Inorganica Chimica Acta
LETTER

Coordination chemistry of sulfonyl amides

3*. Copper(I) and nickel(II) complexes of *N*,*N*′,*N*″,*N*‴-tetramethylsulfonyl-1,4-benzoquinonediimine-2,5-diaminato

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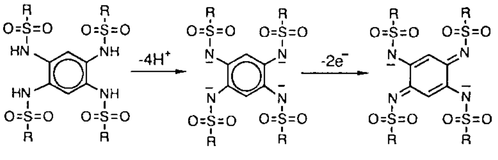
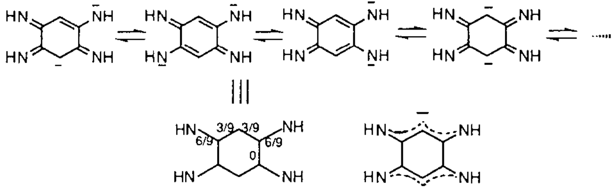
In continuation of our research on the coordination chemistry of sulfonyl amido ligands [1–4], we here report metal complexes in a new series of N-substituted tetrasulfonyl-1,2,4,5-tetraaminobenzene and two novel crystal structures of tetrapyridine-μ-*N*,*N*′,*N*″,*N*‴-tetramethylsulfonyl-1,4-benzoquinonediimine-2,5-diaminato-dicopper(I) and bis(triphenylphosphine)bispyridine-μ-*N*,*N*′,*N*″,*N*‴-tetramethylsulfonyl-1,4-benzoquinonediimine-2,5-diaminato-dicopper(I). (The name is used to describe the oxidation state of the ligand rather than the electronic structure of the ligand.)



The ligand (H_4L) was prepared from the reaction of 1,2,4,5-tetraaminobenzene and methylsulfonyl chloride in a 1:4 ratio in pyridine and subsequently quenched in HCl (15% aq.). The deep blue copper complex was formed by the reaction of copper(II) acetate with ligand (2:1) in pyridine under a dinitrogen atmosphere.

The complex was first thought to be $[Cu_2(II)(\mu\text{-}L1)(py)_4]$, but it characterized as $[Cu_2(I)(\mu\text{-}L2)(py)_4]$ from magnetic measurement (diamagnetic) and X-ray diffraction[†]. Crystal data of $[Cu_2(I)(\mu\text{-}L2)(py)_4]$: $Cu_2S_4O_8N_8C_{30}H_{34}$, triclinic space group $P\bar{1}$, $a = 9.052(1)$, $b = 9.435(5)$, $c = 11.361(1)$ Å, $\alpha = 100.02(3)$, $\beta = 95.56(2)$, $\gamma = 98.18(3)°$, $V = 938.4(6)$ Å^3, $Z = 1$, $D_C = 1.575$ g cm^{-3}, $R_F = 0.029$, $R_{wF} = 0.027$ for 2967 unique data ($2\theta < 50°$) with $I > 2\sigma(I)$ and 304 variables. Data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα ($\lambda = 0.7093$ Å) radiation. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined isotropically.

Figure 1 is an ORTEP drawing of $[Cu_2(I)(\mu\text{-}L2)(py)_4]$. There is a center of inversion between the two copper atoms. Each copper atom is tetrahedrally coordinated by two pyridines and two *ortho*-*N*-sulfonylamido groups. The most interesting feature is the bond pattern observed in the tetraamido benzene ring. The C1–C2–C3–C1′–C2′–C3′ six-membered ring is not aromatic; the bond distance C1–C3 is 1.498(3) Å typical of a single bond, and the bond distances of N1–C1, C1–C2, C2–C3 and C3–N2 are 1.342(3), 1.382(2), 1.384(3) and 1.341(3) Å, respectively, intermediate between the lengths of single and double bonds. These results indicate delocalization, with four bonds in a W shape, and is consistent with the following pattern[††]:



Thus the copper ions are in the +1 state and the complex is diamagnetic.

Further substitution of one pyridine by triphenylphosphine led to the formation of bistriphenylphosphine bispyridine-μ-*N*,*N*′,*N*″,*N*‴-tetramethylsulfonyl-1,4-benzoquinonediimine-2,5-diaminato-dicopper(I), which was also characterized by X-ray diffraction. Crystal data of $[Cu_2(I)(\mu\text{-}L2)(py)_2(Pph_3)_2](py)_2$: $Cu_2S_4P_2O_8N_8C_{66}H_{64}$, triclinic space group $P\bar{1}$, $a = 9.632(2)$, $b = 12.730(3)$, $c = 14.162(21)$ Å, $\alpha = 95.75(2)$, $\beta = 103.04(1)$, $\gamma = 91.06(2)°$, $V = 1681.6(6)$ Å^3, $Z = 1$, $D_C = 1.397$ g cm^{-3}, $R_F = 0.030$, $R_{wF} = 0.026$ for 5056 unique data ($2\theta < 50°$) with $I > 2\sigma(I)$ and 535 variables. Figure 2 is an ORTEP drawing. Comparison with the previous structure indicates that they have essentially identical bond lengths

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*Part 2 is ref. 1.

