drogen sulfide is oxidized to sulfur.

The mechanism of these reactions most probably involves initial outer-sphere electron transfer from the sulfide to ruthenium (eq 8). This may then be followed by rapid reduction of a second

$$L_6Ru^{III} + H_2S \rightarrow L_6Ru^{II} + HS\cdot + H^+ \qquad (8)$$

molecule of ruthenium(III) by HS· or by dimerization to dihydrogen disulfide which may disproportionate (eq 9 and 10).

$$L_6Ru^{III} + HS\cdot \rightarrow L_6Ru^{II} + S^0 + H^+ \qquad (9)$$

$$2HS\cdot \rightarrow H_2S_2 \rightarrow H_2S + S^0 \qquad (10)$$

The ruthenium(II) complexes obtained by the reduction of the ruthenium(III) analogues with hydrogen sulfide can be oxidized by oxygen to produce hydrogen peroxide. This cycle has been demonstrated in the case of $(NH_3)_5Ru^{III}py$ at pH 4. This complex was reduced by hydrogen sulfide to produce its ruthenium(II) analogue quantitatively. After isolation, this complex was oxidized by oxygen to yield the expected amount of hydrogen peroxide.[3] Thus, a two-step, partial reduction of oxygen by hydrogen sulfide to hydrogen peroxide has been demonstrated.

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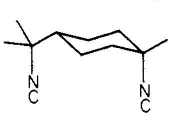
A Binuclear Nickel(II) Encapsulating Agent for Chloride and Bromide Ions

Sir:

The complexation of small cations by using crown ethers and cryptates has found a wide variety of applications in both organic[1] and inorganic chemistry.[2] On the other hand, selective complexation of small anions is relatively unknown, although Lehn and co-workers[3] have found that halides bind strongly to certain protonated cryptates. Here we report experiments that show that a binuclear isocyanide nickel species related to rhodium complexes studied[4,5] previously has the ability to bind chloride and bromide selectively in the presence of larger anions such as thiocyanate. Each halide-containing complex exhibits a fascinating electronic absorption spectrum and also undergoes a one-electron oxidation, producing a mixed-valence Ni(II),Ni(III) binuclear species.

The binuclear Ni(II) complex was prepared by addition of 0.86 g of *p*-1,8-diisocyanomenthane (0.0045 mol), or DMB, dissolved in 30 mL of methanol to a methanol solution of $NiCl_2 \cdot 6H_2O$ (0.54 g, 0.0023 mol). To the resulting orange-red solution was added a filtered methanol solution of KPF_6 (1.1 g, 0.006 mol). The product, a stable orange crystalline solid, was obtained in 84% yield. The IR spectrum of the diamagnetic complex exhibits a band at 2240 cm^{-1} (KBr disk) attributable to $\nu(C{\equiv}N)$; the frequency is similar to those found in the IR spectra of complexes of the type $Ni(CNR)_4^{2+}$.[6,7] The electronic absorption spectrum of the complex (Figure 1), however, is quite different from that of $Ni(CN)_4^{2-}$ [8] or $Ni(CNR)_4^{2+}$,[7] the most striking feature being the very intense (ϵ = 39 400 M^{-1} cm^{-1}) and extremely sharp ($\nu_{1/2}$ = 960 cm^{-1}) band at 320 nm. Chemical analysis supports the formulation $[Ni_2Cl(DMB)_4](PF_6)_3$.[9] A 10^{-3} M nitromethane solution of $[Ni_2Cl(DMB)_4](PF_6)_3$ exhibits a molar conductivity of 260 $\mu\Omega^{-1}$, which is consistent with our formulation of the compound as a 3:1 electrolyte.[10] The analogous bromo complex, $[Ni_2Br(DMB)_4](PF_6)_3$,[11] is obtained by using $NiBr_2$ as starting material.[12]



