



*Dedicated to Professor Ionel Haiduc
on the occasion of his 80th anniversary*

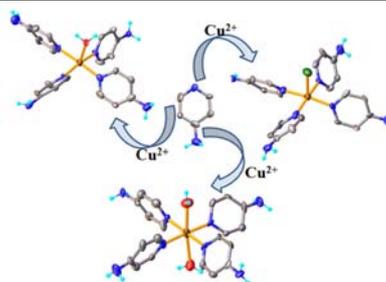
UNEXPECTED CO-CRYSTALLIZATION OF THREE SPECIES OF CU(II) COMPLEXES WITH DIFFERENT COORDINATION GEOMETRY

Mirela-Fernanda ZALTARIOV and Sergiu SHOVA*

“Petru Poni” Institute of Macromolecular Chemistry, Aleea Gr. Ghica Voda 41A, 700487 Iași, Roumania

Received December 16, 2016

A copper(II) compound having an ionic crystal structure resulting from the co-crystallization of three types of complexes in which 4-aminopyridine acts as monodentate ligand was obtained. Physicochemical properties were investigated by spectroscopic (UV-Vis diffuse reflectance, fluorescence, IR) and elemental analyses. Single-crystal X-ray diffraction data revealed different coordination geometry of the Cu^{2+} ion: N_4O or N_4Cl square pyramidal and N_4O_2 octahedral within the complexes.



INTRODUCTION

Metallic complexes with N-donor heterocyclic ligands are of great interest for a wide variety of applications ex. biology, medicine, pharmacology,^{1,2} catalysis and magnetism.³⁻⁵ The number, the nature and the relative position of donor atoms in the structure of such ligands allow a good control of stereochemistry of the metal centers and result in the structural diversity of coordination compounds.

The role of such complexes in many biological systems as components of vitamins or drugs⁶ or as new anti-inflammatory, anti-tumor and antibacterial compounds⁷ was also established. Continued interest in studying such complexes is closely linked to understanding mimic processes of a large number of metalloproteins.⁸

4-aminopyridine and its derivatives⁹ make up an important class of compounds with clinical efficacy

and reduced toxicity as anti-amnesic,¹⁰ in multiple sclerosis by restoration of conduction in demyelinated axons due to rapidly activating voltage gated potassium channels¹ and enhancement of the synaptic transmission,¹¹ while their metal complexes have been found to possess a wide applicability in hydrogenation and epoxidation reactions as asymmetric catalysts.¹²

Here we report on the synthesis, structural characterization and photoluminescence properties in solid state of a new 4-aminopyridine copper(II) compound. The obtained Cu(II) compound showed an unusual structure resulting from the co-crystallization of three different species of complexes.

RESULTS AND DISCUSSION

The copper(II) compound was synthesized by the direct complexation reaction of 4-aminopyridine

* Corresponding author: shova@icmpp.ro

with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in methanol/water mixture. The complex was obtained as single crystals, the structure being confirmed by FTIR, UV-vis diffuse reflectance and fluorescence, as well as by X-ray single-crystal diffraction analyses. In the IR spectrum of Cu(II) compound the band at 1649 cm^{-1} characteristic for stretching vibration of $\text{C}=\text{N}$ of 4-aminopyridine is blueshifted by 10 cm^{-1} due to the coordination of copper ion. The other four bands of pyridine between $1433\text{--}1598\text{ cm}^{-1}$ are also blueshifted confirming the coordination through nitrogen atom from the ring. The stretching bands assigned to the $-\text{NH}_2$ groups at 3302 and 3437 cm^{-1} are also shifted to lower wavenumbers proving the involving of them in the hydrogen bond formation. The presence of the aryl- NH_2 group is also proved by the band at 1354 cm^{-1} , while N-H deformation vibration can be seen at 1616 cm^{-1} in the IR spectrum of Cu(II) compound. The band at 1518 cm^{-1} is assigned to the aromatic $\text{C}=\text{C}$, while the band at 584 cm^{-1} is specific for the ring mode.¹³ The weak band at 392 cm^{-1} is assigned to the stretching vibration of $\text{Cu}-\text{N}$ bond.¹⁴ The presence of the coordinated and solvated water molecules is evidenced by the band at 3449 cm^{-1} .

