corrections were not applied since $\mu = 0.14$ mm^{-1}. The cell parameters were obtained by least-squares refinement of the setting angles of 34 reflections with 2θ greater than 35°. Details of the data collection and crystal cell are presented in Table IV.

The structure was solved by using the program MULTAN.[18] The resulting *E* map revealed all nonhydrogen atoms. The structure was refined with anisotropic thermal parameters and the residual lowered to $R_F = 0.13$. All hydrogens were located in a difference map but were not further refined. Non-hydrogen atoms were refined by block-diagonal least squares with weights based on counting statistics. The scattering curves were taken from the "International Tables for X-ray Crystallography" (1974). Final residuals were $R_F = 0.082$ and $R_{wF} = 0.055$. All calculations were performed by using the NRC PDP8E system of programs.[19] Anisotropic thermal parameters, hydrogen atomic positions, and structure factor tables are included in the supplementary material of this paper.

The boron-11 NMR spectra at 28.7 MHz were obtained with a JEOL FX-90Q spectrometer with D-lock. Chemical shifts were referenced to external $BF_3 \cdot OEt_2$. Perdeuterioacetone was used as a solvent for the low-temperature studies. Probe temperature was monitored with a ^{13}C chemical shift thermometer with use of CCl_4/acetone-d_6.[20] High-field boron-11 spectra were obtained at 126.7 MHz in CD_2Cl_2 solution at the University of California at Los Angeles.

Acknowledgment. We thank the Research Corp. for financial support and the National Science Foundation for an instrument grant toward the purchase of the FT NMR spectrometer. We are also grateful to Paul Behnken of the Department of Chemistry, UCLA, for the high-field boron-11 NMR spectra.

Registry No. $(C_2H_5)_4N^+B_{11}H_{10}S(CH_3)_2^-$, 84642-21-7.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes, hydrogen positional parameters, and anisotropic thermal parameters of non-hydrogen atoms (22 pages). Ordering information is given on any current masthead page.

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Oxygen-17 NMR Study of Nickel(II) in Water–Methanol Solvent

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Received May 7, 1982

The effect of inner-sphere methanol on the lability of remaining water molecules in $Ni(H_2O)_n(CH_3OH)_{6-n}{}^{2+}$ species is of interest in connection with comparisons of various ligands[1] and the general kinetic behavior of solvated ions. Also, the determination of the species present is of essential importance for studied in mixed solvents. In particular Rorabacher[2] and co-workers have done detailed studies of Ni(II) in CH_3OH–H_2O mixtures. Oxygen-17 NMR studies can provide an independent check on species distributions. We have examined a 41.5 wt % CH_3OH solution and find apparently significantly different results on species distribution from those of Rorabacher.

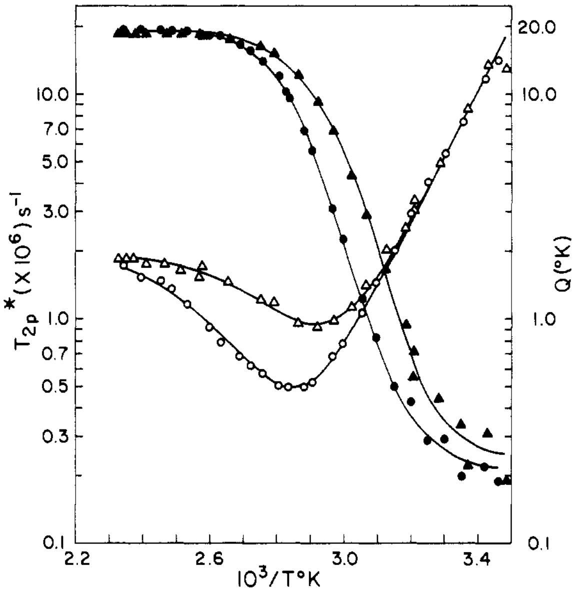

Figure 1. $T_{2p}{}^*$ and Q vs. $10^3/T$ for aqueous Ni(II)–CH_3OH: (▲, △) Q and $T_{2p}{}^*$ at 5.75 MHz; (●, ○) Q and $T_{2p}{}^*$ at 11.5 MHz.

