

*Dedicated to the memory of
Academician Bogdan C. Simionescu (1948–2024)*

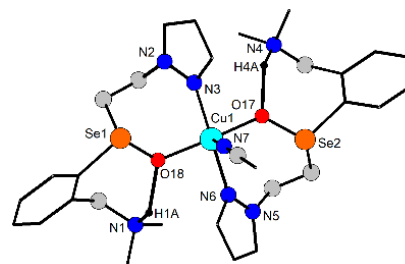
COPPER(II) COMPLEXES OF DIORGANOSELENIUM LIGANDS CONTAINING A PYRAZOLE FUNCTIONALITY

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The copper(II) complexes $[\text{CuL}][\text{ClO}_4]_2$ (**1**) and $[\text{CuL}_2][\text{ClO}_4]_2$ (**2**) were prepared by reacting $\text{Cu}(\text{ClO}_4)_2$ with the heteroleptic diorganoselenide $[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4](\text{CH}_2\text{CH}_2\text{pz})\text{Se}$ (**L**) in the appropriate molar ratio. They were investigated in solution by UV-Vis spectroscopy and mass spectrometry. Crystals of $[\text{Cu}\{\text{Se}(\text{O})(\text{CH}_2\text{CH}_2\text{pz})(\text{C}_6\text{H}_4\text{CH}_2\text{N}(\text{H})\text{Me}_2-2)\}_2(\text{MeCN})][\text{ClO}_4]_4 \cdot \text{MeCN}$ (**2a**) were serendipitously formed during the attempts to grow single-crystals of compound **2**. The molecular structure of **2a** was determined by X-ray diffraction, when a bidentate *N,O* coordination behaviour of the diorganoselenoxide was observed.



INTRODUCTION

A continuously increasing interest was observed in the last decades for hypercoordinated species of main group elements.^{1–3} Among them, a special consideration was given to organoselenium compounds with nitrogen donor atoms, namely diorganodiselenides or diorganoselenides.^{4,5} The $\text{N} \rightarrow \text{Se}$ intramolecular coordination resulted in derivatives with improved stability, which showed a significant enhancement of their catalytic⁶ or biological activity.^{4,5,7} Various organic groups capable to behave as *C,N*- or *N,C,N*-chelating moieties towards the chalcogen atom were employed in organoselenium chemistry, e.g. 2-($\text{RR}'\text{NC}(\text{H})\text{R}''$) C_6H_4 ,^{8–10} 2,6-($\text{RR}'\text{NC}(\text{H})\text{R}''$) $_2\text{C}_6\text{H}_3$)¹¹

($\text{R} = \text{R}'$ or $\text{R} \neq \text{R}'$; $\text{R}, \text{R}' = \text{alkyl}$, $\text{R}'' = \text{H}, \text{Me}$), and such compounds showed even a higher antioxidant activity than ebselen.¹² The presence of both soft (Se) and hard (N) donor atoms made the neutral diorganoselenides, as well as the anionic organoselenolato moieties, versatile ligands for both soft and hard metals. The organic groups attached to selenium have an important influence on the flexibility of the backbone of these species, thus resulting in a chelating or a bridging behaviour towards the metal center.¹³ Compounds with alkyl groups containing a pyrazole functionality, e.g. $[(3,5\text{-dmpz})\text{CH}_2\text{CH}_2]_2\text{Se}$, $[(3,5\text{-dmpz})\text{CH}_2\text{CH}_2]_2\text{Se}_2$,¹⁴ (3,5-dmpz-1-yl)phenyl-based compounds¹⁵ (dmpz = dimethylpyrazole), and 1-(2-chloroethyl)pyrazole-based selenides¹⁶ were used in

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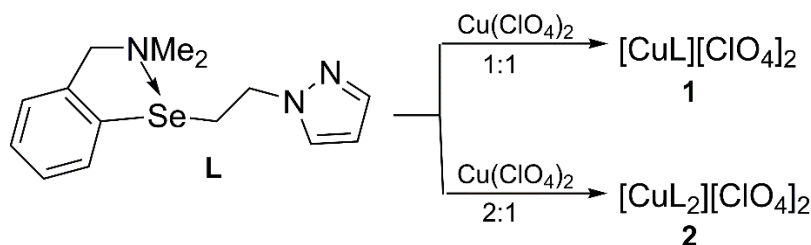
supramolecular architectures,¹⁷ or as ligands in coordination chemistry (*e.g.* Pd, Ru, Ag, Cu, Zn complexes).^{18–22} The presence of pyrazole is expected to have a beneficial influence on the biological properties both of the organoselenium species and their metal complexes, taking into account the own biological activity of the pyrazole functionality.^{23–27}

