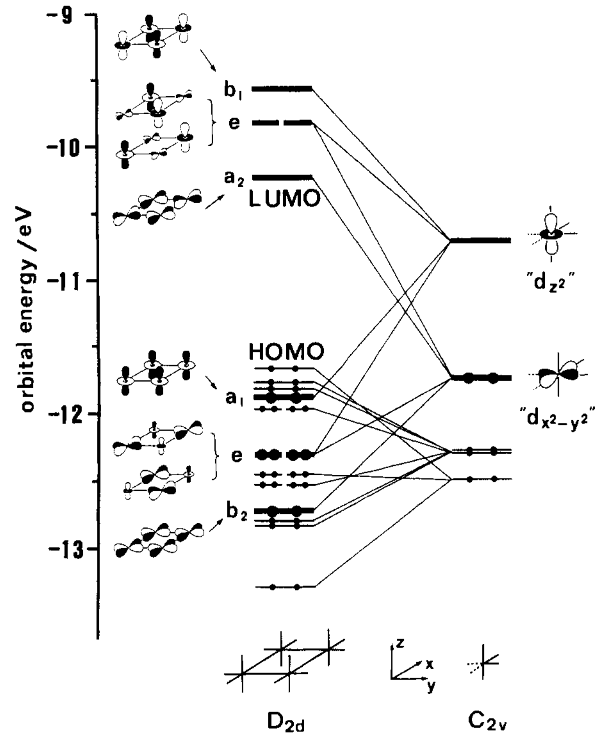

Figure 2. MO interaction diagram for $Pt_4(HCOO)_8$ (**3**) and its quaterly fragment.[12] MO's shown in thick lines are those involving Pt 6dσ orbitals.

Exchange rate is linearly dependent on the complex concentration and rate law 2 is derived.[8] At 25 °C, k_0 and k_1 are 0.36

$$\text{rate} = 4(k_0 + k_1[CH_3COOH])[\text{complex}] \qquad (2)$$

s^{-1} and 4.4 $M^{-1}\ s^{-1}$, respectively, per each reaction site. Substitution of CD_3COO^- for the out-of-plane acetates was not at all observed after a month at 25 °C for the solution of **1** in $CDCl_3$ containing CD_3COOD.

EHMO calculations[9] have been carried out for a model compound, $Pt_4(HCOO)_8$ (**3**), and its fragments,[10,11] where the Pt–O distances are assumed to be 2.01 (out-of-plane) and 2.16 Å (in-plane) as observed for **1**.[2] The MO study reasonably justifies the presence of the Pt–Pt bond and the regioselective substitution reaction.

The MO interaction diagram in Figure 2 shows levels near HOMO–LUMO, which are all associated with Pt 6d orbitals. The MO's shown in thick lines are those derived from dσ orbitals ("$d_{x^2-y^2}$" and "d_{z^2}")[12] of each quaterly fragment. These MO's are associated with the metal–ligand bonds, and therefore their character should relate to the regioselective lability. Four low-lying MO's of these are occupied by eight dσ electrons and result in the Pt–Pt single bonds.[13] With regard to metal–ligand interactions, all four orbitals are of antibonding type, and therefore the occupation of these MO's should weaken the metal–ligand bonds. The lower three orbitals are predominantly of $d_{x^2-y^2}$ character and are antibonding for in-plane ligands, and only the highest one is of d_{z^2} character and antibonding for out-of-plane ligands. The out-of-plane ligands are therefore more tightly bound to each metal ion than the in-plane ligands. The overlap population for the out-of-plane Pt–O bond in **3** was found to be larger than that for the in-plane Pt–O bond.[14]

These MO results indicating that the out-of-plane Pt-O bond is stronger than the in-plane bond are consistent with the observed regioselective ligand substitution as well as with the observed Pt–O distances.[1,2]

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research (No. 63612503) on the Priority Area of Dynamic Interactions and Electronic Processes of Macromolecular Complexes and a Grant-in-Aid for Scientific Research (No. 01430009) from the Ministry of Education, Science and Culture, Japan. We are grateful to Dr. M. Ebihara of the Institute for Molecular Science for the X-ray analysis.

Registry No. **1**, 60383-57-5; **2**·$2CH_2Cl_2$, 123358-56-5; **3**, 123380-75-6; Pt, 7440-06-4.

Supplementary Material Available: Tables of atomic positional and thermal parameters and interatomic distances and bond angles for $Pt_4(\mu\text{-}CH_3COO)_4(\mu\text{-}CCl_3COO)_4\cdot 2CH_2Cl_2$ (2 pages); a table of observed and calculated structure factors (3 pages). Ordering information is given on any current masthead page.

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(8) NMR spectra were recorded on a JEOL JNM GSX-270 FT-NMR spectrometer. The reaction process can be observed by two independent approaches, by irradiating either the methyl signal of the coordinated acetates (in plane) at 2.45 ppm or that of the free acetic acid at 2.02 ppm. Two rate constants at a given reaction condition are in reasonable agreement to each other (maximum difference, 9%).

(9) Calculations were performed with the program FORTICON8: Howell, J.; Rossi, A.; Wallace, D.; Haraki, K.; Hoffmann, R. *QCPE* **1977**, No. 344.

(10) Orbital energies of the fragment MO's were estimated from the calculation in which all the overlaps between Pt atoms were set to be zero.

