temperatures (fast outer-sphere exchange), and the difference $Q_{\mathrm{lim}} - Q_{\mathrm{outer}} = Q_{\mathrm{inner}}$ is the limiting value for inner-sphere fast exchange. If Q_{inner}/H_2O–Ni bond is truly constant, then $\bar{n} = Q_{\mathrm{inner}}(\mathrm{obsd})/3.90$. If $\bar{n}$ is <5, at least some $Ni(H_2O)_4(CH_3OH)_2^{2+}$ must be present. An unique distribution cannot be obtained from these data. The results require that any differences in properties of the species present be small as the data can be well fit with the assumption of only one average single species with 4.91 H_2O/Ni. The constancy of Q from 119 to 160 °C also suggests that $\bar{n}(H_2O)$ is insensitive to temperature. Otherwise, a considerable number of fortuitous compensations would have to be present to account for the data. Jambor[5] has obtained a value of ca. −3 kcal mol^{-1}, using spectrophotometry, for addition of one CH_3OH to hexaaquonickel(II). This result, if correct, would make $\bar{n}(H_2O)$ at our temperatures even larger than the value 5.8 found by Rorabacher[2] at lower temperature. With $\bar{n}(H_2O)$ near 5, our results are in fact going to be quite insensitive to the K's and $\Delta H°$'s for formation of mono- and bis(methanol) complexes since the mono complex is nearly completely formed and only a small amount of bis complex may be present (ca. 10%).

One calculates for a random or statistical distribution of species in our solution, $\bar{n} = 4.3$. Thus water is slightly favored over CH_3OH in the inner sphere. This suggests that $\Delta H°$'s for the stepwise equilibria may be small and thus that the temperature dependence of the species distribution is also small.

The kinetic parameters derived above are quite similar to those for $Ni(H_2O)_6^{2+}$ in water[3] ($k_1 = 3.2 \times 10^4\ s^{-1}$, $\Delta H^{\ddagger} = 13.6$ kcal mol^{-1}, and $\Delta S^{\ddagger} = 7.7$ cal $mol^{-1}\ K^{-1}$). On the face of it, water exchange has been slowed ca. 10% by CH_3OH substituted for H_2O. The exchange parameters for $Ni(CH_3OH)_6^{2+}$ in CH_3OH as found by Luz and Meiboom[6] are $k_1 = 1 \times 10^3\ s^{-1}$, $\Delta H^{\ddagger} = 16$ kcal mol^{-1}, and $\Delta S^{\ddagger} = 8$ cal $mol^{-1}\ K^{-1}$. It is of interest to determine CH_3OH exchange kinetics in the mixed solvent to see if the donor H_2O can labilize CH_3OH.

The $\bar{n}$ value of 4.91 is much lower than expected from Rorabacher's work.[2] We estimate from his data that $\bar{n}$ should be ca. ≥5.8 on the basis of spectrophotometric studies. Our number is subject to the assumption of constancy of the shift produced per H_2O by Ni(II). For an $\bar{n} = 5.8$ to be obtained, Q_{inner}/H_2O would have to be 3.3 rather than 3.9. In fact, the values we find in mixed species tend to be greater than 3.9 rather than less, perhaps up to 4.1. It seems therefore that we have a reasonably good estimate. A check on our result could be made by comparing CH_3OH shifts in $Ni(CH_3OH)_6^{2+}$ with those in the mixed solvent. Since $H_2{}^{17}O$ is difficult to recover from CH_3OH, it would be desirable to use natural-abundance $^{17}OH_2$ and a high-field NMR spectrometer.

The Q_{outer} value of 0.24 is lower than the value 0.48 found[3] for $Ni(H_2O)_6^{2+}$ in H_2O, suggesting that some CH_3OH replaces water in the outer sphere. A more detailed study of outer-sphere shifts and their origin is desirable before reaching very definite conclusions on the point.

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Registry No. Water, 7732-18-5; methanol, 67-56-1.