Over the past years our research was focused on diorganoselenides of type R^1R^2Se ($R^1 = (3,5\text{-dmpz})CH_2CH_2$, $R^2 = (3,5\text{-dmpz})CH_2CH_2$, $2\text{-(}R_2NCH_2)C_6H_4$ ($R = Me, Et$);²⁸ $R^1 = pzCH_2CH_2$, $R^2 = 2\text{-(}Et_2NCH_2)C_6H_4$ or $2\text{-}\{O(CH_2CH_2)_2NCH_2\}C_6H_4$;²⁹ $R^2 = pzCH_2CH_2$,³⁰ and we investigated their coordination ability towards group 11 (Ag, Cu) metals. As a continuation of our work, we report here on the preparation, structural characterization and solution behaviour of two

copper(II) complexes with the heteroleptic ligand $[2\text{-(}Me_2NCH_2)C_6H_4](CH_2CH_2pz)Se$ (**L**), namely the ionic species $[CuL][ClO_4]_2$ (**1**) and $[CuL_2][ClO_4]_2$ (**2**).

RESULTS

The heteroleptic diorganoselenide $(pzCH_2CH_2)(2\text{-}Me_2NCH_2C_6H_4)Se$ (**L**) was reacted both in a 1:1 and a 2:1 molar ratio with $Cu(ClO_4)_2$ in order to obtain the copper(II) complexes $[Cu\{Se(CH_2CH_2pz)(C_6H_4CH_2NMe_2-2)\}][ClO_4]_2$ (**1**) and $[Cu\{Se(CH_2CH_2pz)(C_6H_4CH_2NMe_2-2)\}_2][ClO_4]_2$ (**2**), respectively, as depicted in Scheme 1. In both cases the reaction products were isolated as green solids. The syntheses were performed in acetonitrile.



Scheme 1 – Synthesis of the copper(II) complexes.

The Cu(II) complexes were investigated by mass spectrometry and UV-Vis spectroscopy. Information on the stoichiometry of the copper(II) complexes in solution was obtained by using the continuous variation method (Job's method).^{31,32} The molar ratio metal ions to ligand was changed continuously from 9:1 to 1:9 throughout the series of samples, while the sum of their concentrations was kept constant at 10^{-3} M. The measurements were performed against a blank sample of acetonitrile.

The molar conductivity data for these complexes ($\Lambda_M = 383 \Omega^{-1}\cdot cm^2\cdot mol^{-1}$ and $431 \Omega^{-1}\cdot cm^2\cdot mol^{-1}$ for **1** and **2**, respectively) are higher than the range observed for a 1:2 electrolyte behaviour in 10^{-3} acetonitrile solutions,³³ thus suggesting the existence of a mixture of the desired compound and a protonated species at the nitrogen in the pendant arm of the $2\text{-(}Me_2NCH_2)C_6H_4$ group in the diorganoselenium ligand, as observed by single-crystal X-ray diffraction for **2a**.

The attempts to grow single-crystals for **2** lead to the formation of $[Cu\{Se(O)(CH_2CH_2pz)(C_6H_4CH_2N(H)Me_2-2)\}_2(MeCN)][ClO_4]_4\cdot MeCN$ (**2a**). For this species the molecular structure was determined by single-crystal X-ray diffraction.

DISCUSSION

Spectroscopic investigation

The mass spectra of the solids isolated in the reaction of the ligand **L** and $Cu(ClO_4)_2$, indifferent a 1:1 or a 2:1 ligand/metal molar ratio was used, showed the base peak at m/z 372.0033 thus suggesting the existence of the $[CuL]^{2+}$ cation.

The UV-Vis spectra (Fig. 1) of the copper(II) complexes were recorded in MeCN, and they indicate a similar behaviour for both compounds. The two strong absorption bands around 200–250 nm can be assigned to ligand-centered transitions, while the band in the range 350–400 nm can be assigned to the LMCT transitions determined by the interaction of the diorganoselenium(II) ligand with Cu^{2+} , and the broad bands in the region 700–800 nm, of very low intensity, can be assigned to the $d-d$ transitions of the d^9 Cu^{2+} cations.

