur atoms of the two arms of LMe_2H_4, one oxygen from a water molecule and two oxygens from a bidentate nitrato anion. The environment of the eight-coordinate Cd(2) is similar (Fig. 4), the difference being that the water molecule has been substituted by another nitrato ligand coordinated in a bidentate fashion.

The hepta-coordinate cadmium has a geometry based on a capped distorted octahedron, with the water molecule and the nit-

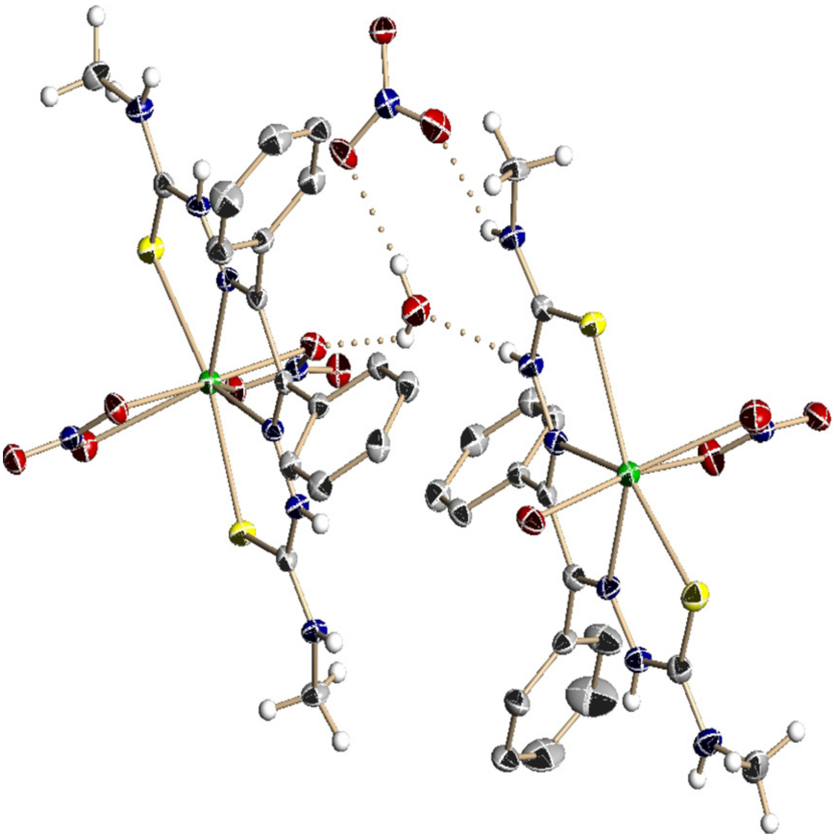

Fig. 2. The crystal structure of **1** at 50% probability including the intermolecular hydrogen bonds.

