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# Synthesis and molecular structure of the first binuclear {(bis-*N*-isophthaloyl ureato) copper(II)pyridine}<sub>2</sub> complex derived from the {(bis-*N*-isophthaloyl-selenoureato) copper(II)}<sub>2</sub> complex by O for Se atom exchange

Axel Rodenstein<sup>a</sup>, James A. Odendal<sup>b</sup>, Reinhard Kirmse<sup>a</sup>, Klaus R. Koch<sup>b,\*</sup>

<sup>a</sup> Universität Leipzig, Institute of Inorganic Chemistry, Johannisallee 29, D-04103 Leipzig, Germany

<sup>b</sup> Department of Chemistry and Polymer Science, University of Stellenbosch, Private Bag XI, Matieland, 7602, South Africa

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### ABSTRACT

The bipodal ligand 3,3,3',3'-tetraethyl-1,1'-isophthaloyl-bis(selenourea)  $(H_2L^1)$  forms a 2:2 copper(II) complex  $[Cu_2(L^1)_2]$ , the crystal and molecular structure and EPR spectrum of which are reported. Treatment of  $[Cu_2(L^1)_2]$  with excess pyridine results in the formation of a novel (bis-*N*-acylureato)copper(II) 1:2 pyridine adduct  $[Cu_2(L^2)_2(py)_2]$ , characterized by single crystal X-ray diffraction and EPR spectroscopy, as a consequence of facile Se replacement by O presumably due to hydrolysis of water present in the mixture. The latter complex forms a one-dimensional supramolecular architecture in the solid state, stabilized via  $\pi$ -stacking interactions between alternate Cu-coordinated pyridine molecules.

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Bipodal 1,3-aryl linked bis-acylthioureas such as 3,3,3',3'-tetraethyl-1,1'-isophthaloylbis(thiourea) result in the facile formation of 2:2 planar metallamacrocyclic complexes of Ni(II) and Pt(II), Pd(II) [1], shown as a general structure (I) below. The corresponding transdichloro-, dibromo- and diiodo-Pt(IV) complexes with such ligands have been prepared by selective oxidation of the 2:2 Pt(II) complexes and structurally characterized [2]. In the context of supramolecular chemistry 2:2 Ni(II) complexes have recently received much recent attention [3], in view of their tendency to form a variety of interesting adducts with heterocyclic nitrogen bases such as pyridine. 4-(dimethylamino)pyridine, pyrazine, 4,4'-bipyridine or 4,4'-transazopyridine resulting in 3D supramolecular assemblies with potential applications as sensors. Subsequently, related 1,3- and 1,4-aryl linked bis-β-diketone derivatives of inter alia Cu(II) and Fe(III) complexes (II) have been prepared, and their supramolecular adducts with for example pyrazine, 4,4'-bipyridine and related molecules have been studied [4]. The synthesis and characterization (based mainly on NMR and EPR spectroscopic evidence) of the corresponding  $[Ni_2(L^1)_2]$  and  $[Cu_2(L^1)_2]$ complexes (III), derived from bipodal acyl-selenourea ligands such as 3,3,3',3'-tetraethyl-1,1'-isophthaloyl-bis(thiourea) ( $H_2L^1$ ) have been recently reported [5].

We here report the crystal and molecular structures of a (bis-*N*-acyl-selenoureato)copper(II) complex, cis-[Cu<sub>2</sub>(L<sup>1</sup>-Se,O)<sub>2</sub>] (Fig. 1a), which