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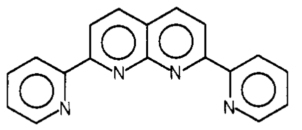
Communications

Crescent-Shaped Dinuclear Complexes: A Dirhodium(II) Complex of the New Tetradentate Ligand 2,7-Bis(2-pyridyl)-1,8-naphthyridine (bpnp), $[Rh_2(bpnp)(\mu\text{-}CH_3CO_2)_3](PF_6)$

Sir:

There is considerable interest in ligand systems that can coordinate two metal centers in close proximity. Such dinuclear complexes may show unusual properties and synergism between the two metals.[1] Described here are the synthesis, spectral characterization, and structure of the first dinuclear complex of the tetradentate ligand 2,7-bis(2-pyridyl)-1,8-naphthyridine[2] (bpnp). The title complex is a derivative of the extensively studied[3] dirhodium(II) tetrakis(μ-carboxylates) and represents the first example of a $LRh_2(O_2CR)_3^+$ ion where L is a neutral bridging ligand. The electrochemistry of this complex is unusually rich, showing not only a reversible one-electron oxidation but also two reversible one-electron reductions in contrast to the tetracarboxylates that undergo irreversible reduction. The combination of the relatively rigid tetradentate ligand and the two metal atoms is crescent shaped (i.e., a "croissant complex"), thus minimizing the steric effects on the metal centers in potential catalytic interactions with substrate molecules.



bpnp

Equimolar quantities of bpnp, tetrakis(μ-acetato)dirhodium(II), and aqueous HCl stirred in methanol under argon give a deep purple solution in minutes. Addition of aqueous ammonium hexafluorophosphate to the air-stable solution and removal of the methanol by heating in air give purple needles of tris(μ-acetato)(2,7-bis(2-pyridyl)-1,8-naphthyridine)dirhodium(II) hexafluorophosphate (I) in >85% yield. Carbon, hydrogen, and nitrogen analyses are in good agreement with the formulation $[Rh_2(bpnp)(O_2CCH_3)_3]PF_6$.[4] Conductivity measurements in nitromethane show this compound to be a 1:1 electrolyte[5] ($\Lambda = 71$ mhos cm^2/mol).

The ^1H NMR spectrum (100 MHz) of I has two singlets for the acetate methyls at δ 1.38 and 2.21 and a complex second-order spectrum in the aromatic region with the integrated ratios 2:1:4, respectively. At 500 MHz, the aromatic region breaks up into six distinct signals of equal areas (δ 8.33, 8.63, 8.96, 9.145, 9.155, and 9.79, respectively). These spectra

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[4] Found by Bernhardt Microanalytical Laboratories (calculated for $C_{24}H_{21}O_6F_6N_4Rh_2P$): % C = 35.10 (35.49); % H = 2.61 (2.60); % N = 6.82 (6.90).

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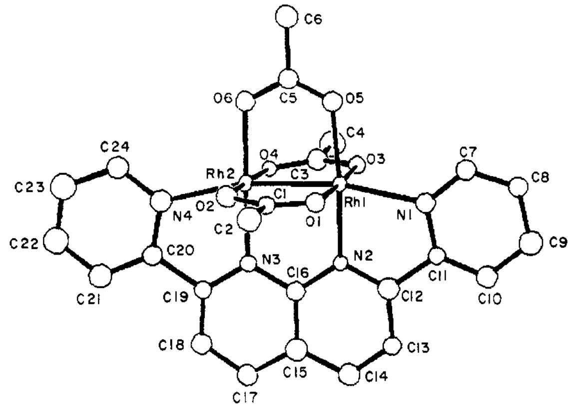

Figure 1. Crystal structure and atom numbering scheme for the tris(μ-acetato)(2,7-bis(2-pyridyl)-1,8-naphthyridine)dirhodium(II) cation.

suggest a solution structure where bpnp symmetrically bridges the two rhodium atoms via the naphthyridine fragment and the methyl protons of the two acetates cis to bpnp are shielded by their proximity to the aromatic ligand. An alternative explanation is that the NMR spectra represent a collection of rapidly equilibrating, less symmetric structures.

The crystal structure of I shown in Figure 1[6] confirms the suggested symmetrical structure. The two rhodium atoms are bridged by the three acetate groups and the naphthyridine fragment of bpnp. The 2-pyridyl groups occupy the axial sites trans to the Rh–Rh bond. The Rh–Rh bond length of 240.5 (2) pm is slightly longer than the 239.6 pm seen in tetrakis(μ-acetato)bis(pyridine)dirhodium(II).[7] The Rh(1)–N(2) and Rh(2)–N(3) bond lengths of 199 (1) and 201 (1) pm are significantly shorter than the rhodium–equatorial nitrogen bond lengths of μ-2-oxypyridine complexes of dirhodium(II)[8] but similar to those in bis(1,10-phenanthroline)bis(μ-formato)dirhodium(II) chloride.[9] The axial Rh(1)–N(1) and Rh(2)–N(4) distances are longer (220 ± 1 pm) than the equatorial Rh–N distances but slightly shorter than the corresponding distance in the bis(pyridine) adduct of tetrakis(μ-acetato)dirhodium(II).[7] The constraint of the 2-pyridyl fragment being bound to the naphthyridine is evident in the average Rh–Rh–N(pyridyl) angle of 166.9 ± 0.1°.

