

New π ligand N,N,N,N',N',N'-hexaallylethylenediaminium (L^{2+}): synthesis and crystal structures of $LBr_2 \cdot 2H_2O$ and its cuprocomplexes $L[Cu^{II}(Br_{0.45}Cl_{3.55})]$, $L[Cu^I_4(Br_{4.55}Cl_{1.45})]$, and $L[Cu^I_4Br_6]$.

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Streszczenie

The alkylation of ethylenediamine with allyl bromide in the presence of a fourfold (with respect to ethylenediamine) molar amount of $NaHCO_3$ in acetone with an ethanol admixture (15:1) affords $LBr_2 \cdot H_2O$ (I), where L^{2+} is the N,N,N,N,N,N'-hexaallylethylenediaminium cation. Single crystals of complexes $L[Cu^{II}(Br_{0.45}Cl_{3.55})]$ (II), $L[(Br_{4.55}Cl_{1.45})]$ (III), and $L[Br_6]$ (IV) are prepared by an electrochemical synthesis from an ethanolic solution of $LBr_2 \cdot 2H_2O$, $CuCl_2 \cdot 2H_2O$ (or $CuBr_2$) at copper wire electrodes. The crystal structures of compounds I–IV are determined by X-ray diffraction analysis. The crystals of complex I are monoclinic: space group $P2_1/n$, $a = 8.544(3)$, $b = 10.404(3)$, $c = 13.350(4)$ Å, $\beta = 97.29(3)^\circ$, $V = 1177.2(6)$ Å³, $Z = 2$. The bromine anions in compound I are bonded to the L^{2+} cations and water molecules through hydrogen contacts $(E)H \cdots Br$ ($E = O, C$) of $2.57(3)$ – $2.86(3)$ Å. The crystals of compounds II–IV are triclinic: space group P . For II: $a = 8.762(4)$, $b = 9.163(4)$, $c = 16.500(6)$ Å, $\alpha = 95.62(4)^\circ$, $\beta = 96.39(4)^\circ$, $\gamma = 111.46(4)^\circ$, $V = 1211.4(9)$ Å³, $Z = 2$; for III: $a = 9.074(4)$, $b = 9.435(4)$, $c = 9.829(5)$ Å, $\alpha = 116.12(4)^\circ$, $\beta = 104.14(4)^\circ$, $\gamma = 100.22(4)^\circ$, $V = 692.3(6)$ Å³, $Z = 1$; for IV isostructural III: $a = 9.084(4)$, $b = 9.404(4)$, $c = 9.869(4)$ Å, $\alpha = 116.31(3)^\circ$, $\beta = 104.00(3)^\circ$, $\gamma = 100.37(3)^\circ$, $V = 692.1(5)$ Å³, $Z = 1$. Unlike the isolated tetrahedral Cu anion in structure II, an original chain anion $(Cu_4)_n$ is observed in the structures of π complexes III and IV.

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