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for

Tetrametallic [2×1+1×2], octametallic double-decker–triple-decker [5×1+3×1], hexametallic quadruple-decker and dimetallic-based one-dimensional complexes of copper(II) and s block metal ions derived from *N*,*N*′-ethylenebis(3-ethoxysalicylaldimine)

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The Coordination Environments of the Copper(II) Centres in 1–6

In the structures of **1**–**6**, there are fifteen crystallographically different copper(II) centres in the salen type N_2O_2 compartment of L^{2-}. The bond lengths and bond angles involving these copper(II) centres are summarized in Table S4. Except the Cu(2) centre in the $Cu^{II}_4Rb^{I}_2$ compound **6**, fourteen other copper(II) centers in **1**–**6** are tetracoordinated by two imine nitrogen atoms and two bridging phenoxo oxygen atoms. The coordination geometry of these fourteen copper(II) centres is approximately square planar. The Cu(2) centre in **6** is pentacoordinated due to additional coordination of the bridging water oxygen atom in the axial position of the approximately square pyramidal coordination environment. Considering all the fifteen cases, the Cu–N(imine)/O(phenoxo) bond distances lie in the range 1.8838(16)–1.961(4) Å. However, in all cases, a Cu–N bond length is slightly longer than its *trans* Cu–O bond distance. In the square $N(imine)_2O(phenoxo)_2$ plane, the ranges of *cisoid* and *transoid* angles are 82.39(13)–96.43(15)º and 171.83(6)–178.60(13)º, respectively. The bond angles [91.12(4)–95.78(5)º] involving the apical water oxygen atom in the coordination environment of Cu(2) in **6** are also very close to 90º. Clearly, the bond angles deviate only little from the ideal values, indicating that coordination environments are almost square pyramidal (for Cu(2) in **6**) or almost square planar (for other fourteen cases). Again, for all the fifteen cases, the ranges of the deviation of the constituent atoms and displacement of the metal centre from the corresponding least-squares $N(imine)_2O(phenoxo)_2$ plane are 0.003–0.104 Å and 0.000–0.0968 Å, respectively, which are in line with only little distortion of the coordination environments.

Table S1

Bond angles (°) in the coordination environments of the potassium(I) centres in $[\{(Cu^{II}L)_2K^{I}\}(ClO_4)]\cdot[\{(Cu^{II}L)_3K^{I}_2(\mu\text{-}ClO_4)\}(ClO_4)]$ (**4**). Symmetry codes: C, 1 – x, y, 1.5 – z; D, –x, y, 1.5 – z.

O(1)–K(1)–O(1C)	98.74(6)	O(5)–K(2)–O(9D)	141.66(5)
O(1)–K(1)–O(2)	51.08(5)	O(5)–K(2)–O(10D)	89.95(5)
O(1)–K(1)–O(2C)	68.71(5)	O(5)–K(2)–O(11)	133.85(6)
O(1)–K(1)–O(3)	101.79(5)	O(6)–K(2)–O(7)	56.16(5)
O(1)–K(1)–O(3C)	84.34(5)	O(6)–K(2)–O(8)	103.20(5)
O(1)–K(1)–O(4)	116.48(5)	O(6)–K(2)–O(9D)	97.22(5)
O(1)–K(1)–O(4C)	127.98(4)	O(6)–K(2)–O(10D)	76.65(5)
O(2)–K(1)–O(2C)	80.88(7)	O(6)–K(2)–O(11)	170.09(7)
O(2)–K(1)–O(3)	59.11(5)	O(7)–K(2)–O(8)	51.14(4)
O(2)–K(1)–O(3C)	129.56(5)	O(7)–K(2)–O(9D)	73.34(5)
O(2)–K(1)–O(4)	104.21(5)	O(7)–K(2)–O(10D)	103.87(5)
O(2)–K(1)–O(4C)	174.27(5)	O(7)–K(2)–O(11)	113.94(6)
O(3)–K(1)–O(3C)	170.70(8)	O(8)–K(2)–O(9D)	83.90(5)
O(3)–K(1)–O(4)	53.18(5)	O(8)–K(2)–O(10D)	139.33(5)
O(3)–K(1)–O(4C)	117.84(5)	O(8)–K(2)–O(11)	67.46(6)
O(4)–K(1)–O(4C)	70.85(7)	O(9D)–K(2)–O(10D)	56.29(5)
O(5)–K(2)–O(6)	53.54(5)	O(9D)–K(2)–O(11)	78.91(7)
O(5)–K(2)–O(7)	101.62(5)	O(10D)–K(2)–O(11)	107.99(7)
O(5)–K(2)–O(8)	123.26(5)		

Table S2
Bond angles (°) in the coordination environments of the potassium(I) centre in $[Cu^{II}LK^{I}(\mu\text{-}PF_6)]_n$ (**5**).
Symmetry code: E, –1 + x, y, z.