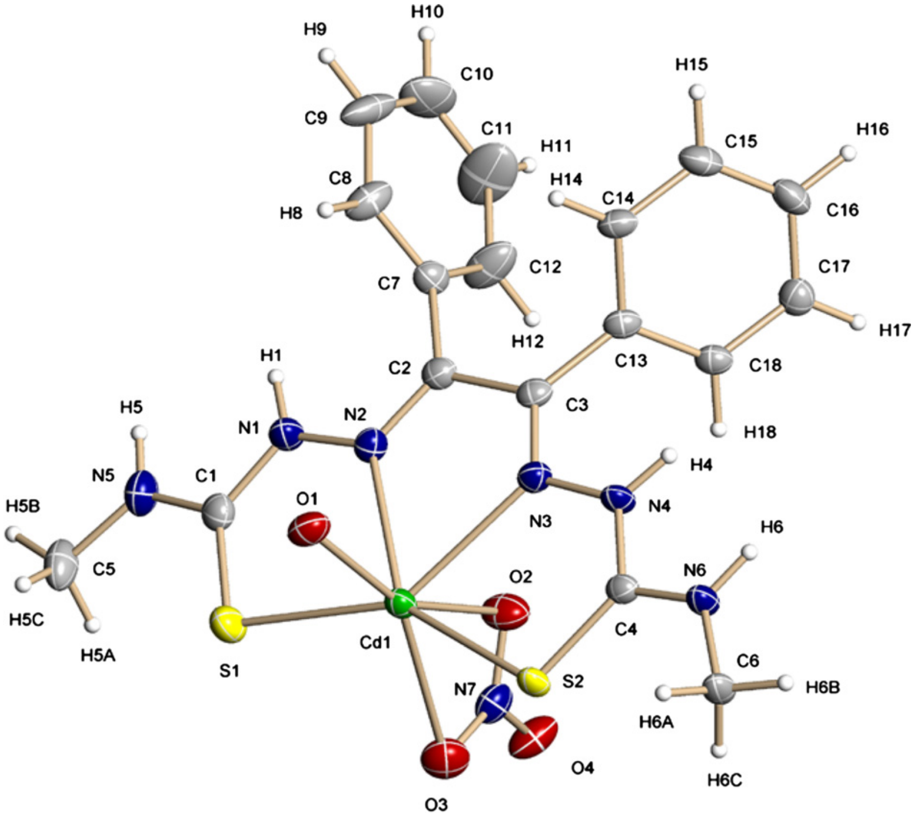

Fig. 3. The molecular structure of the complex cation in **1** with ellipsoids at 50%.

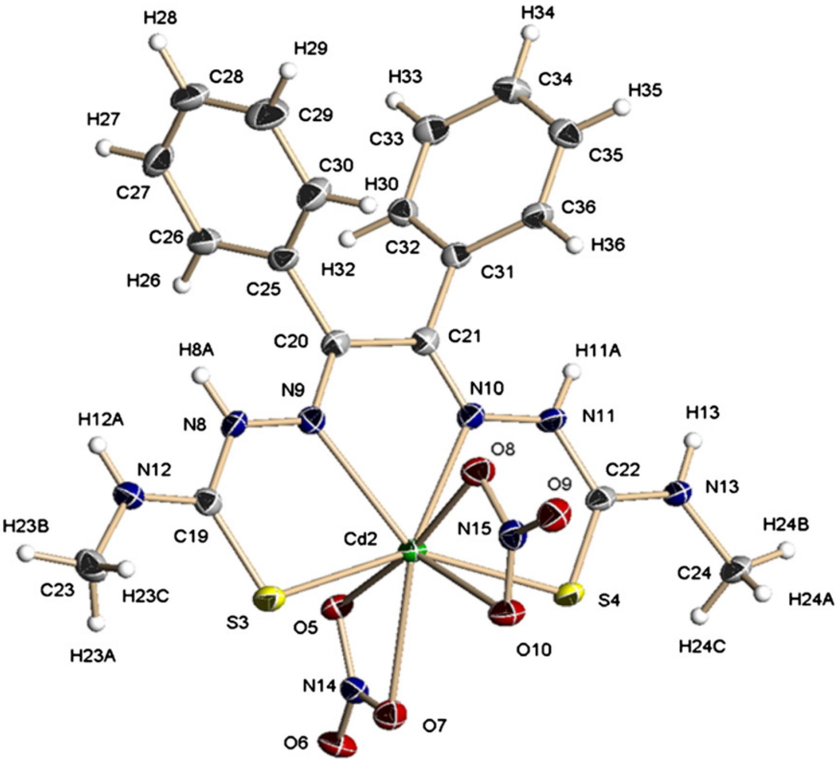

Fig. 4. The molecular structure of the neutral unit in **1** with ellipsoids at 50%.

rato group located above and under the tetradentate ligand, which is virtually planar (Fig. 3). The angle of 173.35° formed by the N atom of the bidentate nitrato group, the Cd atom and the water molecule is very close to that expected for a *trans* disposition. The Cd(1)–OH_2 bond length [2.320(3) Å] (see Table 2) is in the range observed in other Cd(II) complexes that contain nitrato ions and water molecules in their coordination sphere [20]. The Cd–O distances from the bidentate nitrato group, at 2.484(3) and 2.647(3) Å, fall within the range observed for Cd(II) compounds containing bidentate nitrato ligands and show a significant asymmetry $\delta = 0.16$ Å, which is of the same order as those observed in other cadmium complexes [14].

Cd(2) is eight-coordinate, with two nitrogen and two sulfur atoms from the benzil bis(thiosemicarbazone) ligand and four oxygen atoms from two bidentate nitrato ions (Fig. 4), which is not a common coordination number for Cd(II). The arrangement of the eight atoms around the Cd(II) centre corresponds to a distorted dodecahedron, with the angle between the N_2S_2Cd and O_4Cd planes very close to 90°. The Cd–O distances show two asymmetrically bidentate nitrato ligands with short Cd–O distances of 2.425(3) and 2.393(3) Å, and longer ones of 2.598(3) and 2.698(3) Å [33,34].