undergoes an interesting Se by O atom-exchange reaction in the bound ligand  $(L^1)$  when  $[Cu_2(L^1)_2]$  is treated with excess pyridine, to result in a novel five-coordinate (bis-*N*-acylureato)copper(II)-bis-pyridine complex  $[Cu_2(L^2)_2(py)_2]$  (Scheme 1). The ligand 3,3,3',3'-tetraethyl-1,1'-isophthaloyl-bis(selenourea)  $(H_2L^1)$  and its  $[Cu_2(L^1)_2]$  complex were synthesized in the absence of light according to a recently published procedure [5]. The highly light-sensitive products were isolated in good yields as a pale red solid  $(H_2L^1)$ , and brown crystals of  $[Cu_2(L^1)_2]$  respectively [6]. The ligand 3,3,3',3'-tetraethyl-1,1'-isophthaloyl-bis(selenourea) was characterized by means of conventional spectroscopic methods, with the <sup>77</sup>Se{<sup>1</sup>H} NMR spectrum of H<sub>2</sub>L<sup>1</sup> showing a single resonance at  $\delta$ (<sup>77</sup>Se) = 496 ppm in CDCl<sub>3</sub> relative to  $(CH_3)_2$ Se. In the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of  $H_2L^1$  the symmetrical satellites corresponding to  ${}^{1}J_{CSe} = 219$  Hz about the  ${}^{13}$ C peak at 180 ppm peak confirm the presence of the C = Se unit. The NH group was detected as a broad band at 3190  $\rm cm^{-1}$  in the IR spectrum and as a broad singlet in the <sup>1</sup>H NMR spectrum of H<sub>2</sub>L<sup>1</sup>.

The brown, paramagnetic complex  $[Cu_2(L^1)_2]$  is prepared by the reaction of  $H_2L^1$  with copper(II)acetate  $\cdot H_2O$  in ethanol in the absence of light in 76% yield and re-crystallized from chloroform/acetonitrile [6]. The ESI(TOF) mass spectrum of  $[Cu_2(L^1)_2]$  supports the molecular structure by a base peak at 1100.9 amu associated with a  $[M+H]^+$  species. Suitable crystals of  $[Cu_2(L^1)_2]$  were characterized by single crystal X-ray diffraction [7] showing this complex to be a 2:2 metallamacrocyclic complex with  $C_i$  as shown in Fig. 1a. Interestingly, in this 2:2 complex the Se atoms coordinated to the copper lie significantly above and below the mean plane defined by the Cu1,O1, O2 and Cu1a,O1a,O2a atoms. Essentially as shown in Fig. 1b, the two Se

<sup>\*</sup> Corresponding author. Tel.: +27 218083020; fax: +27 218083342. *E-mail address:* krk@sun.ac.za (K.R. Koch).

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**Fig. 1.** a) Molecular structure of [Cu<sub>2</sub>(L<sup>1</sup>)<sub>2</sub>]. Selected bond lengths (Å): Cu1–O1 1.947(3), Cu1–Se1 2.366(1), Cu1–O2 1.953(3), and Cu1–Se 2 2.359(1). Atoms are described by thermal ellipsoids at the 50% probability level. b) Shown also is a representation of the structure (H atoms and ethyl chains deleted for clarity) to illustrate Se atoms above and below the plane of the complex.

atoms significantly protrude above the mean plane of the metallamacrocyclic complex, with the dihedral angles defined by C1–N1–C2–Se1/ C21–N3–C22–Se2 (and the symmetry related ones) being 8.6(1)°, resulting in the Se atoms being relatively exposed to a possible reaction with ambient water as indicated in Scheme 1 (*vide infra*).

Although the *intra*-molecular metal–metal distance Cu1–Cu1a of 7.69(1)Å in  $[Cu_2(L^1)_2]$  is comparatively large, the presence of an electron spin interaction might be anticipated [8]. This is confirmed by

the EPR spectrum of  $[Cu_2(L^1)_2]$ , which shows a hyperfine structure (hfs) septet due to *intra*-molecular exchange interactions between the two Cu<sup>2+</sup> centres (Fig. 2). The isotropic g value of 2.077 and a Cu hfs coupling constant of  $39.2 \cdot 10^{-4}$  cm<sup>-1</sup> is consistent with a (CuO<sub>2</sub>Se<sub>2</sub>)<sub>2</sub> coordination unit [5,8]. *Inter*-molecular exchange interactions can most probably be excluded in view of the low concentration of [Cu<sub>2</sub>(L<sup>1</sup>)<sub>2</sub>] in this solution (c≈10<sup>-3</sup> M). The expected <sup>77</sup>Se hfs splitting could unfortunately not be detected in view of the relatively broad



Scheme 1. Structural motifs of known 2:2 metallamacrocyclic complexes and synthesis of Cu(II) complexes herein.