O(1)–K(1)–O(4)	172.38(5)
O(1)–K(1)–O(2)	57.22(4)
O(1)–K(1)–O(3)	118.41(4)
O(1)–K(1)–F(1)	90.36(6)
O(1)–K(1)–F(2E)	86.91(6)
O(2)–K(1)–O(3)	61.25(4)
O(2)–K(1)–O(4)	118.90(4)
O(2)–K(1)–F(1)	100.19(6)
O(2) –K(1)–F(2E)	108.29(5)
O(3)–K(1)–O(4)	57.82(5)
O(3)–K(1)–F(1)	102.84(6)
O(3)–K(1)–F(2E)	110.07(5)
O(4)–K(1)–F(1)	96.93(6)
O(4)–K(1)–F(2E)	88.47(5)
F(1)–K(1)–F(2E)	143.90(6)
Cu(1)–O(2)–K(1)	104.30(6)
Cu(1)–O(3)–K(1)	105.11(6)

Table S3

Bond angles (°) in the coordination environments of the rubidium(I) centre in $[\{(Cu^{II}L)_2Rb^{I}(\mu\text{-}H_2O)\}_2](BPh_4)_2\cdot 2CH_3COCH_3$ (**6**).

Symmetry code: G, −x, 2 − y, 1 − z.

O(1)–Rb(1)−O(2)	52.26(3)	O(3)–Rb(1)−O(7)	77.67(3)
O(1)–Rb(1)−O(3)	101.81(3)	O(3)–Rb(1)−O(8)	63.39(3)
O(1)–Rb(1)−O(4)	121.89(3)	O(3)–Rb(1)−O((9G)	117.44(3)
O(1)–Rb(1)−O(5)	78.80(3)	O(4)–Rb(1)−O(5)	131.63(3)
O(1)–Rb(1)−O(6)	69.75(3)	O(4)–Rb(1)−O(6)	167.69(3)
O(1)–Rb(1)−O(7)	103.29(3)	O(4)–Rb(1)−O(7)	116.01(3)
O(1)–Rb(1)−O(8)	146.22(3)	O(4)–Rb(1)−O(8)	74.81(3)
O(1)–Rb(1)−O((9G)	126.73(3)	O(4)–Rb(1)−O((9G)	110.65(3)
O(2)–Rb(1)−O(3)	55.93(3)	O(5)–Rb(1)−O(6)	50.73(3)
O(2)–Rb(1)−O(4)	102.20(3)	O(5)–Rb(1)−O(7)	97.28(3)
O(2)–Rb(1)−O(5)	122.22(3)	O(5)–Rb(1)−O(8)	113.38(3)
O(2)–Rb(1)−O(6)	81.64(3)	O(5)–Rb(1)−O((9G)	59.14(3)
O(2)–Rb(1)−O(7)	70.71(3)	O(6)–Rb(1)−O(7)	53.86(3)
O(2)–Rb(1)−O(8)	97.73(3)	O(6)–Rb(1)−O(8)	93.14(3)
O(2)–Rb(1)−O((9G)	125.91(3)	O(6)–Rb(1)−O((9G)	58.77(3)
O(3)–Rb(1)−O(4)	52.30(3)	O(7)–Rb(1)−O(8)	45.77(3)
O(3)–Rb(1)−O(5)	174.94(3)	O(7)–Rb(1)−O((9G)	56.65(3)
O(3)–Rb(1)−O(6)	124.64(3)	O(8)–Rb(1)−O((9G)	54.25(3)

Table S4. Bond Lengths (Å) and Bond Angles (°) of the Coordination Environments of the Copper(II) Centres in **1**–**6** Symmetry code, D, –x, y, 1.5 – z.