The presence of two distances for Cd–N and Cd–S bonds in each unit agrees with the distorted geometry. The Cd–N distances are not identical in both units, but they are in the range expected for a cadmium imine bond. The average bond lengths of Cd–S bonds in the seven and eight-coordinate structures are 2.583 and 2.609 Å, respectively, the difference of which arises from the increase in coordination number of the cadmium(II) ion in this complex. Similar variations are observed for the Cd–N distances.

The pseudomacrocyclic coordination mode of the ligand affords three five-member chelate rings. The bis(thiosemicarbazone) cores can be considered planar with a maximum deviation from the

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

Cd(1)–O(1)	2.320(3)	Cd(2)–O(7)	2.598(3)
Cd(1)–N(2)	2.429(3)	Cd(2)–S(4)	2.6070(15)
Cd(1)–N(3)	2.438(3)	Cd(2)–S(3)	2.6110(14)
Cd(1)–O(2)	2.484(3)	Cd(2)–O(10)	2.698(3)
Cd(1)–S(2)	2.5753(14)	S(1)–C(1)	1.690(4)
Cd(1)–S(1)	2.5912(14)	S(2)–C(4)	1.699(4)
Cd(1)–O(3)	2.647(3)	C(1)–N(1)	1.367(5)
Cd(2)–O(8)	2.393(3)	C(2)–N(2)	1.297(5)
Cd(2)–O(5)	2.425(3)	C(3)–N(3)	1.295(5)
Cd(2)–N(9)	2.439(3)	C(4)–N(4)	1.368(5)
Cd(2)–N(10)	2.457(3)		
O(1)–Cd(1)–N(2)	84.65(10)	O(8)–Cd(2)–N(10)	79.49(9)
O(1)–Cd(1)–N(3)	88.09(10)	O(5)–Cd(2)–N(10)	93.36(9)
N(2)–Cd(1)–N(3)	65.50(10)	N(9)–Cd(2)–N(10)	65.13(10)
O(1)–Cd(1)–O(2)	157.43(10)	O(8)–Cd(2)–O(7)	138.40(8)
N(2)–Cd(1)–O(2)	74.24(10)	O(5)–Cd(2)–O(7)	50.78(8)
N(3)–Cd(1)–O(2)	76.07(10)	N(9)–Cd(2)–O(7)	134.52(9)
O(1)–Cd(1)–S(2)	92.81(8)	N(10)–Cd(2)–O(7)	132.63(9)
N(2)–Cd(1)–S(2)	138.92(8)	O(8)–Cd(2)–S(4)	96.55(8)
N(3)–Cd(1)–S(2)	73.45(8)	O(5)–Cd(2)–S(4)	86.78(7)
O(2)–Cd(1)–S(2)	97.83(8)	N(9)–Cd(2)–S(4)	138.07(7)
O(1)–Cd(1)–S(1)	88.53(8)	N(10)–Cd(2)–S(4)	72.99(7)
N(2)–Cd(1)–S(1)	73.75(8)	O(7)–Cd(2)–S(4)	74.94(7)
N(3)–Cd(1)–S(1)	139.25(8)	O(8)–Cd(2)–S(3)	91.53(7)
O(2)–Cd(1)–S(1)	93.06(8)	O(5)–Cd(2)–S(3)	90.04(7)
S(2)–Cd(1)–S(1)	147.29(3)	N(9)–Cd(2)–S(3)	73.39(8)
O(1)–Cd(1)–O(3)	151.97(9)	N(10)–Cd(2)–S(3)	138.50(7)
N(2)–Cd(1)–O(3)	115.23(10)	O(7)–Cd(2)–S(3)	78.85(7)
N(3)–Cd(1)–O(3)	117.52(10)	S(4)–Cd(2)–S(3)	148.50(3)
O(2)–Cd(1)–O(3)	49.62(9)	O(8)–Cd(2)–O(10)	49.98(8)
S(2)–Cd(1)–O(3)	84.60(8)	O(5)–Cd(2)–O(10)	139.23(8)
S(1)–Cd(1)–O(3)	79.23(8)	N(9)–Cd(2)–O(10)	121.93(9)
O(8)–Cd(2)–O(5)	170.79(8)	N(10)–Cd(2)–O(10)	118.26(9)
O(8)–Cd(2)–N(9)	78.20(10)	O(7)–Cd(2)–O(10)	88.50(8)
O(5)–Cd(2)–N(9)	93.58(9)	S(4)–Cd(2)–O(10)	79.53(7)
S(3)–Cd(2)–(10)	82.66(7)		