**Fig. 2.** X-band EPR spectra of  $[Cu_2(L^1)_2]$  in toluene and  $[Cu_2(L^2)_2(py)_2]$  in pyridine at T=370 K. The S=½ specie is highlighted with "\*" and S=1 with "+". Experimental error:  $g_0 = \pm 0.002$ ;  $a_0 = \pm 0.5$ .

EPR lines obtained. Superposition of lines might be expected based on the presence of a hyperfine quartet structure resulting from "monomeric"  $Cu^{2+}$  centres. In the latter case the same  $g_0$  value as found for the  $Cu^{2+}-Cu^{2+}$  pair is expected, although the <sup>63,65</sup>Cu hfs coupling constant  $a_0$  will be approximately twice as large as that of the  $Cu^{2+}-Cu^{2+}$  pair. This phenomenon of a typical chemical equilibrium of copper complexes with chalcogenoureato ligands in solution was recently described [5,8]. The weak signals at low-field, 292 mT, and at high-field, 335 mT, arise from decomposition products.

Dissolution of  $[Cu_2(L^1)_2]$  in excess pyridine (as solvent) results in a green solution, from which an unexpected product consisting of blue crystals of  $[Cu_2(L^2)_2(py)_2]$  can be isolated after a two day period at room temperature. Evidently the selenium donor atoms of the coordinated  $L^1$  are replaced by an oxygen donor atom forming a novel *bis-N*-acylureato ligand system  $L^2$  which remains bound to Cu(II). Apparently, the ligand  $L^1$ -fragment of the relatively unstable (bis-*N*-acylselenoureato)copper (II) complex,  $[Cu_2(L^1)_2]$  undergoes O for Se atom replacement under these conditions, presumably as a result of hydrolysis of water present in this solution. This process is presumably accompanied by the formation



Fig. 3. a) Molecular structure of  $[Cu_2(L^2)_2(py)_2]$  [7]. Selected bond lengths (Å): Cu1–O1 1.946(1), Cu1–O2 1.919(1), Cu1–O5 1.938(1), Cu1–O6 1.930(1), Cu1–N9 2.262(1), Cu2–O3 1.932(1), Cu2–O4 1.922(1), Cu2–O7 1.922(1), Cu1–O8 1.935(1), and Cu2–N10 2.296(1). b) One-dimensional supramolecular arrangement of  $[Cu_2(L^2)_2(py)_2]$ . The  $\pi$ -stacking interactions are represented in a distance of 3.34(1)Å between the pyridine rings. Atoms are described by thermal ellipsoids at the 50% probability level.

of intermediate  $[H_2Se]^{\ddagger}$ , which decomposes immediately to form elemental red selenium, which can be identified as a by product of this reaction. The possible mechanism of this reaction is as yet unclear and it has not been studied in any detail. The blue crystals isolated from this mixture is a novel pyridine adduct  $[Cu_2(L^2)_2(py)_2]$  as characterized by single crystal X-ray diffraction, the molecular structure of which is shown in Fig. 3 [7]. Unfortunately the solid complex  $[Cu_2(L^2)_2(py)_2]$  rapidly loses pyridine on exposure to air at ambient temperatures, which is indicative of only weak pyridine coordination to copper(II) in this compound.