DMB

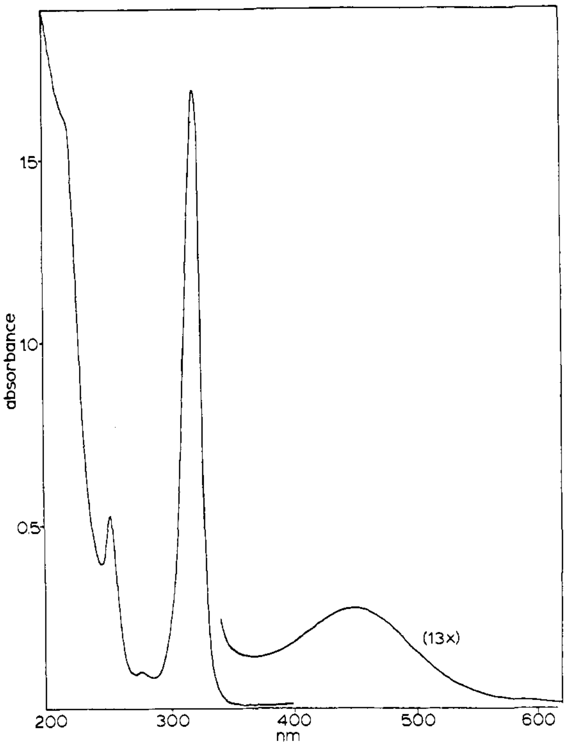


Figure 1. Electronic absorption spectrum of 0.043 mM $[Ni_2Cl(DMB)_4](PF_6)_3$ in acetonitrile solution at 25 °C.

The geometry of DMB as a bridging ligand is such that the two metals are far enough apart to encapsulate a Cl^- or Br^-. In $Ni_2(CN)_4(DMB)_2$, the Ni-Ni distance is 4.33 Å[13] whereas in $Rh_2(DMB)_4^{2+}$ the Rh-Rh distance is 4.48 Å.[14] Far-infrared spectra of several salts of the $Ni_2X(DMB)_4^{3+}$ complexes exhibit sharp, intense bands attributable to Ni-X stretches at 210 (X = Cl) and 158 cm^{-1} (X = Br). The fact that the IR bands are observable in the $Ni_2X(DMB)_4^{2+}$ complexes supports our placement of the halide in a bridging position.[15] Further evidence that the system is effectively centrosymmetric comes from Raman spectral measurements on $Ni_2Cl(DMB)_4^{3+}$; an intense band due to the symmetric Ni-Cl-Ni stretch is observed at 284 cm^{-1}.

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(1) (a) Pederson, C.; Frensdorff, H. K. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 16. (b) Lehn, J. M. *Acc. Chem. Res.* **1978**, *11*, 49.

(2) Tehan, F. J.; Barnett, B. L.; Dye, J. L. *J. Am. Chem. Soc.* **1974**, *96*, 7203.

(3) Graf, E.; Lehn, J. M. *J. Am. Chem. Soc.* **1976**, *98*, 6403.

(4) Lewis, N. S.; Mann, K. R.; Gordon, J. G., II; Gray, H. B. *J. Am. Chem. Soc.* **1976**, *98*, 7461.

(5) (a) Mann, K. R.; Lewis, N. S.; Miskowski, V. M.; Erwin, D. K.; Hammond, G. S.; Gray, H. B. *J. Am. Chem. Soc.* **1977**, *99*, 5525. (b) Miskowski, V. M.; Sigal, I. S.; Mann, K. R.; Gray, H. B.; Milder, S. J.; Hammond, G. S.; Ryason, P. R. *Ibid.* **1979**, *101*, 4383.

(6) Miller, J. S.; Balch, A. L. *Inorg. Chem.* **1972**, *11*, 2069.

(7) Stephany, R. W.; Drenth, W. *Recl. Trav. Chim. Pays-Bas* **1972**, *91*, 1453.

(8) Cowman, C. D.; Ballhausen, C. J.; Gray, H. B. *J. Am. Chem. Soc.* **1973**, *95*, 7873.

(9) All analyses were performed by the Caltech Microanalytical Laboratory. Anal. Calcd for $[Ni_2Cl(DMB)_4](PF_6)_3$: C, 42.73; H, 5.39; N, 8.31. Found: C, 42.51; H, 5.17; N, 8.05.

(10) Geary, W. J. *Coord. Chem. Rev.* **1971**, *1*, 81.

(11) Anal. Calcd for $[Ni_2Br(DMB)_4](PF_6)_3$: C, 41.37; H, 5.22; N, 8.04. Found: C, 41.64; H, 5.35; N, 8.10.

(12) Preliminary experiments indicate that fluoride also forms a complex. Iodide, however, tends to substitute readily for the isocyanide ligands, initially forming dark blue $[Ni_2I_3(DMB)_3]BPh_4$ and ultimately brown $Ni_2I_4(DMB)_2$. Details of these reactions will be reported later.

(13) Gray, H. B.; Gladfelter, W. L., to be submitted.

(14) Mann, K. R., personal communication.