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[†] The Ag(I) analogue was also determined. Crystal data of $[Ag_2(I)(\mu\text{-}L2)(py)_4]$: $Ag_2S_4O_8N_8C_{30}H_{34}$, triclinic space group $P\bar{1}$, $a = 9.217(2)$, $b = 9.252(5)$, $c = 11.343(3)$ Å, $\alpha = 97.85(3)$, $\beta = 94.05(5)$, $\gamma = 96.55(3)°$, $V = 948.3(6)$ Å^3, $Z = 1$, $D_C = 1.714$ g cm^{-3}, $R_F = 0.029$, $R_{wF} = 0.022$ for 2685 unique data ($2\theta < 50°$) with $I > 2\sigma(I)$ and 236 variables. The structure reveals the same bond pattern as the Cu(I) complex.

[††] The observed delocalization pattern is similar to that in the bridge ligand of the dianion of 2,5-dihydroxy-1,4-benzoquinone [5].

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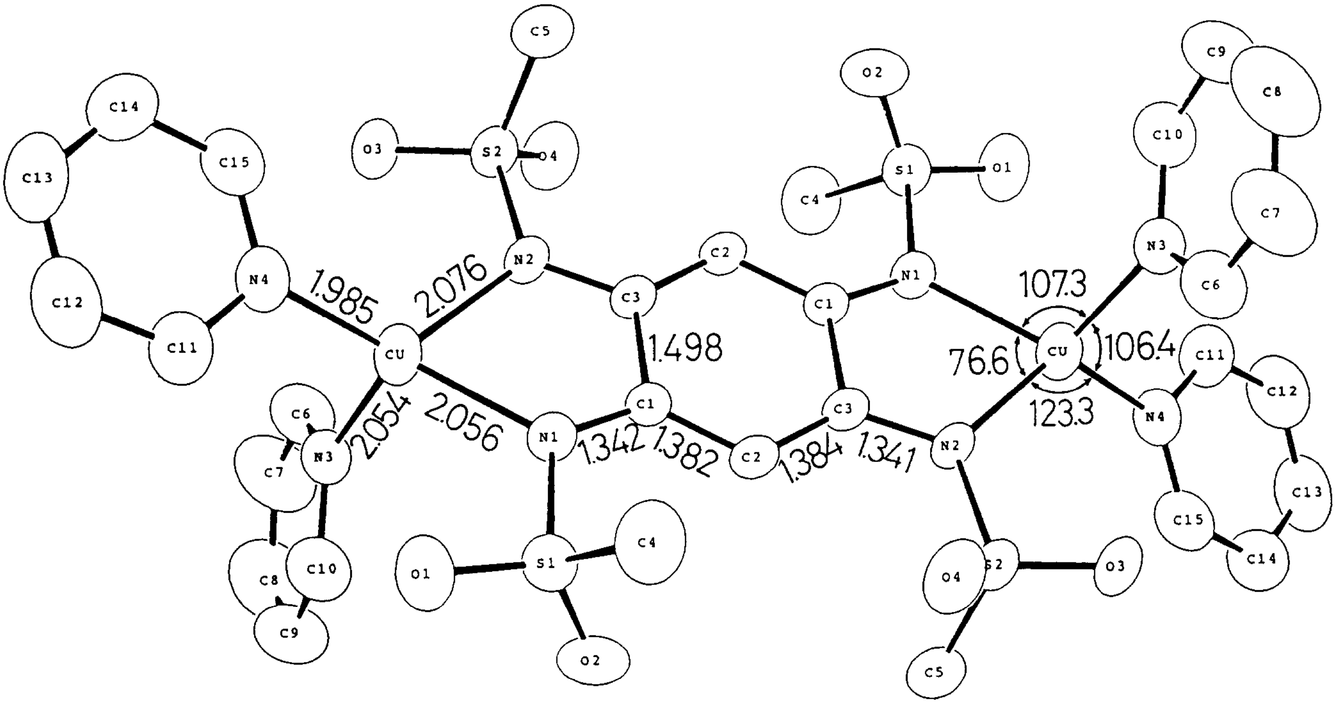

Fig. 1. ORTEP drawing of the complex $[Cu_2(I)(\mu\text{-}L2)(py)_4]$ with 50% probability. The standard deviations of bond lengths and angles shown are in the range 0.002–0.003 Å and 0.08–0.09°, respectively.