Compound	Cu–Centre	Bond lengths		Bond angles	
1	Cu(1)	Cu(1)–N(1)	1.939(3)	N(1)–Cu(1)–O(3)	177.82(11)
		Cu(1)–N(2)	1.940(3)	N(2)–Cu(1)–O(2)	176.79(11)
		Cu(1)–O(2)	1.901(2)	N(1)–Cu(1)–N(2)	84.40(12)
		Cu(1)–O(3)	1.900(2)	N(1)–Cu(1)–O(2)	92.70(11)
				N(2)–Cu(1)–O(3)	93.47(11)
				O(2)–Cu(1)–O(3)	89.44(10)
	Cu(2)	Cu(2)–N(3)	1.911(3)	N(3)–Cu(2)–O(8)	178.29(11)
		Cu(2)–N(4)	1.926(3)	N(4)–Cu(2)–O(7)	178.60(13)
		Cu(2)–O(7)	1.889(2)	N(3)–Cu(2)–N(4)	86.43(13)
		Cu(2)–O(8)	1.894(2)	N(3)–Cu(2)–O(7)	94.96(12)
				N(4)–Cu(2)–O(8)	94.80(12)
				O(7)–Cu(2)–O(8)	83.81(10)
	Cu(3)	Cu(3)–N(5)	1.940(3)	N(5)–Cu(3)–O(13)	177.48(12)
		Cu(3)–N(6)	1.942(3)	N(6)–Cu(3)–O(12)	177.29(10)
		Cu(3)–O(12)	1.895(2)	N(5)–Cu(3)–N(6)	85.16(12)
		Cu(3)–O(13)	1.893(2)	N(5)–Cu(3)–O(12)	93.33(11)
				N(6)–Cu(3)–O(13)	92.37(11)
				O(12)–Cu(3)–O(13)	89.16(10)
2	Cu(1)	Cu(1)–N(1)	1.9477(15)	N(1)–Cu(1)–O(3)	176.07(6)
		Cu(1)–N(2)	1.9292(15)	N(2)–Cu(1)–O(2)	176.71(6)
		Cu(1)–O(2)	1.9106(12)	N(1)–Cu(1)–N(2)	84.51(6)
		Cu(1)–O(3)	1.9075(13)	N(1)–Cu(1)–O(2)	92.67(6)
				N(2)–Cu(1)–O(3)	92.40(6)
				O(2)–Cu(1)–O(3)	90.49(5)
	Cu(2)	Cu(2)–N(3)	1.9172(15)	N(3)–Cu(2)–O(8)	176.86(6)
		Cu(2)–N(4)	1.9317(15)	N(4)–Cu(2)–O(7)	176.81(6)
		Cu(2)–O(7)	1.8894(12)	N(3)–Cu(2)–N(4)	85.13(6)
		Cu(2)–O(8)	1.8991(12)	N(3)–Cu(2)–O(7)	94.31(6)
				N(4)–Cu(2)–O(8)	93.75(6)
				O(7)–Cu(2)–O(8)	86.97(5)
	Cu(3)	Cu(3)–N(5)	1.9388(15)	N(5)–Cu(3)–O(13)	176.51(6)
		Cu(3)–N(6)	1.9406(15)	N(6)–Cu(3)–O(12)	176.53(6)
		Cu(3)–O(12)	1.9018(13)	N(5)–Cu(3)–N(6)	84.40(6)
		Cu(3)–O(13)	1.9139(12)	N(5)–Cu(3)–O(12)	93.35(6)
				N(6)–Cu(3)–O(13)	92.12(6)
				O(12)–Cu(3)–O(13)	90.13(5)
3	Cu(1)	Cu(1)–N(1)	1.932(4)	N(1)–Cu(1)–O(3)	176.04(15)
		Cu(1)–N(2)	1.961(4)	N(2)–Cu(1)–O(2)	176.46(16)
		Cu(1)–O(2)	1.936(3)	N(1)–Cu(1)–N(2)	84.56(18)
		Cu(1)–O(3)	1.901(3)	N(1)–Cu(1)–O(2)	92.35(15)
				N(2)–Cu(1)–O(3)	92.53(16)
				O(2)–Cu(1)–O(3)	90.47(14)