(15) The IR spectra of $[NiX(diphos)_2]ClO_4$ (X = Cl, Br) complexes do not exhibit Ni-X bands; we assume they are extremely weak.

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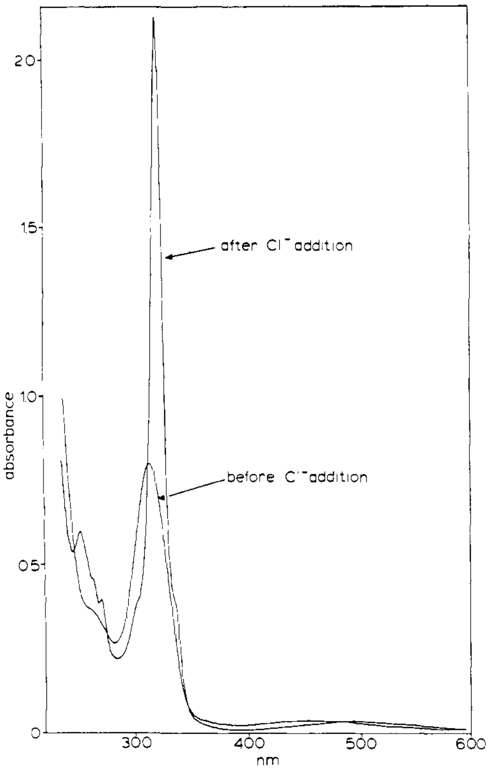

Figure 2. Spectral changes that occur after addition of 1.5 μmol of $Ph_4As^+Cl^-$ to a 10-mL acetonitrile solution containing 1.024 μmol of $[Ni_2(DMB)_4](ClO_4)_4$ and 1.036 μmol of NaSCN at 25 °C.

Importantly, titration of the halide-free complex,[16] $Ni_2(DMB)_4^{4+}$, with $Ph_4As^+Cl^-$ in acetonitrile gives a formation constant of 1.5×10^6 M^{-1} at 25 °C. For comparison, the formation constant of $NiCl^+$ in acetonitrile is 10^4 M^{-1}.[17] Further Cl^- addition has little effect on the spectrum until greater than 2 equiv have been added, at which time a steady decrease in absorbance occurs as more Cl^- is added ($NiCl_4^{2-}$ is the eventual product). Addition of SCN^- in acetonitrile to $Ni_2(DMB)_4^{4+}$ results in a visible spectrum similar to that of each of the halo complexes, indicative of square-pyramidal Ni(II).[18] [The thiocyanate complex also exhibits a peak at 310 nm, although it is less intense and much broader than in $Ni_2X(DMB)_4^{3+}$ (X = Cl, Br).] The absorbance maximizes after addition of 2 equiv of SCN^-. *Addition of 1 equiv of Cl^- to these solutions results in nearly quantitative formation of $Ni_2Cl(DMB)_4^{3+}$* (Figure 2). The remarkable preference for Cl^- over SCN^- suggests strongly that the former ion occupies the unique binding site in $Ni_2(DMB)_4^{4+}$.

The intense band at 320 nm has been studied at 20 K in poly(methyl methacrylate) films containing $Ni_2X(DMB)_4^{3+}$. Two vibrational progressions with spacings of 436 and 2174 cm^{-1} are resolved for the chloro complex. Results for the bromo complex are essentially the same. The vibrations involved are clearly the Ni–C and C≡N stretches, respectively, strongly implying that the electronic transition involves Ni(II) → π*(CNR) charge transfer. Simple theoretical considerations suggest that the transition responsible for the 320-nm system is related to the $d_{z^2} \rightarrow \pi^*(CN)$ transitions that fall at 286[8] and 277 nm[7] in the spectra of $Ni(CN)_4^{2-}$ and $Ni(CNR)_4^{2+}$, respectively. Specifically, the 320-nm band is assigned $^1A_{1g} \rightarrow {}^1A_{2u}[a_{2u}(d_{z^2}(-) \rightarrow a_{1g}[\pi^*,p_z(+)])]$ in the $Ni_2Cl(DMB)_4^{3+}$ complex.