The purity of the product was further evidenced by elemental analysis.

X-Ray crystallography

According to X-ray crystallography the copper(II) compound has an ionic crystal structure

which is built up due to co-crystallization of three types of complexes with 4-aminopyridine (NH_2Py) as monodentate ligands towards Cu^{2+} ion in N_4O or N_4Cl square pyramidal and N_4O_2 octahedral coordination geometry. The asymmetric part of the unit cell (Fig. 1) comprises four complex cations: $[\text{Cu}(\text{NH}_2\text{Py})_4(\text{H}_2\text{O})_2]^{2+}$ (**1**), two of $[\text{Cu}(\text{NH}_2\text{Py})_4(\text{H}_2\text{O})]^{2+}$ (**2**), $[\text{Cu}(\text{NH}_2\text{Py})_4\text{Cl}]^+$ (**3**), one non-coordinated 4-aminopyridine and seven water molecules trapped in the crystal structure. Seven positive charges provided by four complex cations are balanced by seven negative charge non-coordinated chloride anions. The X-ray molecular structure of complex cations is illustrated in Figs. 2-4. In the complex cation **1** (Fig. 2) the copper atom adopts a slightly distorted octahedral environment formed by four pyridine nitrogen of 4-aminopyridine ligands and two water molecules coordinated in trans positions. The $[\text{Cu}(\text{NH}_2\text{Py})_4(\text{H}_2\text{O})_2]^{2+}$ cation, showing close geometrical parameters, has been also observed in the crystal structure of diaquatetrakis(4-aminopyridine)copper(II)di(o-sulfobenzimidate) dehydrate compound.¹⁵ The copper atoms in co-crystallized complex cations $[\text{Cu}(\text{NH}_2\text{Py})_4(\text{H}_2\text{O})]^{2+}$ (**2**) and $[\text{Cu}(\text{NH}_2\text{Py})_4\text{Cl}]^+$ (Figs. 3-4) are in square-pyramidal coordination with $\text{Cu}-\text{O}1_w$ of $2.309(3)\text{ \AA}$ and $\text{Cu}-\text{Cl}$ of $2.638(3)\text{ \AA}$, respectively. The crystal structures of pure molecular complex $[\text{Cu}(\text{NH}_2\text{Py})_4\text{Cl}_2] \cdot \text{H}_2\text{O}$,¹⁶ and $[\text{Cu}(\text{NH}_2\text{Py})_4\text{Cl}] \cdot \text{CH}_3\text{OH}$,¹⁷ formed by mono-cations are also reported.

