A versatile ligand for coordination chemistry: metal complexes of alkyl- or arylsulfonfonyl amides

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Amide groups are considered to be poorly coordinating systems due to the delocalization of the lone pair electrons on the nitrogen atom and the electron-withdrawing ability of the carbonyl, sulfonfonyl or phosphonfonyl groups.

The chemistry of

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\begin{align*}
\text{O} & \quad \text{R} \\
\text{H} & \quad -\text{NR} \\
-\text{C} & \quad -\text{NH}
\end{align*}
\]

complexes has been extensively explored, whereas few studies on metal complexes of

\[
\begin{align*}
\text{O} & \quad \text{R} \\
\text{S} & \quad -\text{NH} \\
\text{O} & \quad \text{R}
\end{align*}
\]

have been reported. The p-tolylsulfonamide group in 1-(4-tolyl-sulfonfonyl)-1,4,8,11-tetraazacyclotetradecan (Tscyclam) has been used to reduce the coordination power of cyclam; the crystal structure of \([\text{Ni(Tscyclam)(H_2O)}_2]\text{Cl}_2\) shows that the Ni-N (amide) distance is 0.3 Å longer than the Ni-N (amine) distances [1]. On the other hand, the effects mentioned above may increase the acidity of the amidic hydrogen so that the amides could become anions in basic solution; the latter are good σ donors. Thus high-valent metal complexes are expected to be formed with multiamido ligands.

This work describes the synthesis of amido complexes of three different classes: mono-, di-N-substituted o-phenylenediamine and N-substituted 2-aminopyridine. Their crystal structures are also reported.

The first example of these ligands is \(N\text{-}(p\text{-tolylsulfonfonyl})\text{-o-phenylenediamine (2)}\) which was prepared from the reaction of o-phenylenediamine and \(p\text{-tolylsulfonfonyl chloride in a 1:1 ratio in pyridine and subsequently quenched in HCl (15%, aq.}\). The product was recrystallized from ethanol. (Mass: \(m/z\) 262; IR: \(\nu(N-H) 3466, 3385, 3210 \text{ cm}^{-1}; \nu(S=O) 1151 \text{ cm}^{-1}\)) The metal complexes (M = Co, Ni, Cu) were prepared by the reaction of metal acetates with excess ligand in small amounts of dmf. The copper complex has been characterized by X-ray diffraction. Crystal data of \([\text{Cu(L2)(dmf)}]_2\text{(dmf)}\): Cu_{37}O_{2N_{2}}C_{37}H_{47}, triclinic space group \(P1\), \(a = 11.965(3)\), \(b = 12.752(4)\), \(c = 12.757(2)\) Å, \(\alpha = 85.43(2)\), \(\beta = 84.05(2)\), \(\gamma = 84.22(2)\), \(V = 1921(1)\) Å³, \(Z = 2\), \(D_c = 1.41 \text{ g cm}^{-3}\), \(\rho = 0.063\), \(R_{wp} = 0.058\) for 4122 unique data with \(I > 2\sigma(I)\) and 425 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 included as fixed contributions. Figure 1 is an ORTEP drawing of the [Cu(L2)(dmf)] molecule. The copper ion is coordinated by two deprotonated bidentate ligands (L2) in a square-planar base with one dmf molecule in an axial position. The Cu-N (amide) distances, 2.032(5) and 2.041(5) Å, are slightly larger than the Cu-N (amine) distances, 1.975(5) and 1.982(5) Å.
Fig. 1. ORTEP drawing of the molecule [Cu(L2)2·dmf] with 50% probability. Pertinent bond lengths (Å) and bond angles (°): Cu-N1 2.041(5), Cu-N2 1.982(5), Cu-N3 2.032(5), Cu-N4 1.975(6), N1-C1 1.412(8), N2-C6 1.449(9), N3-C7 1.410(9), N4-C12 1.451(9); O5-Cu-N1 91.3(2), O5-Cu-N2 101.2(2), O5-Cu-N3 98.3(2), O5-Cu-N4 90.8(2), N1-Cu-N2 80.6(2), N1-Cu-N3 170.1(2), N1-Cu-N4 98.5(2), N2-Cu-N3 96.2(2), N2-Cu-N4 168.0(2), N3-Cu-N4 82.7(2).