Both $Ni_2X(DMB)_4^{3+}$ complexes react with I_2 in acetonitrile; addition of $Ph_4As^+I_3^-$ produces black microcrystalline products in 50–60% yields. These species contain none of the original counterion (PF_6^-, BPh_4^-, or BF_4^-) and are formulated as $[Ni_2X(DMB)_4](I_3)_4$ (X = Cl, Br).[19] IR spectral measurements show that the Ni–Cl–Ni stretch is at 228 cm^{-1}, whereas Ni–Br–Ni is at 165 cm^{-1}. The increase in this stretching frequency in each case is consistent with removal of an electron from the $a_{2u}[d_{z^2}(-)]$ Ni–X–Ni antibonding orbital. These species exhibit corrected molar susceptibilities (χ_m^{corr}) of 3.379×10^{-3} cgs units (X = Cl) and 3.690×10^{-3} cgs units (X = Br). (The magnetic moments are 2.82 and 3.00 μ_B, respectively.) A frozen acetonitrile solution (4 K) of the bromo complex shows an EPR signal with $g_{\parallel} = 2.20$, $g_{\perp} = 2.05$, and $A_{\parallel}(Br) = 185$ G. The large Br hyperfine coupling constant is similar to the value of 169 G recently obtained for $[Ni(diphos)_2Br_2]PF_6$.[20] The UV-vis spectrum of $[Ni_2Br(DMB)_4](I_3)_4$ is characteristic of I_3^-, except for a distinct shoulder at 320 nm. Details will be reported later.

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(16) This complex is a tractable white powder prepared from $Ni(ClO_4)_2 \cdot 6H_2O$ and DMB. The infrared spectrum indicates the presence of a small amount of an unbound isocyanide group. Anal. Calcd for $[Ni_2(DMB)_4](ClO_4)_4 \cdot 2H_2O$: C, 43.92; H, 5.85; N, 8.54. Found: C, 43.87; H, 6.02; N, 8.52.

(17) Nash, C. P.; Jenkins, M. S. *J. Phys. Chem.* **1964**, *68*, 356.

(18) Preer, J. R.; Gray, H. B. *J. Am. Chem. Soc.* **1970**, *92*, 7306.

(19) Anal. Calcd for $[Ni_2Cl(DMB)_4](I_3)_4$: C, 23.66; H, 2.98; N, 4.60. Found: C, 23.53; H, 2.95; N, 4.24. Calcd for $[Ni_2Br(DMB)_4](I_3)_4$: C, 23.23; H, 2.93; N, 4.52. Found: C, 23.46; H, 3.02; N, 4.62.

(20) Sethulakshmi, C. N.; Subramainan, S.; Bennett, M. A.; Manoharan, P. T. *Inorg. Chem.* **1979**, *18*, 2520.

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Hydrophobic Effect of the CH_2 Group: Enthalpy and Entropy Contributions

Sir:

Several workers[1-3] have analyzed the CH_2 increment to the free energy of partition of *n*-alkanes between water and an organic solvent into a favorable gas → organic solvent contribution and an unfavorable gas → water contribution. More recently, I showed[4] that the free energy of solution of rare gases and gaseous alkanes in nonaqueous solvents could be correlated through 1 and 2, where R_G is a solute parameter and l_G and d_G are parameters

$$\Delta G_s^\circ \text{ (in solvent)} = m\Delta G_s^\circ \text{ (in benzene)} + c \qquad (1)$$

$$\Delta G_s^\circ \text{ (in solvent)} = l_G R_G + d_G \qquad (2)$$

characteristic of the solvent.[5] When these equations were applied to solution in water, it was found that ΔG_s° values for rare gases were well correlated but that values for the *n*-alkanes were always more positive than those calculated by using the "rare gas line" (see Figure 1).[6] The difference may be taken as a measure of the hydrophobic effect of alkanes, and in this way, the unfavorable gas → water CH_2 contribution of 0.18 kcal mol^{-1} was dissected into a favorable normal solvent effect of 0.36 kcal mol^{-1} and an

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(1) R. Wolfenden and C. A. Lewis, *J. Theor. Biol.*, **59**, 231 (1976).

(2) R. D. Cramer III, *J. Am. Chem. Soc.*, **99**, 5408 (1977).

(3) J. H. Rytting, L. P. Huston, and T. Higuchi, *J. Pharm. Sci.*, **67**, 615 (1978).

(4) M. H. Abraham, *J. Am. Chem. Soc.*, **101**, 5477 (1979).

(5) The parameters R_G, l_G, and d_G are identical with the terms *R*, *l*, and *d* used previously.[4]

(6) In Figure 1 are also plotted points for the inorganic gases H_2, N_2, O_2, and CO; these solutes behave similarly to the rare gases in all solvents, including water.

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