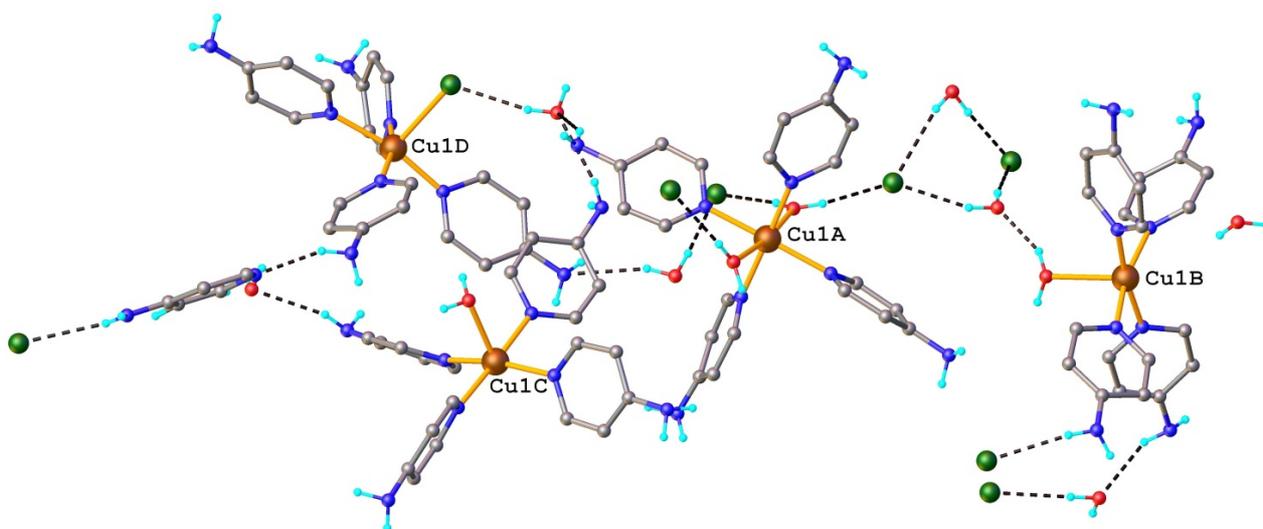


Fig. 1 – View of the asymmetric part in the crystal structure of copper(II) complex.

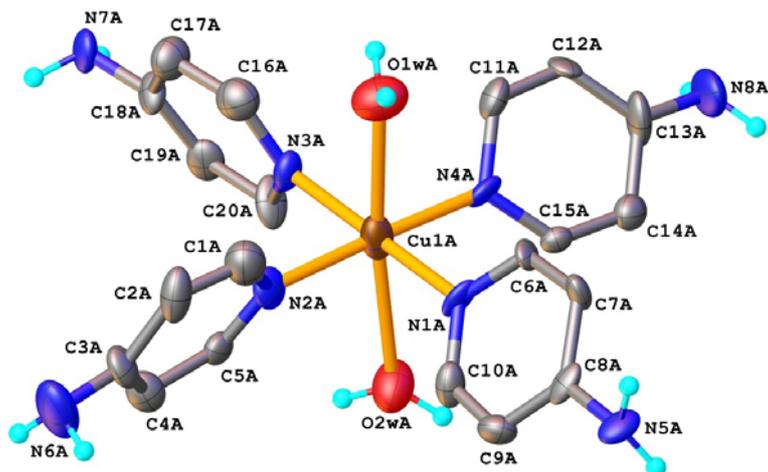


Fig. 2 – The structure of $[\text{Cu}(\text{NH}_2\text{Py})_4(\text{H}_2\text{O})_2]^{2+}$ complex cation. Thermal ellipsoids are drawn at 30% probability level. Non-relevant H-atoms are omitted for clarity.

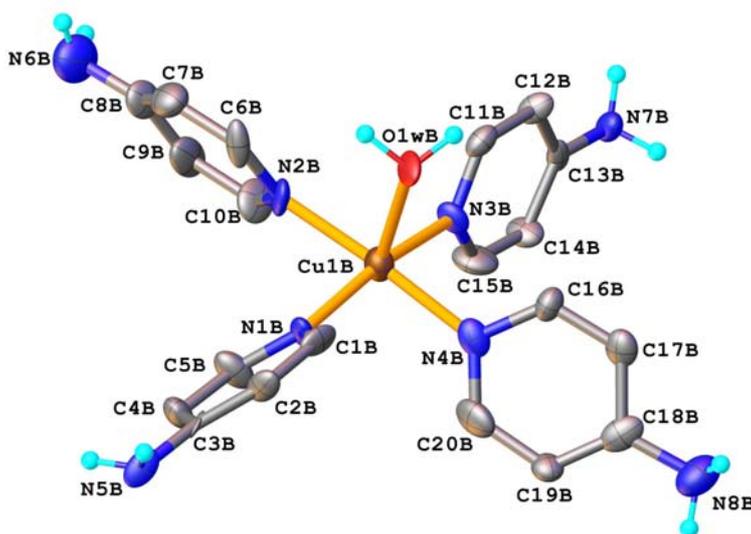


Fig. 3 – The structure of $[\text{Cu}(\text{NH}_2\text{Py})_4(\text{H}_2\text{O})_2]^{2+}$ complex cation. Thermal ellipsoids are drawn at 30% probability level. Non-relevant H-atoms are omitted for clarity.