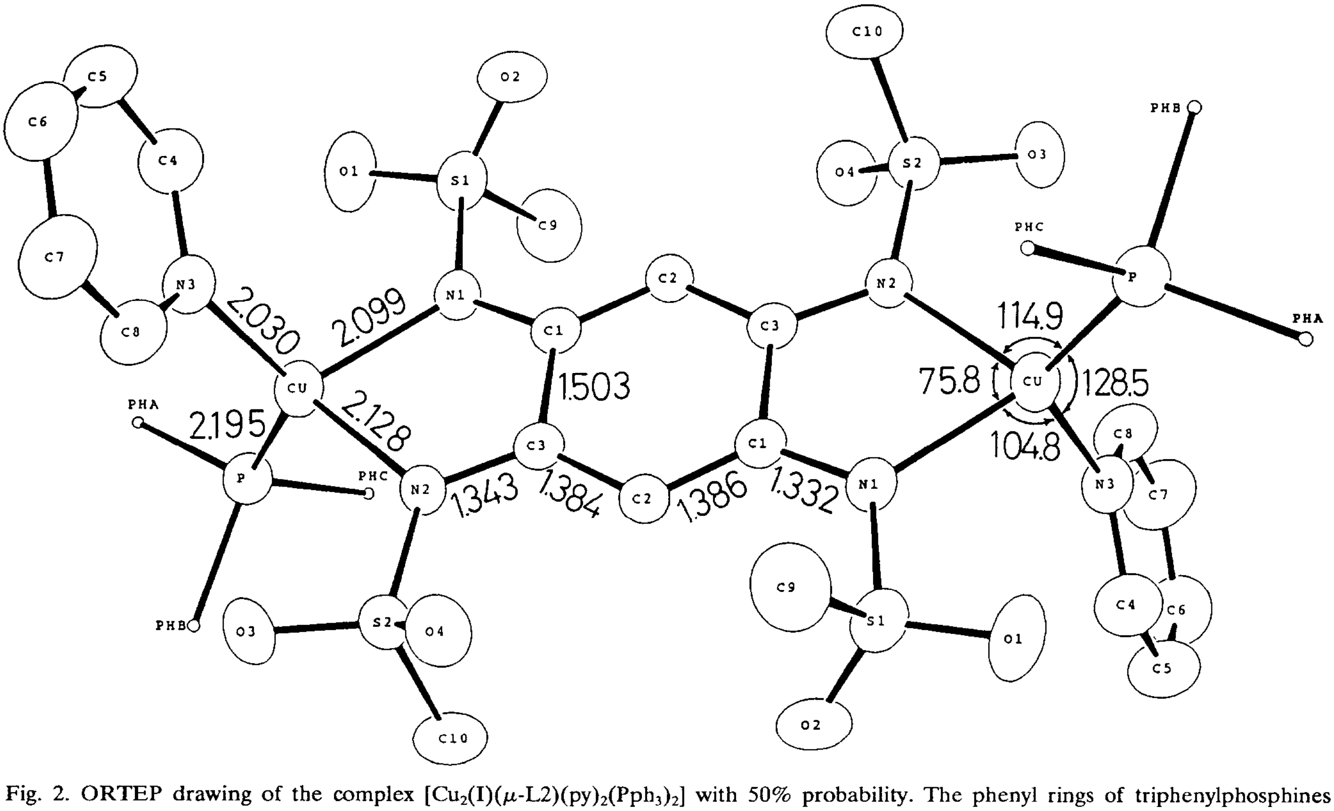

Fig. 2. ORTEP drawing of the complex $[Cu_2(I)(\mu\text{-}L2)(py)_2(Pph_3)_2]$ with 50% probability. The phenyl rings of triphenylphosphines except the attached carbon atoms have been omitted for clarity. The standard deviations of bond lengths and angles shown are in the ranges 0.002–0.003 Å and 0.05–0.07°, respectively.

in the bridged ligand and slightly longer Cu–N bonds in the coordination sphere. The latter is attributed to the minimization of steric hindrance between the crowded triphenylphosphine ligand and the other coordinated moieties.

The Ni analogue has a different chemistry. The pink–red complex was formed by the reaction of nickel(II) acetate with ligand (2:1) in pyridine under a dinitrogen atmosphere. Its UV–Vis spectrum (UV–Vis: 590 (6.9×10^2), 550 (6.21×10^2), 426 ($\epsilon=2.48\times10^3$ M^{-1} cm^{-1}) nm) is similar to that of $[Ni(II)(py)_2(L3)]$ (L3 = *N*,*N*′-dimethylsulfonyl-*o*-phenylenediaminato) [2]. It characterized as $[Ni_2(II)(py)_4(\mu\text{-}L1)]^0$. When dioxygen was bubbled through the solution of complex $[Ni_2(II)(py)_4(\mu\text{-}L1)]^0$, it turned deep blue and the complex ion $[Ni_2(II)(py)_4(\mu\text{-}L2)]^{2+}$ was formed. Further structural characterization is in progress.

An attempt is being made to isolate the one-dimensional polymer $[Ni(II)(\mu\text{-}L2)]_n$.

Acknowledgement

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