Compound	Cu–Centre	Bond lengths		Bond angles	
3	Cu(2)	Cu(2)–N(3)	1.907(4)	N(3)–Cu(2)–O(8)	175.20(15)
		Cu(2)–N(4)	1.913(4)	N(4)–Cu(2)–O(7)	172.49(15)
		Cu(2)–O(7)	1.897(3)	N(3)–Cu(2)–N(4)	85.98(17)
		Cu(2)–O(8)	1.891(3)	N(3)–Cu(2)–O(7)	96.43(15)
				N(4)–Cu(2)–O(8)	95.79(15)
				O(7)–Cu(2)–O(8)	82.39(13)
	Cu(3)	Cu(3)–N(5)	1.945(4)	N(5)–Cu(3)–O(14)	177.83(16)
		Cu(3)–N(6)	1.924(4)	N(6)–Cu(3)–O(13)	176.57(16)
		Cu(3)–O(13)	1.898(3)	N(5)–Cu(3)–N(6)	84.93(18)
		Cu(3)–O(14)	1.927(3)	N(5)–Cu(3)–O(13)	92.15(16)
				N(6)–Cu(3)–O(14)	93.04(16)
				O(13)–Cu(3)–O(14)	89.90(14)
4	Cu(1)	Cu(1)−N(1)	1.920(2)	N(1)–Cu(1)–O(3)	173.94(9)
		Cu(1)−N(2)	1.940(2)	N(2)–Cu(1)–O(2)	175.97(8)
		Cu(1)−O(2)	1.8838(16)	N(1)–Cu(1)–N(2)	85.93(9)
		Cu(1)−O(3)	1.9010(16)	N(1)–Cu(1)–O(2)	94.21(8)
				N(2)–Cu(1)–O(3)	92.46(8)
				O(2)–Cu(1)–O(3)	87.81(7)
	Cu(2)	Cu(2)−N(3)	1.933(2)	N(3)–Cu(2)–O(7)	177.88(8)
		Cu(2)−N(4)	1.9231(19)	N(4)–Cu(2)–O(6)	177.84(8)
		Cu(2)−O(6)	1.8950(16)	N(3)–Cu(2)–N(4)	84.98(8)
		Cu(2)−O(7)	1.8968(16)	N(3)–Cu(2)–O(6)	93.88(8)
				N(4)–Cu(2)–O(7)	93.48(8)
				O(6)–Cu(2)–O(7)	87.61(7)
	Cu(3)	Cu(3)−N(5)	1.938(3)	N(5)–Cu(3)–O(10D)	173.59(9)
		Cu(3)−O(10)	1.9067(18)	N(5–Cu(3) –N(5D)	85.06(17)
				N(5)–Cu(3)–O(10)	93.66(10)
				O(10)–Cu(3)–O(10D)	88.30(10)
5	Cu(1)	Cu(1)–N(1)	1.9345(17)	N(1)–Cu(1)–O(3)	176.67(7)
		Cu(1)–N(2)	1.9403(15)	N(2)–Cu(1)–O(2)	176.23(8)
		Cu(1)–O(2)	1.9115(12)	N(1)–Cu(1)–N(2)	84.45(7)
		Cu(1)–O(3)	1.9100(14)	N(1)–Cu(1)–O(2)	93.42(6)
				N(2)–Cu(1)–O(3)	93.03(7)
				O(2)–Cu(1)–O(3)	89.22(6)
6	Cu(1)	Cu(1)−N(1)	1.9255(14)	N(1)–Cu(1)–O(3)	178.27(6)
		Cu(1)−N(2)	1.9267(15)	N(2)–Cu(1)–O(2)	176.92(6)
		Cu(1)−O(2)	1.8981(11)	N(1)–Cu(1)–N(2)	85.13(7)
		Cu(1)−O(3)	1.9033(11)	N(1)–Cu(1)–O(2)	94.08(6)
				N(2)–Cu(1)–O(3)	93.15(6)
				O(2)–Cu(1)–O(3)	87.63(5)

Compound	Cu–Centre	Bond lengths		Bond angles	
6	Cu(2)	Cu(2)−N(3)	1.9427(14)	N(3)–Cu(2)–O(7)	171.83(6)
		Cu(2)−N(4)	1.9456(14)	N(4)–Cu(2)–O(6)	175.71(6)
		Cu(2)−O(6)	1.9214(11)	O(9)–Cu(2)–N(3)	95.78(5)
		Cu(2)−O(7)	1.9262(11)	O(9)–Cu(2)–N(4)	92.59(5)
		Cu(2)−O(9)	2.4044(12)	O(9)–Cu(2)–O(6)	91.12(4)
				O(9)–Cu(2)–O(7)	92.09(5)
				N(3)–Cu(2)–N(4)	84.42(6)
				N(3)–Cu(2)–O(6)	93.07(5)
				N(4)–Cu(2)–O(7)	93.03(5)
				O(6)–Cu(2)–O(7)	88.98(5)