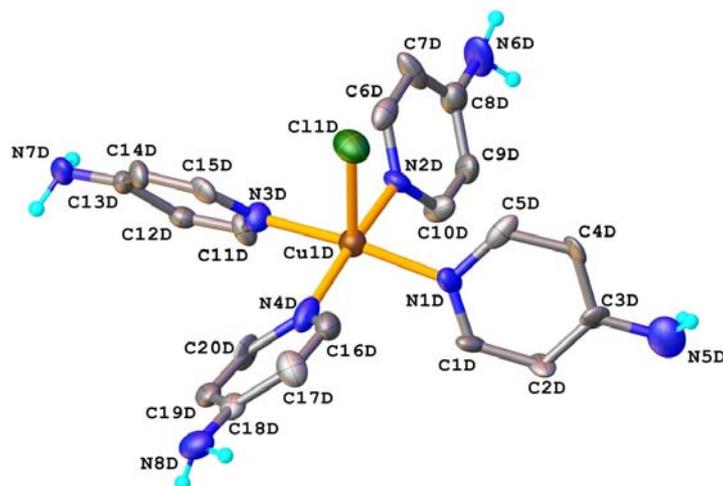


Fig. 4 – The structure of $[\text{Cu}(\text{NH}_2\text{Py})_4\text{Cl}]^+$ complex cation. Thermal ellipsoids are drawn at 30% probability level. Non-relevant H-atoms are omitted for clarity.

Photoluminescence properties

The optical properties of the copper(II) compound were obtained by means of electronic absorption and fluorescence spectroscopy in solid state. The diffuse reflectance spectrum shows that the Cu(II) compound has two main absorptions, with thresholds at about 550 nm and 1150 nm. The sub-bands in the UV region can be assigned to superposed $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions in pyridine ring (240 nm) and to two ligand-to-metal charge transfer bands (362 and 468 nm) in two distinct Cu(II) coordination geometries. The same bimodal profile is observed in the low energy region, where the d-d transition of Cu(II) ions in a low and high coordination geometries gave rise to two sub-bands at 716 and 875 nm (Figure 6a). It is possible that the absorption band at 716 nm is corresponding to the Cu(II) ions in the square – pyramidal geometry, while the band at 875 nm

would correspond to the most coordinated complex (Fig. 5a).¹⁸

The fluorescence spectra of the copper(II) compound under excitation at 430 nm consists of a succession of azure (487 nm), emerald green (534 nm) and yellowish green (572 nm) emissions. The redshift of the emission energy is connected to the coordination geometry of the Cu(II) ions (Fig. 5b).

Using the Tauc's equation for determining the band gap, two values of E_g were obtained, corresponding to the two main sections of the absorbance spectrum. For the region bellow 600 nm, the E_g value is 3.7 eV, while for the visible – near IR region, the band gap shifted to the red, reaching 1.91 eV. Two values for the band gap energy can be connected to the two modes of coordination of Cu(II) ions in the unit cell, that would be similar to two different compositions of the compound (Fig. 5c).