The visible absorption spectrum of I in methanol shows several intense bands with λ_{max} values of 565 nm (ϵ = 3.1 × 10^3 L mol^{-1} cm^{-1}), 525 (sh), and 435 (1.30 × 10^3). The tetrakis(μ-carboxylato)dirhodium(II) complexes display two bands of comparable wavelengths, the lower energy band assigned as a π^*(Rh–Rh) to σ^*(Rh–Rh) transition.[10] However, the molar extinction coefficient for the low-energy band of I is more than an order of magnitude larger and the band maximum shifts to longer wavelengths in less polar solvents, suggesting a charge-transfer assignment.

Cyclic voltammetry in acetonitrile with tetra-*n*-butylammonium perchlorate as supporting electrolyte shows three reversible one-electron waves for I. A reversible oxidation is seen at 1.28 V vs. SSCE,[11] and two reversible reductions are seen at –0.57 and –1.21 V vs. SSCE. In comparison, free bpnp is reversibly reduced in the same medium at –1.56 V (vs. SSCE). Bis(ligand) adducts of tetrakis(μ-acetato)dirhodium(II) show a reversible oxidation (one electron) at ca. 1.0 V vs. SCE but are irreversibly reduced (two electrons) at potentials more negative than –0.7 V vs. SCE.[12]

Preliminary studies show I to form a catalyst for the water gas shift reaction in 20% water/pyridine solutions, with turnover frequencies of over 100 mol of CO_2 day^{-1} (mol of I)$^{-1}$ at 100 °C and 1 atm of CO. The homogeneous solution formed retains this activity for at least 2 weeks. However, the turnover frequency for hydrogen formation is consistently lower than that for CO_2 by about 25%, suggesting the possibility that hydrogenation of pyridine is a side reaction in this system.

The preparation of naphthyridine derivative complexes of the type $L_xRh_2(OAc)_{4-x}{}^{x+}$ by refluxing the rhodium(II) tetraacetate dimer and the desired naphthyridine with acid equimolar to the naphthyridine appears to be general. We have now also prepared complexes where x = 4 (L = 1,8-naphthyridine) and x = 2 (L = 2-(2-pyridyl)-1,8-naphthyridine). These complexes and their properties will be discussed in a later paper.

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Registry No. [$Rh_2(bpnp)(O_2CCH_3)_3$]PF_6, 84810-84-4; Rh, 7440-16-6; tetrakis(μ-acetato)dirhodium(II), 15956-28-2.

Supplementary Material Available: Listings of positional and thermal parameters for I (3 pages). Ordering information is given on any current masthead page.

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(6) Crystal data: $C_{24}H_{21}O_6F_6N_4Rh_2P$, M_r = 821.21, tetragonal, $I4_1cd$, a = b = 2872.0 (14) pm, c = 1390.6 (5) pm, V = 11470 × 10^6 pm^3, Z = 16, density calculated = 1.881 g/cm^3, density observed = 1.879 g/cm^3, Syntex P1 diffractometer, Mo Kα, λ = 0.71969 Å, T = 115 K; 5725 reflections collected of which 2146 were unique ($I > 3\sigma(I)$); total number of parameters varied 167. The structure was solved by direct methods and difference Fourier syntheses. Full-matrix least-squares refinement with anisotropic thermal parameters for the two rhodium atoms and isotropic thermal parameters for the remaining non-hydrogen atoms converged at R = 0.068 and R_w = 0.086. The hexafluorophosphate group was severely disordered; accordingly it was treated as a rigid group in the refinement. The ring hydrogen atoms were calculated by assuming sp^2 geometry and kept fixed during the refinement. No attempts were made to locate the hydrogen atoms of the acetate moieties. The largest peak in the final difference map, 2.0 e/Å^3, is associated with the disordered anion.

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(11) Saturated sodium chloride calomel electrode, at 23 °C.

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