Experimental Section

$Ni(ClO_4)_2 \cdot 6H_2O$ was prepared by recrystallizing the G. F. Smith reagent. It was analyzed by EDTA titration. Water enriched in oxygen-17 at about 4 atom %, originally obtained from Mound Laboratories, Monsanto, Inc., was purified by distillation. The methanol was Baker Analyzed reagent grade as was the perchloric acid used. $Zn(ClO_4)_2 \cdot 6H_2O$ was from G. F. Smith and was used as obtained. The nickel sample was 0.0495 M in Ni(II), 0.01 M in $HClO_4$, 29.22 M in H_2O, and 11.65 M in CH_3OH (41.5% CH_3OH by weight). The zinc blank solution had the same concentrations present. The sample and blank were each placed in 12.5 mm o.d. thick-wall Pyrex glass tubes, which were sealed with a torch.

The NMR equipment and procedures were those described before.[3] The measured line broadenings and shifts of $H_2{}^{17}O$ were converted to $T_{2p}{}^*$ and Q via the relations

$$1/T_{2p}{}^* \equiv 2\pi(W_s - W_0)m(H_2O)/m(Ni)$$

$$Q \equiv TSm(H_2O)/m(Ni)$$

where W_s and W_0 are the half-widths (in Hz) at half-maximum absorption for sample and blank and m is the molality. T is in K, and S is the relative frequency shift $(\nu_s - \nu_0)/\nu_0$, where ν_s refers to the nickel sample frequency and ν_0 to the zinc blank frequency. The data were interpreted with Swift and Connick's equations[4] modified to correspond to our use of $T_{2p}{}^*$ and Q.

Results and Discussion

Figure 1 shows the results of the measurements at two fields. The solid lines are obtained by fitting the data at both fields to the complete Swift–Connick equations with use of a weighted nonlinear least-squares program. The parameters obtained were as follows: $k_1(25\ °C) = 2.77 \times 10^4$ s^{-1}, $\Delta H^* = 12.79$ kcal mol^{-1}, $\Delta S^* = 4.8$ cal mol^{-1} K^{-1}, $T_{2M}(144\ °C) = 9.5 \times 10^{-6}$ s, E_a for $T_{2M} = 0.21$ kcal mol^{-1}, $Q_{lim} = 19.39$ K, $Q_{outer} = 0.24$ K. A field dependence for T_{2M} was not needed to obtain a good fit. These values are computed with use of $\bar{n}$ for H_2O/Ni in $Ni(H_2O)_n(CH_3OH)_{6-n}{}^{2+}$ equal to 4.91. This value was obtained by assuming the limiting Q_{inner} for a single Ni–OH_2 interaction to be 3.90 K on the basis of empirical observations,[1,3] suggesting that this quantity remains constant, independent of the nature and number of non-water ligands present. Thus $\bar{n} = (19.39 - 0.24)/3.90$. Here Q_{lim} is the high-temperature (fast-exchange) limiting value observed for the solution, Q_{outer} is the outer-sphere value found at low

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temperatures (fast outer-sphere exchange), and the difference $Q_{\text{lim}} - Q_{\text{outer}} = Q_{\text{inner}}$ is the limiting value for inner-sphere fast exchange. If Q_{inner}/H_2O–Ni bond is truly constant, then $\bar{n} = Q_{\text{inner}}(\text{obsd})/3.90$. 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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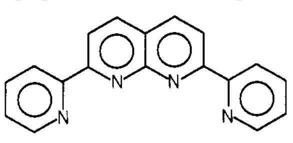
Communications

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 ^{1}H 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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