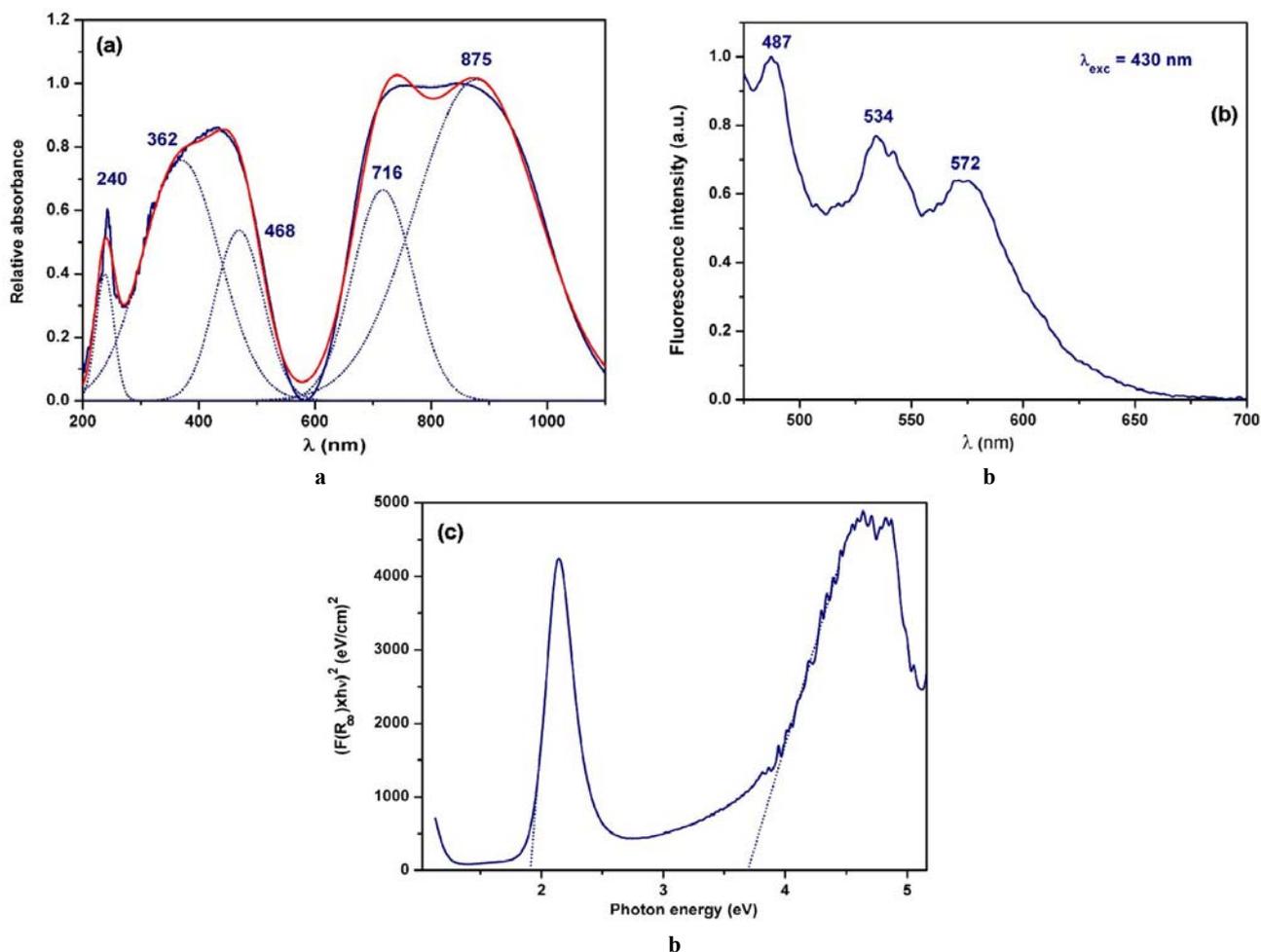


Fig. 5 – Spectral characteristics of the Cu(II) compound: (a) Normalized diffuse reflectance spectra; (b) normalized fluorescence spectra; (c) The Tauc plot of $[F(R_{\infty}) \times hv]^2$ vs. photon energy.

EXPERIMENTAL

Materials and measurements

para-aminopyridine (Aldrich), Copper(II) chloride dihydrate (Aldrich), methanol (Chimopar) and diethyl ether (Chimopar), were used as received.

Fourier transform infrared (FT-IR) spectra were recorded using a Bruker Vertex 70 FT-IR spectrometer. Registrations were performed in the transmission mode in the range 400–4000 cm⁻¹ at room temperature with a resolution of 2 cm⁻¹ and accumulation of 32 scans.

UV-Vis absorption spectra measurements of the compound in solid state were carried out using the diffuse reflectance accessory on a Specord 200 spectrophotometer. The optical band gaps of the compound was determined from the diffuse reflectance spectra. The DRS spectrum was converted in absorbance using the Kubelka Munk equation

$F(R_{\infty}) = \left[\frac{(1 - R_{\infty})^2}{2R_{\infty}} \right]$, where R_{∞} is reflectance of the sample with infinite thickness. The optical band gap was obtained by using the Tauc's expression

$F(R_{\infty}) \times hv = A (hv - E_g)^{1/2}$ for materials with direct or indirect band gap, respectively, and A is a material constant.¹⁹

The plot $[F(R_{\infty}) \times hv]^2$ vs. photon energy hv allows the evaluation of the optical band gap by extrapolating the linear part of the plot to the energy axis.

