A New Co-ordinating Role for a Metal Salicylaldimine

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Air oxidation of $(CuIpy)_4$ (py = pyridine) in acetone in the presence of Ni(mepren) (H_2mepren = *N,N'*-1,3-propylenebis-salicylidineamine) yields the ionic complex $[\{Ni(OH)\}_2\{Ni(H_2O)_2(mepren)\}_2](Cu_2I_4)$, the cation of which contains the nickel salicylaldimine molecules co-ordinated in a novel fashion to $[Ni\text{-}\mu\text{-}(OH)]_2^{2+}$.

Of all the synthetic strategies which have been devised for the preparation of heterobimetallic complexes, perhaps the simplest is that which exploits the Lewis basicity of metal salicylaldimines, thereby enabling them to form donor bonds with appropriate Lewis acid metal species.[1] The range of heterobimetallic adducts prepared in this way is extensive and comprehensive studies of their magnetic properties have contributed significantly to our understanding of magnetic exchange between dissimilar metal centres. Although the structural chemistry of these adducts is surprisingly varied, the

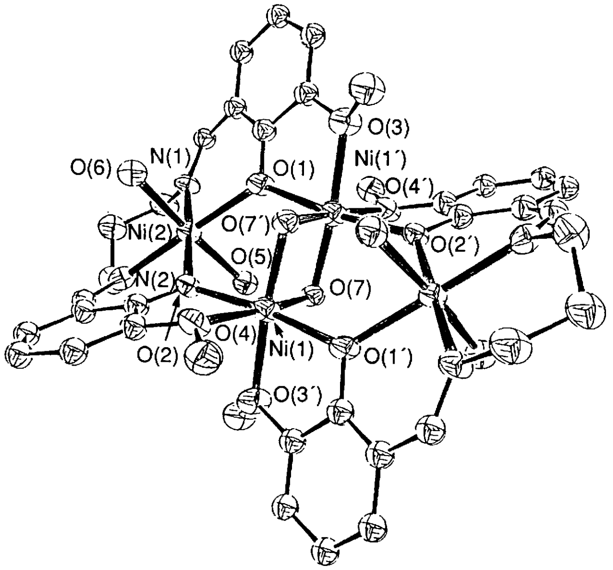

Figure 1. ORTEP plot of the asymmetric unit of the cation of (**1**) (acetone molecules omitted for clarity). Selected dimensions: Ni(2)–O(1) 2.106(6), Ni(2)–O(2) 2.122(6), Ni(2)–O(5) 2.064(7), Ni(2)–O(6) 2.131(7), Ni(2)–N(1) 2.055(8), Ni(2)–N(2) 2.076(8), Ni(1)–O(2) 2.026(6), Ni(1)–O(4) 2.143(8), Ni(1)–O(7) 2.010(7), Ni(1)–O(3′) 2.078(7), Ni(1)–O(1′) 2.037(6), Ni(1)–O(7′) 1.988(7), Ni(1)–Ni(1′) 2.804(1) Å; O(1)–Ni(2)–O(2) 93.9(2), N(1)–Ni(2)–O(1) 86.4(3), N(2)–Ni(2)–N(1) 93.6(3), O(2)–Ni(2)–N(2) 86.1(3), O(5)–Ni(2)–O(6) 173.6(3)°.

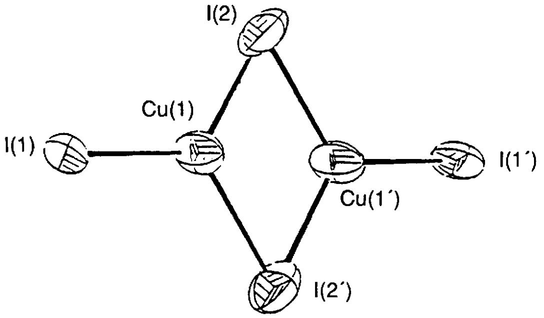

Figure 2. ORTEP plot of the asymmetric unit of the anion of (**1**). Selected dimensions: Cu(1)–I(1) 2.511(2), Cu(1)–I(2) 2.598(2), Cu(1)–I(2′) 2.573(2), Cu(1)–Cu(1′) 2.683(2) Å; I(1)–Cu(1)–I(2) 117.7(1), I(1)–Cu(1)–I(2′) 124.7(1), I(2)–Cu(1)–I(2′) 117.5(1) Å.

role of the metal salicylaldimine is invariant, behaving as a bidentate donor ligand to the Lewis acid metal.[2—6] This communication focuses attention on a novel alternative co-ordinating role for a metal salicylaldimine which could be exploited in the synthesis of new homo- and hetero-metallic compounds.

When Ni(mepren) (H_2mepren = *N,N*′-1,3-propylenebis-salicylidineamine) and $(CuIpy)_4$ (py = pyridine) were reacted in refluxing acetone for 24 h, a green solid was obtained which had relatively low solubility in acetone. Recrystallization of this product from acetone yielded turquoise, dark green, and brown crystals. The IR spectra of these three materials suggest that they are original reaction products. The brown crystalline material was identified as Cu(mepren). *X*-Ray microprobe analysis indicated that the turquoise and dark green crystals contained both nickel and copper. The structures of both compounds were established by single crystal diffraction studies.† Both are $[\{Ni(OH)\}_2\{Ni(H_2O)_2(mepren)\}_2](Cu_2I_4)$, the difference between them being that the turquoise compound, (**1**), contains four hydrogen-bonded acetone molecules per formula unit whereas the green compound contains two hydrogen-bonded molecules of metal salicylaldimine per formula unit.