The coordination sphere of copper(II)atom in  $[Cu_2(L^2)_2(py)_2]$  displays a square pyramidal 5-coordinate geometry involving two chelating O,O donor atom sets of *N*-acylureato fragments of L<sup>2</sup> bound equatorially to Cu (II) with the coordinated pyridine molecules in apical positions *anti* to one another. The bound pyridine molecule on alternate sides of the planar  $[Cu_2(L^2)_2]$  unit, generate an infinite one-dimensional supramolecular chain stabilized through  $\pi$ -stacking interactions between adjacent pyridine moieties in the crystal lattice shown in Fig. 3b. The crystal and molecular structure of  $[Cu_2(L^2)_2(py)_2]$  described here is remarkably similar to the corresponding  $[Cu_2(L)_2(py)_2]$ ·py derived from 1,3-aryl linked *bis*- $\beta$ diketone (L) derivatives reported by Clegg et al. [4]. The pyridine adducts of related *bis*- $\beta$ -diketonatocopper(II) complexes previously been described also show loss of pyridine from the solid complex [4,9].

The paramagnetic copper(II) complex  $[Cu_2(L^2)_2(py)_2]$  was examined by EPR spectroscopy in pyridine solution. The formation of 'CuO<sub>4</sub>N' coordination units in  $[Cu_2(L^2)_2(py)_2]$  is accompanied by drastic changes in the EPR spectrum compared to the 'CuSe<sub>2</sub>O<sub>2</sub>' core of  $[Cu_2(L^1)_2]$  in toluene solution; the g<sub>0</sub> value of the former increases significantly while a<sub>0</sub> decreases significantly with respect to the Se,O coordinated Cu<sup>2+</sup> centres in the planar  $[Cu_2(L^1)_2]$  (Fig. 2). This indicates noticeable changes in the spin-density distribution within the Se,O chelated coordination sphere of  $[Cu_2(L^1)_2]$  compared to the 'CuO<sub>4</sub>N' coordination sphere of  $[Cu_2(L^2)_2]$  $(py)_2$  in the pyridine solution. Spin-exchange interactions were not observed in the broad EPR spectrum of the  $[Cu_2(L^2)_2(py)_2]$  with the 'CuO<sub>4</sub>/ CuO<sub>4</sub>N' core in pyridine solution. Presumably in pyridine solutions at 370 K, pyridine exchange processes may result in equilibria between [Cu<sub>2</sub>  $(L^2)_2(py)_2]$ ,  $[Cu_2(L^2)_2(py)]$  and  $[Cu_2(L^2)_2]$  in view of the relatively low stability found for the isolated  $[Cu_2(L^2)_2(py)_2]$  complex (vide infra), which may account for the broad poorly resolved EPR spectrum obtained; such exchange processes in the solution are likely also to affect any equilibrium between "dimeric" and "monomeric Cu<sup>2+</sup> "centres in such solution, while pyridine coordination to the 'CuO<sub>4</sub>' core in  $[Cu_2(L^2)_2]$  to result in  $[Cu_2(L^2)_2]$  $(py)_2$  isolated here, will certainly prevent *inter*-molecular spin-exchange. Further study will be required to resolve such issues. Similar results have been observed in previous EPR studies of pyridine adducts of substituted 2,4-pentanedionatocopper(II) complexes [10,11].

In conclusion, the novel binuclear  $[Cu_2(L^2)_2(py)_2]$  complex derived from the relatively unstable *cis*- $[Cu_2(L^1-Se,O)_2]$  complex, which in the presence of pyridine results in the relatively rapid elimination of red selenium accompanied by the O for Se atom exchange to yield the first example of a metallamacrocyclic copper(II) complex (isolated as a five-coordinate Cu(II) *bis*-pyridine adduct) containing a bipodal chelating *N*,*N*,*N*<sup>'''</sup>-tetraethyl-*N'*,*N*<sup>''</sup>-isophthaloylbis(urea) anion fragment as ligand. This  $[Cu_2(L^2)_2(py)_2]$  complex crystallizes in onedimensional supramolecular arrays in the solid state.

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### Appendix A. Supplementary material

X-ray crystallographic files in CIF format for the supplementary crystallographic data for  $[Cu_2(L^1)_2]$  and  $[Cu_2(L^2)_2(py)_2]$  have been

submitted to the Cambridge Crystallographic Data Centre with reference numbers CCDC 780953 and CCDC 780954 at www.ccdc.ac. uk/data\_request/cif.