In order to obtain information on the ligand to metal ratio in complex **2**, the continuous variation method was employed. In the UV-Vis spectra recorded for the Job Plot experiments, the band at 735 nm was studied. Initially the maximum of the

curve representing the absorption at 735 nm = $f(\text{molar fraction})$ was found at a value of 0.5, indicating the formation of a 1:1 complex, but after

13 days the maximum of this curve shifted to a value of 0.33, thus indicating the formation of a 2:1 complex (Fig. 2).

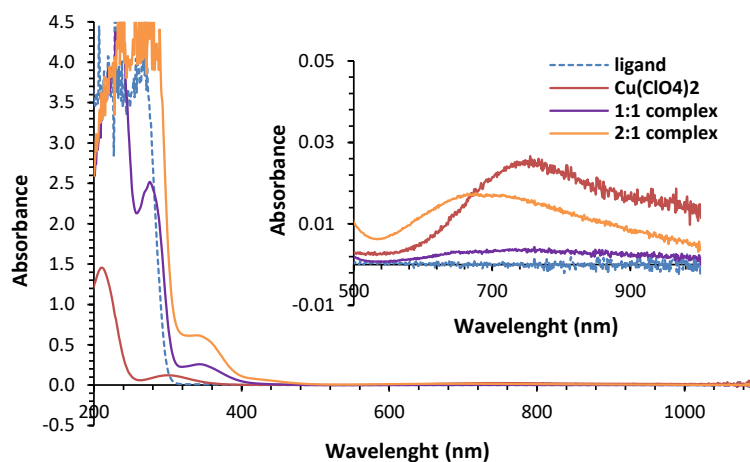


Fig. 1 – UV-Vis spectra of the starting materials and complexes **1** and **2** in 10^{-3} M MeCN solutions. Insight: the region 500–900 nm corresponding to d-d transitions.

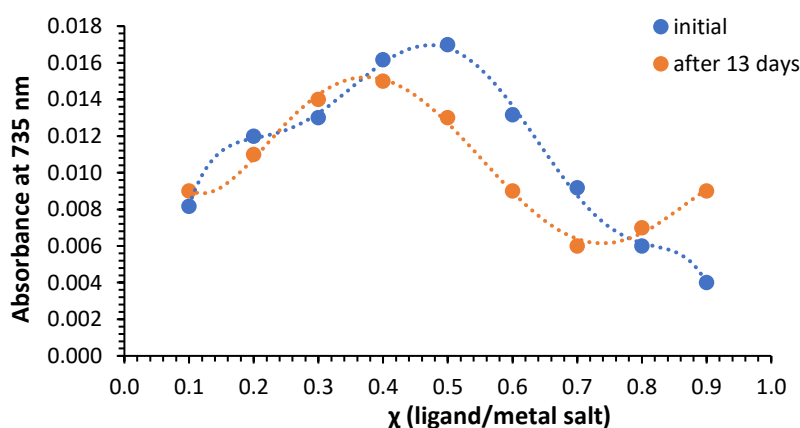


Fig. 2 – Evolution of the Job's plot for the formation of complex **2**. The absorbance at 735 nm was considered.

Such a behaviour suggests that the first ligand **L** unit easily coordinates to copper, while the second one only after once the $[\text{CuL}]^{2+}$ species is formed. Moreover, taking into account that the reaction was performed in MeCN solutions, we can consider the initial formation of $[\text{Cu}(\text{MeCN})_n][\text{ClO}_4]_2$, followed by substitution of the acetonitrile by molecules of ligand **L**. Both the UV-Vis spectrum of a solution of $\text{Cu}(\text{ClO}_4)_2$ in acetonitrile and the mass spectra of compounds **1** and **2** show the existence of $[\text{Cu}(\text{MeCN})_n]^{2+}$ ($n = 1, 2$) species. We have to mention here that our attempts to perform the reactions in methanol resulted in mixtures of compounds which showed a fast further decomposition.