The asymmetric unit of (**1**) is shown in Figures 1 and 2. The complex contains the $[Ni\text{-}(\mu\text{-}OH)]_2^{2+}$ cation.‡ This is significant since, although $[Cu\text{-}(\mu\text{-}OH)]_2^{2+}$ is a well established species, its nickel analogue does not appear to have been encountered in any previous crystallographic study; di(μ-hydroxo)organonickel species, on the other hand, do exist.[7] The generation of $[Ni\text{-}(\mu\text{-}OH)]_2^{2+}$ in the present reaction was facilitated by the displacement of Ni^{2+} by Cu^{2+} ions from the nickel salicylaldimine complex [Cu(mepren) was a reaction product]. In complex (**1**) $[Ni\text{-}(\mu\text{-}OH)]_2^{2+}$ is centrosymmetric and has two co-ordinated molecules of $Ni(H_2O)_2$(mepren).

It is the mode of co-ordination of these nickel Schiff-base complexes which is of particular interest. Rather than acting as a bidentate donor ligand to one metal (as has been the case in every other bimetallic adduct of this general class) each Schiff-base complex in (**1**), by adopting a bridging role, behaves as a bidentate ligand to each of the nickel atoms in the di(μ-hydroxo) cation. Thus, the phenolic oxygens of a nickel Schiff-base complex form donor bonds to two separate metals, and at the same time the pronounced umbrella conformation adopted by the complex facilitates further methoxy donor bond formation to each of the metals. As each nickel salicylaldimine behaves similarly in centrosymmetric fashion, the nickel ions of the di(μ-hydroxo) species achieve octahedral geometry. The core of the structure is composed of an eight membered centrosymmetric ring of alternating nickel and oxide ions. The nickel ions of the di(μ-hydroxo) species and the oxide ions are essentially coplanar while the nickel ions of the salicylaldimine complexes are removed from this plane to produce a chair conformation. The oxygen and nickel ions of the di(μ-hydroxo) species define a plane which is essentially perpendicular to the planar section of the eight membered ring. An acetone molecule is hydrogen bonded to each of the water molecules co-ordinated to nickel, but more signifi-

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† *Crystal data*: $C_{50}H_{74}N_4O_{18}I_4Ni_4Cu_2$, $M = 1888.62$, monoclinic space group $P2_1/c$, $a = 11.1326(13)$, $b = 17.6495(23)$, $c = 17.1053(20)$ Å, $\beta = 95.173(10)°$, $U = 3347.24$ Å^3, $D_c = 1.87$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 35.21$ cm^{-1}, 2772 reflections with $I > 3\sigma I$, using a CAD4 diffractometer and Mo-K_α radiation, $2\theta_{max.} = 48°$. The structure was solved by direct methods, SHELX86,[8] and refined with 188 variable parameters using SHELX76.[9] Following full matrix refinement with metal, iodine, oxygen, nitrogen, and carbon atoms of acetone refined anisotropically and no absorption correction applied, $R = 5.23$ and $R_w = 5.52\%$. Maximum and minimum excursions in the final $F_o - F_c$ difference map were 0.93 and −0.79 e Å^{-3} respectively. The ORTEP program[10] was used to produce the diagrams in Figures 1 and 2. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

‡ Metal analysis confirmed that nickel rather than copper had to be involved in the di(μ-hydroxy) species.

cantly, the chair conformation of the core brings one water oxygen, O(5), within 2.55 Å from a hydroxide oxygen, O(7), and a hydrogen atom of the water was located between the two oxygens thus demonstrating the presence of a very strong intramolecular hydrogen bond.

This unexpected mode of co-ordination of the nickel Schiff-base complex is achieved without any apparent molecular strain; the umbrella conformation is commonly encountered, and both the bond lengths and bond angles about nickel are similar to those which we have found in other high-spin nickel salicylaldimines. Furthermore, apart from the angle of 78.5(3)° [for O(4)–Ni(1)–O(2) and O(4′)–Ni(1′)–O(2′)], other angles about the nickel atoms of the di(μ-hydroxo) species deviate no more than 5° from the true octahedral value, and the Ni–O donor bond lengths compare well with the Cu–O bond lengths of 2.30(1) and 1.98(1) Å in Cu(salen)·$CuCl_2$ (H_2salen = *N*,*N′*-ethylenebis-salicylidineamine). It would be surprising therefore if this bridging role of a metal salicylaldimine could not be realized with other bimetallic species, including perhaps metal–metal bonded species. Our initial investigations of these possibilities have led to the isolation of 1 : 1 adducts of the distannoxane $(SnBu^nCl_2)_2O$ with a range of metal salicylaldimine complexes (which, in fact, do not have methoxy substituents) and ^{119}Sn Mössbauer parameters present very convincing evidence for the presence of only one tin environment in each adduct. The most logical conclusion to be drawn from these observations, particularly in the light of the structure described, is that here also are further examples of metal salicylaldimines adopting a bridging role.

We thank the Commissioners of Irish Lights for financial support (J. F. G.).

Received, 15th March 1990; Com. 0/01154A

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