Table 3
Intermolecular hydrogen bonds (Å, °) in complex **1**

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	<(DHA)
O(14)–H(14B)···O(5)	0.73(6)	2.35(5)	2.929(4)	136(5)
O(14)–H(14A)···O(12)	0.82(6)	2.14(6)	2.961(5)	173(6)
N(13)–H(13)···N(16)#1	0.88	2.58	3.427(4)	161.2
N(13)–H(13)···O(12)#1	0.88	1.97	2.833(4)	167.3
N(12)–H(12A)···O(9)#2	0.88	2.23	2.995(4)	145.7
N(11)–H(11A)···O(11)#1	0.88	2.14	2.926(4)	147.9
N(8)–H(8A)···O(9)#2	0.88	2.24	3.028(4)	148.4
N(6)–H(6)···O(13)	0.88	2.20	2.882(4)	133.5
N(5)–H(5)···O(4)#3	0.88	2.21	2.989(5)	147.5
N(4)–H(4)···O(14)	0.88	2.09	2.877(4)	148.4
N(1)–H(1)···O(4)#3	0.88	2.21	2.976(4)	144.6

Symmetry transformations used to generate equivalent atoms: #1 $x + 1, y, z$; #2 $-x + 1, -y + 1, -z + 1$; #3 $-x + 2, -y + 2, -z$.

main plane of 0.0760 Å for C(3) in the seven-coordinate unit and a 0.0616 Å deviation for the N(9) atom in the eight-coordinate one. In accordance with the symmetry of the ligand, the bond distances and angles in both thiosemicarbazone moieties in both units are very similar. The bond lengths agree well with an imine–thione form of the ligand, but with considerable electronic delocalisation through the thiosemicarbazone backbone. Thus, the thione bond distances of ca. 1.69 Å are intermediate between a theoretical C–S single and double bond (1.82 and 1.56 Å, respectively) as occurs with the N–N– bonds (ca. 1.35 vs. 1.44 Å calculated for a single N–N) and the three C–N bonds of each 4-methyl-3-thiosemicarbazone branch.

The two units are connected through hydrogen bonds involving the amino groups, the non-coordinated nitrate ion and the crystallization water molecule (Fig. 2). Finally, the molecules are held together in the crystal packing through an extended network of intermolecular hydrogen bonds involving the same groups (see Table 3).

4. Conclusions

The importance of the working conditions in the structure of coordination complexes from a bis(thiosemicarbazone) is reflected in the complexes obtained by the reaction of cadmium nitrate and benzil bis(4-methyl-3-thiosemicarbazone). Complex **1** is obtained in methanol and it contains two different types of Cd(II) ions. The Cd(1) atom is seven-coordinate by two nitrogen and two sulfur atoms from the ligand and three oxygens from a bidentate nitrato ligand and one water molecule, but the Cd(2) coordination sphere expands to eight by the exchange of the water molecule by an additional bidentate nitrato group. Both units are linked to a nitrate ion and a water molecule by hydrogen bonds. Complex **2** is synthesised in the presence of lithium hydroxide, so the ligand is doubly deprotonated and the cadmium(II) atom could be penta-coordinate in a binuclear structure. To the best of our knowledge, complex **1** is the first thiosemicarbazone complex containing eight-coordinate Cd(II). Moreover, it also is the first example in which two cadmium ions show seven and eight coordination in two independent units within the same crystal.

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Appendix A. Supplementary data

CCDC 670708 contains the supplementary crystallographic data for **1**. 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. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2008.04.036.