The molar conductivity of the two species in 10^{-3} M solutions, higher than the expected values in

the range $220\text{--}300 \Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ suggest a mixture of the desired 1:2 ratio between complex cations and ClO_4^- anions, with species having more anions which counterbalance a higher charge than $2+$ of the cations. Taking into account the single-crystal X-ray structure of **2a**, we can assume that in acetonitrile solution, due to the presence of water from the starting copper(II) salt, at least a partial hydrolysis took place, with the formation of perchloric acid, which further determined the protonation of the nitrogen in the pendant arm of the $2\text{-(Me}_2\text{NCH}_2\text{)C}_6\text{H}_4$ group, thus resulting in an increase of the charge of the complex cation. We can also presume that the presence of perchloric acid in solution is responsible for the oxidation of selenium from Se(II) to Se(IV), with the formation of a diorganoselenium(IV) oxide as neutral ligand.

X-ray diffraction studies

Crystal and molecular structure of $[\text{Cu}\{\text{Se}(\text{O})(\text{CH}_2\text{CH}_2\text{pz})(\text{C}_6\text{H}_4\text{CH}_2\text{N}(\text{H})\text{Me}_2-2)\}_2(\text{MeCN})][\text{ClO}_4]_4\text{MeCN}$ (**2a**)

By leaving the mother solution of **2** to crystallize

by slow diffusion of Et₂O into MeCN, an unexpected compound was obtained, showing two molecules of diorganoselenium oxide coordinated to Cu²⁺. The ortep-like diagram of the cation is depicted in Fig. 3, while selected bond lengths and angles are shown in Table 1.

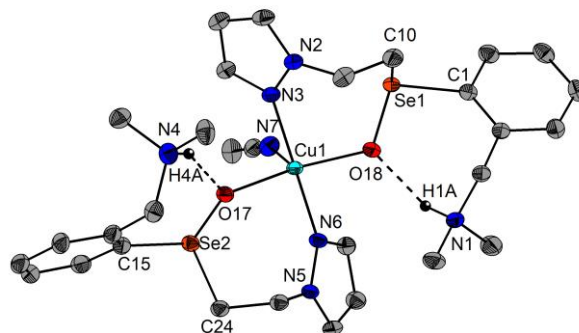


Fig. 3 – Thermal ellipsoids representation of the cation $[\text{Cu}\{\text{Se}(\text{O})(\text{CH}_2\text{CH}_2\text{pz})(\text{C}_6\text{H}_4\text{CH}_2\text{N}(\text{H})\text{Me}_2-2)\}_2(\text{MeCN})]^{4+}$ at 50% probability level. Hydrogen atoms, except those attached to nitrogen, were omitted for clarity.

Table 1

Selected interatomic distances (Å) and angles (°) in **2a**.

Interatomic distances (Å)		Angles (°)	
N3–Cu1	2.029(4)	O17–Cu1–O18	161.08(13)
N6–Cu1	2.017(4)	O17–Cu1–N6	94.42(14)
N7–Cu1	2.244(4)	O18–Cu1–N6	84.80(14)
O17–Cu1	1.968(3)	O17–Cu1–N3	86.03(14)
O18–Cu1	1.969(3)	O18–Cu1–N3	95.07(14)
O17–Se2	1.717(3)	N6–Cu1–N3	178.97(15)
O18–Se1	1.711(3)	O17–Cu1–N7	98.38(14)
		O18–Cu1–N7	100.50(14)
		N6–Cu1–N7	88.65(15)
		N3–Cu1–N7	90.37(15)
O17...H4A	1.7826	O18–Se1–C1	102.40(17)
O18...H1A	1.9466	O18–Se1–C10	99.77(19)
		C1–Se1–C10	98.62(18)
		O17–Se2–C15	103.31(17)
		O17–Se2–C24	100.25(17)
		C15–Se2–C24	95.60(19)

The compound has a ionic structure, with $[\text{Cu}(\text{MeCN})\{\text{Se}(\text{O})(\text{CH}_2\text{CH}_2\text{pz})(\text{C}_6\text{H}_4\text{CH}_2\text{N}(\text{H})\text{Me}_2-2)\}_2]^{4+}$ cations counterbalanced by $[\text{ClO}_4]^-$ anions. A second MeCN molecule is also present in the crystal, but it is not involved in any interactions. The copper(II) centre is penta-coordinated by the two oxygen atoms attached to selenium, two nitrogen atoms from the pyrazole rings of the two ligand molecules and a nitrogen atom from the coordinated acetonitrile molecule, thus resulting in a distorted square-pyramid coordination geometry ($\tau = 0.30$)³⁴ around the metal centre, with the nitrogen from the acetonitrile molecule in apical position, at 2.40 Å above the N₂O₂ plan. The N_{pz}...Cu distances are slightly longer than those observed in the related