(1:2). The ligand was recrystallized from ethanol. (Mass: m/z 416; IR: ν(N-H) 3313, 3217 cm⁻¹, ν(S=O) 1161, 1145 cm⁻¹.) The reaction of H2L3 and metal ions (M=Co(II), Ni(II), Cu(II)) in pyridine led to the isolation of [M(L3)2]²⁻ [2]. The anionic complexes, [M(L3)2]²⁻, were synthesized by addition of NEt₃ to the acetonitrile solution of metal ions and H2L3. The products (HNEt₃)₂[M(L3)₂] were characterized by single-crystal X-ray analysis. Both bis(N,N'-bis(methylsulfonyl)-o-phenylenediiminato)cuprate(II), [Cu(L3)²]²⁻ and bis(N,N'-bis(p-tolylsulfonyl)-o-phenylenediiminato)cuprate(II), [Cu(L3)²]²⁻, have been determined. The former has lower R values and is presented in Fig. 2. Crystal data of (HNEt₃)₂[Cu(L3)²]: CuS₄O₆N₆H₄, orthorhombic, space group P2₁2₁2₁, a = 12.232(3), b = 16.304(4), c = 18.320(9) Å, V = 3654(2) Å³, Z = 4, Dₐ = 1.43 g/cm³, R_p = 0.059, R_w = 0.056 for 2874 unique data with I > 2σ(I) and 355 parameters. Crystal data of (HNEt₃)₂[Cu(L3)²]: CuS₄O₆N₆H₄, trigonal, space group P3₁2₁, a = 17.433(5), c = 20.700(6) Å, V = 4658(2) Å³, Z = 3, Dₐ = 1.39 g/cm³, R_p = 0.094, R_w = 0.113 for 1144 unique data with I > 2σ(I), 287 parameters. Figure 2 is an ORTEP drawing of the anionic complex [Cu(L3)²]²⁻. The copper ion has a distorted tetrahedral geometry. The dihedral angle between the N1-Cu-N2 and N3-Cu-N4 planes is 73.1(3)°. The average Cu-N distance, 1.985(8) Å, is normal by comparison with four-coordinate copper complexes.

The third ligand, HL4, was prepared similarly. The reaction of Cu(OAc)₂ with HL4 led to the formation of dinuclear [Cu₂(L4)₄]. The result of the X-ray structural analysis is shown in Fig. 3. Crystal data of [Cu₂(L4)₄]: Cu₂S₄O₆N₆C₄H₄, monoclinic, space group P2₁/c, a = 15.762(12), b = 15.552(5), c = 20.505(11) Å, β = 104.14(7)°, V = 4874(5) Å³, Z = 4, D = 1.47 g/cm³, R_p = 0.050, R_w = 0.049 for 5142 unique data with I > 2σ(I). The binuclear Cu₂(L4)₄ molecule has the expected struc-
ture of the copper(II) acetate type without the axial ligands. The only closely related structure is \([\text{Cu}_2(dpt)_4] \) (dpt = 1,3-di-phenyltriazenato) [3]. Both structures have small Cu–Cu distances, 2.441(2) Å for \([\text{Cu}_2(dpt)_4]\) and 2.516(2) Å for \([\text{Cu}_2(L4)_4]\) and both are diamagnetic at room temperature. The four nitrogen atoms coordinated to one copper ion are planar but the copper atoms lie 0.2 Å out of those planes. The two N4-planes of this complex are almost parallel, but when the structure is viewed down the Cu–Cu line two sets of coordinating nitrogen atoms are twisted from the eclipsed position by 17.3(2)°.

Further exploration of ligands of this new type is under way.

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References