References

[1] J.E. Fegusson, The Heavy Elements: Chemistry Environmental Impact and Health Effects, Pergamon Press, Oxford, 1990.
[2] G. Parkin, Chem. Rev. 104 (2004) 699.
[3] Y.Q. Huang, B. Ding, H.B. Song, B. Zhao, P. Ren, P. Cheng, H.G. Wang, D.Z. Liao, S.P. Yan, Chem. Commun. (2006) 4906.
[4] L. Yi, B. Ding, B. Zhao, P. Cheng, D.Z. Liao, S.P. Yan, Z.H. Jiang, Inorg. Chem. 43 (2004) 33.
[5] L. Yi, B. Ding, B. Zhao, P. Cheng, D.Z. Liao, S.P. Yan, Z.H. Jiang, H.B. Song, H.G. Wang, J. Chem. Soc., Dalton Trans. (2006) 665.
[6] M. Kadarkaraisamy, A.G. Sykes, Polyhedron 26 (2007) 1323.
[7] D. Sriram, P. Yogeeswari, R. Thirumurugan, R.K. Pavana, J. Med. Chem. 49 (2006) 3448.
[8] H. Beraldo, D. Cambino, Mini-Rev. Med. Chem. 4 (2004) 31.
[9] N.C. Kasuga, K. Onodera, S. Nakano, K. Hayashi, K. Nomiya, J. Inorg. Biochem. 100 (2006) 1176.
[10] F. Zani, D.G. Calatayud, E. López-Torres, M.A. Mendiola, J.R. Procopio, EUROBIC 8 Conference Book, Aveiro, Portugal, 2006, p. 153, ISBN: 989-20-0305-5.
[11] E. Bermejo, A. Castiñeiras, L.M. Fostiak, I. García Santos, J.K. Swearingen, D.X. West, Polyhedron 23 (2004) 2303.
[12] E. López-Torres, M.A. Mendiola, J. Rodríguez-Procopio, M.T. Sevilla, E. Colacio, J.M. Moreno, I. Sobrados, Inorg. Chim. Acta 323 (2001) 130.
[13] M.R. Bermejo, A.M. González-Noya, M. Martínez-Calvo, R. Pedrido, M. Maneiro, M.I. Fernández, E. Gómez-Fórneas, Z. Anorg. Allg. Chem. 633 (2007) 1911.
[14] A. Tamayo, E. Oliveira, B. Covelo, J. Casabó, L. Escrische, C. Lodeiro, Z. Anorg. Allg. Chem. 633 (2007) 1809.
[15] J. Granifo, M.T. Garland, R. Baggio, Inorg. Chem. Commun. 7 (2004) 77.
[16] M.A. Ali, A.H. Mirza, W.B. Ejau, P.V. Bernhardt, Polyhedron 25 (2006) 3337.
[17] J. Chakraborty, B. Samanta, G. Pilet, S. Mitra, Inorg. Chem. Commun. 10 (2007) 40.
[18] H-S. Wang, W. Shi, J. Xia, H.-B. Song, H.-G. Wang, P. Cheng, Inorg. Chem. Commun. 10 (2007) 856.
[19] D.B. Cordes, L.R. Hanton, Inorg. Chem. Commun. 8 (2005) 967.
[20] G. Anantharaman, M.G. Walawalkar, R. Murugaved, B. Gäbor, R. Herbst-Irmer, M. Baldus, B. Angerstein, H.W. Roesky, Angew. Chem., Int. Ed. 42 (2003) 4482.
[21] J.S. Casas, A.E. Castellano, M.S. García-Tasende, A. Sánchez, J. Sordo, J. Zukerman-Schpector, Z. Anorg. Allg. Chem. 523 (1997) 825.
[22] D.G. Calatayud, E. López-Torres, M.A. Mendiola, Inorg. Chem. 46 (2007) 10434. and refs therein.
[23] D.G. Calatayud, F.J. Escolar, E. López-Torres, M.A. Mendiola, Helv. Chim. Acta 90 (2007) 2201.
[24] G.M. Sheldrick, Acta Crystallogr., Sect. A 46 (1990) 467.
[25] G.M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, Universität Göttingen, Göttingen, Germany, 1997.
[26] E. López-Torres, M.A. Mendiola, C.J. Pastor, B. Souto Pérez, Inorg. Chem. 43 (2004) 5222.
[27] P.S. Marchetti, S. Bank, T.W. Bell, M.A. Kennedy, P.D. Ellis, J. Am. Chem. Soc. 111 (1989) 2063.

[28] M.F. Summers, Coord. Chem. Rev. 86 (1988) 43.
[29] R. Pedrido, M.R. Bermejo, M.J. Romero, M. Vázquez, A.M. González-Moya, M. Maneiro, M.J. Rodríguez, M.I. Fernández, J. Chem. Soc., Dalton Trans. (2005) 572.
[30] R. Pedrido, M.J. Romero, M.R. Bermejo, A.M. González-Moya, I. García-Lema, G. Zaragoza, Chem. Eur. J. 14 (2008) 500.
[31] D.L. Reger, S.M. Meyers, S.S. Mason, A.L. Rheingold, B.S. Haggerty, P.D. Ellis, Inorg. Chem. 34 (1995) 4996.
[32] M.L. Helm, L.L. Hill, J.P. Lee, D.G. Van Derveer, G.J. Grant, J. Chem. Soc., Dalton Trans. (2006) 3534.
[33] S.A. Barnett, A.J. Blake, N.R. Champness, C. Wilson, J. Chem. Soc., Dalton Trans. (2005) 3852.
[34] E.R. Acuña-Cueva, R. Faure, N.A. Illán-Cabeza, S.B. Jiménez-Pulido, M.N. Moreno-Carretero, M. Quirós-Olozábal, Inorg. Chim. Acta 342 (2003) 209.