copper(II) complexes $[\text{CuCl}_2\{\text{Se}(\text{CH}_2\text{CH}_2\text{pz})_2\}]$, $[\text{Cu}(\text{OCIO}_3)_2\{\text{Se}(\text{CH}_2\text{CH}_2\text{pz})_2\}(\text{H}_2\text{O})]$ and $[\text{Cu}(\text{NO}_3)_2\{\text{Se}(\text{CH}_2\text{CH}_2\text{pz})_2\}]$ (range 1.945(5) – 1.991(5) Å).³⁰ The nitrogen atoms in the pendant arms are protonated, thus raising the charge of the cation to +4 and justifying the presence of four $[\text{ClO}_4]^-$ anions per each cation in the crystal. The values of the Se–O bonds of 1.717(3) and 1.711(3) Å are slightly longer than that observed in phenoxaselenine oxide (1.6615(16) Å),³⁵ but smaller than the sum of the covalent radii of the elements ($\Sigma r_{\text{cov}}(\text{Se},\text{O}) = 1.86 \text{ Å}$)³⁶, thus suggesting a double character of these bonds. The bond angles around selenium are in accordance with a distorted pseudo-tetrahedral coordination geometry. The O,N

bidentate coordination behaviour of the oxidized L ligand resulted in two N_2C_2SeOCu chelate rings of seven members.

Two strong intramolecular hydrogen bonds (1.782 and 1.946 Å *vs.* $\Sigma r_{vdw}(O,H) = 2.60\text{--}2.85$ Å³⁶) between the hydrogen atoms in the pendant arms and the oxygen atoms attached to selenium are present in the cation.

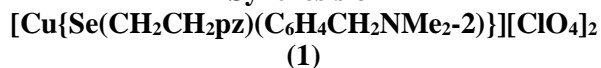
EXPERIMENTAL

Materials and methods

The diorganoselenide (pzCH₂CH₂)(2-Me₂NCH₂C₆H₄)Se was prepared by a literature procedure.²⁹ All starting materials for the diorganoselenide and copper perchlorate hexahydrate, were procured from Sigma-Aldrich and were used without further purification. Melting points were measured in open capillary tubes with an Electrothermal 9200 apparatus and are not corrected. Elemental analyses were performed on a Flash EA 1112 analyzer. ESI+ mass spectra were recorded on a Thermo Scientific Orbitrap XL spectrometer equipped with a standard ESI/APCI source. The molar conductivity of 10⁻³ M solutions in DMSO was determined with a TDS Meter CON 510 conductometer. UV-Vis spectra were recorded in MeCN solutions on a Thermo Electron Nicolet Evolution 300 spectrometer. λ_{max} values are given in nm. Information on the stoichiometry of the copper complexes in solution was obtained by using the continuous variation method. The molar concentration of both components (metal ions : ligand molar ratio) was changed continuously from 9:1 to 1:9 throughout a series of samples, while the sum of their concentrations was kept constant at 1 mM. The measurements were performed against a blank sample of MeCN.

Caution: Copper perchlorate as well as the perchlorate metal complexes are potentially explosive and should be handled with care and in small quantities.

Synthesis of



A solution of Cu(ClO₄)₂·6H₂O (75 mg, 0.198 mmol, 98% purity) in 5 mL of acetonitrile was added dropwise to a clear colourless solution of [2-(Me₂NCH₂)C₆H₄]SeCH₂CH₂pz (61.2 mg, 0.198 mmol) in 10 mL of acetonitrile. The resulting clear green solution was stirred for 60 min at room

temperature. Upon evaporation of the solvent under vacuum a green oily product was obtained. Washing with Et₂O (6 × 3 mL) gave a light mint green solid which was dried under vacuum for several hours. Yield: 90.6 mg (80%); M.p.: 86–87°C; ESI+ MS (MeCN): *m/z* (%) 372.0034 (50) [CuL]²⁺, 310.0818 (100) [L + H]⁺, 265.0239 (10) [L–NMe₂]⁺, 214.0131 (20) [L²–CH₂CH₂pz]⁺, 144.9822 (55) [Cu(MeCN)₂]⁺, 103.9554 (60) [Cu(MeCN)]⁺; UV-Vis (MeCN, 10⁻³ M): 233, 276, 346, 729(w) nm. Λ_M (MeCN, 10⁻³ M): 383.0 Ω⁻¹·cm²·mol⁻¹.