Crystallographic measurements for copper(II) compound were carried out with an Oxford-Diffraction XCALIBUR E CCD diffractometer equipped with graphite-monochromated Mo-K α radiation. The unit cell determination and data integration were carried out using the CrysAlis package of Oxford Diffraction.²⁰ All structures were solved by direct

methods using SHELXS-97²¹ and refined by full-matrix least-squares on F_o^2 with SHELXL-97²² with anisotropic displacement parameters for non-hydrogen atoms. All H atoms attached to carbon were introduced in idealized positions ($d_{CH} = 0.96 \text{ \AA}$) using the riding model with their isotropic displacement parameters fixed at 120% of their riding atom. Positional parameters of the H attached to O and N atoms were obtained from difference Fourier syntheses and verified by the geometric parameters of the corresponding hydrogen bonds. The main crystallographic data together with refinement details are summarized in Table 1.

CCDC 1518794 contains the supplementary crystallographic data for this contribution. These data can be obtained free of charge via 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 deposit@ccdc.ca.ac.uk).

Synthesis of copper(II) compound

To a solution of CuCl₂·2H₂O (0.170 g, 1 mmol) in water (5 mL) a solution of 4-aminopyridine (0.094 g, 1 mmol) was added dropwise and the resulting mixture was stirred at room temperature for 30 min. and then at reflux for 1h. Green crystals appeared after three days. The crystals were filtered off, washed with methanol and diethylether and dried in air at room temperature (0.048 g, 52 %). Anal. Calcd for C₈₅H₁₁₀Cl₈Cu₄N₃₄O₄ (M_r 2209.81 g/mol): C, 46.2; H, 5.02; N, 21.55. Found: C, 46.22; H, 5.13; N, 21.73. IR ν_{max} (KBr), cm⁻¹: 3449s, 3339vs, 3223s, 3086w, 3059w, 2567w, 1639vs, 1616s, 1557w, 1518s, 1456m, 1402w, 1354m, 1285m, 1209s, 1061m, 1028s, 853w, 826s, 584s, 561m, 523m, 444s, 392w.

Table 1

Crystallographic data, details of data collection and structure refinement parameters.

Empirical formula	C ₈₅ H ₁₂₄ Cl ₈ Cu ₄ N ₃₄ O ₁₁
Molecular weight, g/mol	2335.93
Temperature (K)	200
Crystal system	trigonal
Space group	$P3_2$
a , (Å)	20.496(3)
b , (Å)	20.496(3)
c , (Å)	22.455(4)
α , (°)	90
β , (°)	90
γ , (°)	120
V , (Å ³)	8169.2(3)
Z	3
D_{calc} (g/cm ³)	1.424
μ , (mm ⁻¹)	1.036
θ_{min} , θ_{max} (°)	4.936 to 46.512
Crystal size (mm)	0.25 × 0.15 × 0.15
Reflections collected/unique (R_{int})	74509/15567 (0.1111)
Data/restraints/parameters	15567/97/1269
R_1^a ($I > 2\sigma(I)$)	0.0750
wR_2^b (all data)	0.1592
GOF ^c	1.060
$\Delta\rho_{max}$ and $\Delta\rho_{min}$ (e/Å ³)	0.88/-0.42
Flack parameter	-0.010(9)

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, ^b $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$.

^cGOF = $\{ \sum [w(F_o^2 - F_c^2)^2] / (n - p) \}^{1/2}$, where n is the number of reflections and p is the total number of parameters refined.

CONCLUSIONS

A copper(II) compound with 4-aminopyridine as monodentate ligand has been prepared and characterized. The compound showed an unusual structure where three species of complexes in which Cu^{2+} ions adopt different coordination geometry and one 4-aminopyridine molecule are co-crystallized in the same crystal. Photophysical studies revealed that the copper(II) compound exhibit strong absorptions and fluorescence in concordance with the structure confirmed by X-ray diffraction.