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- [6] Synthesis of H2L1 A solution of isophthaloyl dichloride (0.83 g, 4.17 mmol) in 15 mL of acetone was added to a solution of KSeCN (1.20 g, 8.33 mmol) in 25 mL of acetone, which was not dried before. The mixture was stirred at room temperature for 15 min. During this time, an orange suspension was formed. Thereafter, diethylamine (0.61 g, 8.33 mmol) was added dropwise. The mixture was heated to reflux for 2 h, after which it was allowed to cool. A red solution with an orange-red precipitate was obtained. The mixture was transferred to a beaker containing 150 mL water and 5 mL hydrochloric acid and was left to stand in the fridge overnight. The solid was filtered off and washed with water. Recrystallization from ethanol gave pale red, light sensitive crystals of H2L. Yield 1.50 g (74%). 1H NMR (300 MHz, CDCl3): δ [ppm]: 1.25 (t, 3J = 6.9 Hz, 12H, CH3); 1.33 (t, 3] = 6.9 Hz, 12H, CH3); 3.54 (q, 3] = 6.9 Hz, 4H, CH2); 4.06 (q, 3] = 6.9 Hz, 4H, CH2); 7.49 (t, 3] = 7.8 Hz, 1H, ar-H); 7.98 (d, 3] = 7.8 Hz, 2H, ar-H); 8.35 (s, 1H, ar-H); 9.64 (s, 2H, NH). 13C-{1H} NMR (75 MHz, CDCl3): 8 [ppm]: 11.6 (s, CH3); 12.9 (s, CH3); 48.2 (s, CH2); 50.9 (s, CH2); 127.3 (s, ar-C); 129.4 (s, ar-C); 132.7 (s, ar-C); 132.8 (s, ar-C); 162.0 (s, C=O); 180.6 (s, C=Se, 2JCSe=219.1 Hz). 77Se-{1H} NMR (76 MHz, CDCl3):  $\delta$  [ppm]: 495.9 (s, C=Se); IR (KBr) [cm<sup>-1</sup>]:  $\nu$ (N-H) 3189 (w), v (C=O) 1694 (s), v (C=Se) 1530 (s). Synthesis of [Cu<sub>2</sub>(L<sup>1</sup>)<sub>2</sub>]:  $H_2L$  (0.49 g, 1.00 mmol), dissolved in 25 mL ethanol, was added to a solution of Cu  $(CH_3COO)_2 \cdot H_2O$  (0.20 g, 1.00 mmol) in 40 mL of ethanol. The colour of the solution turned immediately to brown and after stirring the reaction solution at 60 °C for 15 min, a microcrystalline solid was obtained. The solid was filtered off and washed with water. The product was recrystallized from a chloroform/ acetonitrile mixture. Yield 0.42 g (76%). M.p. 160 °C (decomposition); positive ESI-MS (m/z): 1100.9[M+H]<sup>+</sup>; IR (KBr)  $[cm^{-1}]$ :  $\nu$ (CO) 1588(s),  $\nu$ (CSe) 1492 (s); Calculation for C<sub>36</sub>H<sub>48</sub>Cu<sub>2</sub>N<sub>8</sub>O<sub>4</sub>Se<sub>4</sub>: C, 39.32; H, 4.40; N, 10.19. Found: C, 39.10; H, 4.38; N, 10.07. Synthesis of [Cu<sub>2</sub>(L<sup>2</sup>)<sub>2</sub>(py)<sub>2</sub>]: [Cu<sub>2</sub>(L<sup>1</sup>)<sub>2</sub>] (0.10 g, 0.09 mmol) was dissolved in 1 mL pyridine. The colour of the solution turned to green. The mixture was left to stand 2 days at room temperature. Thereafter, blue crystals of the product and a red solid of the byproduct were obtained. The product, which is unstable beyond the solvent, was characterized by X-ray diffraction and EPR spectroscopy.