Synthesis of [Cu{Se(CH₂CH₂pz)(C₆H₄CH₂NMe₂-2)}₂][ClO₄]₂ (2)

A solution of Cu(ClO₄)₂·6H₂O (35.8 mg, 0.094 mmol, 98% purity) in 5 mL of acetonitrile was added dropwise to a clear colourless solution of [2-(Me₂NCH₂)C₆H₄]SeCH₂CH₂pz (58.5 mg, 0.189 mmol) in 10 mL of acetonitrile. The resulting clear green solution was stirred for 30 min at room temperature. Upon evaporation of the solvent under vacuum a green foam was obtained. Washing with Et₂O (6 × 3 mL) gave a light green solid which was dried under vacuum for several hours. Yield: 83 mg (88%); M.p.: 72–73°C; ESI+ MS (MeCN): *m/z* (%) 372.0033 (100) [CuL]²⁺, 310.0817 (75) [L+H]⁺, 265.0240 (35) [L–NMe₂]⁺, 214.0130 (25) [L–CH₂CH₂pz]⁺, 103.9554 (10) [Cu(MeCN)]⁺; UV-Vis (MeCN, 10⁻³ M): λ [nm] 220, 275, 353, 735(w). Λ_M (MeCN, 10⁻³ M): 431 Ω⁻¹·cm²·mol⁻¹.

Crystal structure determination

Single crystals suitable for X-ray diffraction for [Cu{Se(O)(CH₂CH₂pz)(C₆H₄CH₂N(H)Me₂-2)}₂(MeCN)][ClO₄]₄·MeCN (**2a**) were obtained by slow diffusion of Et₂O into an acetonitrile solution. The crystals were mounted on MiTeGen microMounts cryoloops and data were collected on a Bruker D8 VENTURE diffractometer using Mo-K α radiation ($\lambda = 0.71073$ Å) from a μ S 3.0 microfocus source with multilayer optics, at low temperature (100 K). The structures were refined with anisotropic thermal parameters for non-H atoms. Hydrogen atoms were placed in fixed, idealized positions and refined with a riding model and a mutual isotropic thermal parameter. For structure solving and refinement the Bruker APEX3 Software Package was used.³⁷ The drawings were created using the Diamond program.³⁸ The details of the crystal structure determination and refinement are given in Table 2.

Table 2
X-ray crystal data and structure refinement for compound **2a**

Empirical formula	C ₃₂ H ₄₆ Cl ₄ CuN ₈ O ₁₈ Se ₂
Formula weight	597.01
Temperature (K)	100
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P 21
Unit cell dimensions	
a (Å)	11.1092(8)
b (Å)	16.7894(14)
c (Å)	12.7165(11)
α (°)	90
β (°)	106.357(3)
γ (°)	90
Volume (Å ³)	2275.8(3)
Z	4
D _c (g/cm ³)	1.742
Absorption coefficient (mm ⁻¹)	2.395
F(000)	1206
Crystal size, mm	0.10 x 0.08 x 0.06
θ range for data collections (°)	2.263 to 28.280°
Reflections collected	105023
Independent reflections	11282 [R(int) = 0.0848]
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	11282 / 1 / 598
Goodness-of-fit on F ²	1.055
Final R indices [F ² > 2σ(F ²)]	R1 = 0.0348, wR2 = 0.0878
R indices (all data)	R1 = 0.0373, wR2 = 0.0897
Largest diff. peak and hole, eÅ ⁻³	0.987 and -0.786

CONCLUSIONS

The copper(II) complexes [CuL][ClO₄]₂ (**1**) and [CuL₂][ClO₄]₂ (**2**) were obtained as green solids, by reacting the neutral ligand [2-(Me₂NCH₂)C₆H₄](CH₂CH₂pz)Se (**L**) with Cu(ClO₄)₂ in a 1:1 and a 2:1 molar ratio, respectively. Both compounds are ionic species and they behave as 1:2 electrolytes in solution. The single-crystal X-ray diffraction studies upon [Cu{Se(O)(CH₂CH₂pz)(C₆H₄CH₂N(H)Me₂-2)}₂(MeCN)][ClO₄]₄·MeCN (**2a**), formed by a hydrolysis/oxidation process, revealed a *N,O* coordination behavior of the diorganoselenium oxide towards copper(II).

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Supplementary material. CCDC 2450487 contains the supplementary crystallographic data for compound **2a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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