Acknowledgements: This work was supported by a grant of the Ministry of National Education, CNCS – UEFISCDI, PN-III-P2-2.1-PED-2016, Contract 130PED/2017. We also like to acknowledge Dr. Mihaela Avadanei for helpful discussions on the photoluminescence properties.

REFERENCES

1. K. C. Hayes, *CNS Drug Rev.*, **2004**, *10*, 295–316.
2. L. Friggeri, L. Scipione, R. Costi, M. Kaiser, F. Moraca, C. Zamperini, B. Botta, R. Di Santo, D. De Vita, R. Brun and S. Tortorella, *ACS Med. Chem. Lett.*, **2013**, *4*, 538–541.
3. M. Lenze, E. T. Martin, N. P. Rath and E. B. Bauer, *ChemPlusChem*, **2013**, *78*, 101 – 116.
4. U. García-Couceiro, O. Castillo, A. Luque, J. P. García-Terán, G. Beobide and P. Roman, *Eur. J. Inorg. Chem.*, **2005**, 4280–4290.
5. B. Dojer, A. Pevec, M. Jagodic, M. Kristl and M. Drogenik, *Inorg. Chim. Acta*, **2012**, *383*, 98–104.
6. G. Cavagiolo, L. Benedetto, E. Boccaleri, D. Colangelo, I. Viano and D. Osella, *Inorg. Chim. Acta*, **2000**, *305*, 61–68.
7. F. Xu, T. Tao, Q.-Q. Liu, J. Geng and W. Huang, *Inorg. Chim. Acta*, **2012**, *392*, 465–468.
8. E. V. Rybak-Akimova, A. Y. Nazarenko, L. Chen, P. W. Krieger, A. M. Herrera, V. V. Tarasov and P. D. Robinson, *Inorg. Chim. Acta*, **2001**, *324*, 1–15.
9. J. M. McBride, D. T. Smith, S. R. Byrn, R. B. Borgens and R. Shi, *Neurosci.*, **2007**, *148*, 44–52.
10. A. Andreani, A. Leoni, A. Locatelli, R. Morigi, M. Rambaldi, C. Pietra and G. Villetti, *Eur. J. Med. Chem.*, **2000**, *35*, 77–82.
11. E. Jankowska, A. Lundberg, P. Rudomin and E. Sykova, *Brain Res.*, **1982**, *240*, 117–129.
12. G. Chelucci, *Coord. Chem. Rev.*, **2013**, *257*, 1887–1932.
13. O. O. E. Onawumi, O. O. P. Faboya, O. A. Odunola, T. K. Prasad and M. V. Rajasekharan, *Polyhedron*, **2008**, *27*, 113–117.
14. K. Nakamoto, “Infrared and Raman Spectra of Inorganic and Coordination Compounds”, John Wiley & Sons, 1986. doi:10.1021/ja00904a075.
15. P. Naumov, G. Jovanovski, M. G. B. Drew and S. W. Ng, *Inorg. Chim. Acta*, **2001**, *314*, 154–162.
16. H.-K. Fun, A. Sinthya, S. R. Jebasa and S. Devadasan, *Acta Cryst.*, **2008**, *E64*, 853–854.
17. B. B. Ivanova and H. Mayer-Figg, *J. Coord. Chem.*, **2005**, *58*, 653–659.
18. M. Elleb, J. Meullemeestre, M.-J. Schwing-Weill and F. Vierling, *Inorg. Chem.*, **1982**, *21*, 1477–1483.
19. A. Dolgonos, T. O. Mason and K. R. Poeppelmeier, *J. Solid State Chem.*, **2016**, *240*, 43–48.
20. CrysAlisRED, Oxford Diffraction Ltd., Version 1.171.36.32, **2003**.
21. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, **2009**, *42*, 339–341.
22. G. M. Sheldrick, SHELXS, *Acta Cryst.*, **2008**, *A64*, 112–122.