- [7] Structure determination of [Cu<sub>2</sub>(L<sup>1</sup>)<sub>2</sub>]: C<sub>36</sub>H<sub>48</sub>Cu<sub>2</sub>N<sub>8</sub>O<sub>4</sub>Se<sub>4</sub> (M = 1099.74); triclinic, space group *P*-1 (No. 2); T = 100(2) K, a = 8.3300(15)Å, b = 10.2834(19)Å, c = 12.1590(20)Å,  $\alpha = 81.280(2)^\circ$ ,  $\beta = 80.142(2)^\circ$ ,  $\gamma = 87.315(2)^\circ$ , V = 1014.1(3)Å<sup>3</sup>, Z = 1,  $D_c = 1.801$  Mg/m<sup>3</sup>,  $\mu$ (MoK<sub> $\alpha$ </sub>) = 4.687 mm<sup>-1</sup>, brown prism from CHCl<sub>3</sub>/ CH<sub>3</sub>CN,  $0.11 \times 0.05 \times 0.03$  mm<sup>3</sup>, $\Theta$  range for data collection  $1.72-24.70^{\circ}$ , F(000) = 546; 8875 collected, 3438 unique, and 2753 observed ( $I > 2\sigma(I)$ ) diffractions, 244 parameter, final  $R_1 = 3.63\%$  for observed diffractions,  $wR_2 = 9.14\%$  for all data, GOF = 1.045, residual electron density + 1.953 and  $-0.769 \text{ e} \cdot \text{Å}^{-3}$ . Structure determination of [Cu<sub>2</sub>(L<sup>2</sup>)<sub>2</sub>(py)<sub>2</sub>]:The low temperature X-ray structure was obtained immediately after isolation.  $C_{46}H_{58}Cu_2N_{10}O_8$  (M = 1006.10); triclinic, space group P-1 (No.2); T = 100(2) K, a = 12.4854(5) Å, b = 12.8161(5) Å,  $\dot{A}^{3}$ , Z = 2,  $D_{c} = 1.5.4141(6)$ ,  $\dot{A}_{c} = 74.810(1)^{\circ}$ ,  $\beta = 87.576(1)^{\circ}$ ,  $\gamma = 86.650(1)^{\circ}$ , V = 2375.3(2) $\dot{A}^{3}$ , Z = 2,  $D_{c} = 1.407$  Mg/m<sup>3</sup>,  $\mu$ (MoK<sub> $\alpha$ </sub>) = 0.958 mm<sup>-1</sup>, blue prism from pyridine,  $0.20 \times 0.04 \times 0.01 \text{ mm}^3$ ,  $\Theta$  range for data collection  $1.65-28.19^\circ$ , F(000) = 940; 27534 collected, 10,655 unique, and 9241 observed  $(I > 2\sigma(I))$  diffractions, 595 parameter, final  $R_1 = 2.84\%$  for observed diffractions,  $wR_2 = 7.78\%$  for all data, GOF = 1.030, residual electron density +0.408 and  $-0.268 \text{ e} \cdot \text{Å}^{-3}$ . Diffraction data were collected on a Bruker-Nonius SMART Apex diffractometer equipped with fine-focus sealed tube and a 0.5 mm Monocap collimator (monochromated MoK $\alpha$  radiation,  $\lambda = 0.71073$  Å). Data were captured with a CCD (Charge-Coupled Device) area-detector with the generator powered at 40 kV and 30 mA. A constant stream of nitrogen gas is produced by an Oxford Cryogenics Cryostat (700 Series Cryostream Plus) coupled to the diffractometer for low temperatures (100 K). The structures were solved by direct methods (SHELXS-97 [12]) and refined by full-matrix least-squares on F<sup>2</sup> (SHELXL-97 [12]). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed and refined in their theoretical positions. The molecular structures were visualized by Diamond, Version 3.2e [13].
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