(11) For discussions on fragment MO's, see: Elian, M.; Hoffman, R. *Inorg. Chem.* **1975**, *14*, 1058–1076. The quarterly fragment MO's of our complex are similar to those of MCl_4 rather than those of $M(CO)_4$. It should be noted that the coordination axes are taken in a different way from those in the above literature.

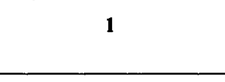
(12) The "$d_{x^2-y^2}$" and "d_{z^2}" orbitals actually contain some contributions of s and p orbitals, but for simplicity are designated as such.

(13) These four MO's are of bonding type with respect to Pt–Pt interaction, giving four Pt–Pt single bonds to stabilize the Pt_4 core, although the strong interaction takes place only in the b_2 orbital.

(14) This was the case even when the in- and out-of-plane Pt–O distances were assumed to be equal (2.01 or 2.16 Å).

Redox Regulation in Ruthenium(II) Complexes of 2,6-Bis(*N*-pyrazolyl)pyridine Ligands: Synthetically Versatile Analogues of 2,2′:6′,2″-Terpyridine

The redox reactions of ruthenium(II) complexes containing 2,2′:6′,2″-terpyridine (**1**) have been extensively investigated.[1-10]



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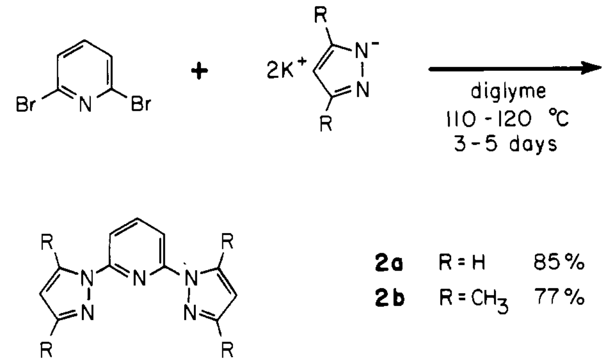
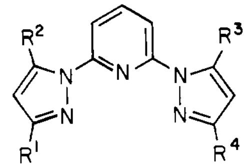
Scheme I



In order to fully exploit the rich redox chemistry of ruthenium terpyridine complexes, it would be desirable to modify or "tune"[11] the properties and reactivity of these complexes through the use of substituted terpyridine ligands. Unfortunately, the synthesis of substituted terpyridines is quite difficult.[9-10] We report here the synthesis of a new family of planar tridentate ligands based on 2,6-bis(*N*-pyrazolyl)pyridine (**2**). The ligands are structural analogues of 2,2′:6′,2″-terpyridine; however, unlike the familiar polypyridine ligand, the substituents on the 2,6-bis(*N*-pyrazolyl)pyridine ligand can be easily varied. Therefore, the redox properties of complexes containing these ligands can be conveniently and rationally regulated through ligand design, as illustrated here by the bis-chelated ruthenium(II) complexes of the parent ligand, bpp ($R^1 = R^2 = R^3 = R^4 = H$) and the methyl-substituted derivatives, Me_2-bpp ($R^1 = R^2 = Me$ and $R^3 = R^4 = H$) and Me_4-bpp ($R^1 = R^2 = R^3 = R^4 = Me$).



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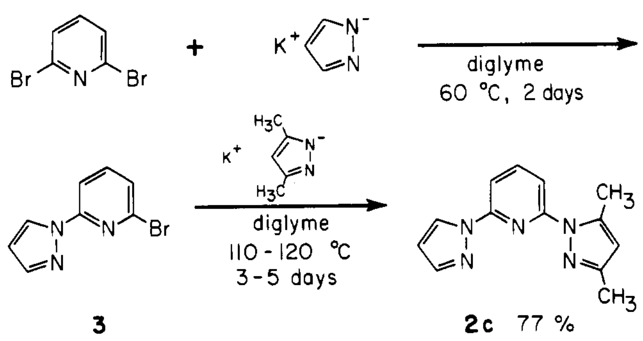
The symmetric ligands **2a** and **2b** were synthesized as shown in Scheme I. A solution of 2,6-dibromopyridine and the pyrazolate salt[12] in diglyme was heated at 110–130 °C for 3–5 days. Evaporation of the solvent and addition of water precipitated the crude ligands, which were recrystallized once from methanol/water and once from dichloromethane/hexanes. The long reaction times are necessary due to the sluggish displacement of the second bromide. The slow displacement of the second bromide is advantageous in that it permits isolation of the monosubstituted bromopyridine (**3**), enabling the convenient synthesis of the unsymmetric Me_2-bpp ligand (**2c**), as illustrated in Scheme II. Satisfactory analyses were obtained for all of the tridentate ligands (Table I),[22] and the ^1H and ^{13}C NMR spectra are consistent with the assigned structures.

The bis-chelated ruthenium(II) complexes were synthesized from $RuCl_3{\cdot}3H_2O$ by routes strictly analogous to published procedures for the preparation ruthenium 2,2′:6′,2″-terpyridine (tpy) complexes.[2b,4a,b] The complexes were characterized by elemental analysis (Table II),[22] electronic spectroscopy, and cyclic voltammetry. The complexes exhibited reversible $Ru^{III/II}$ couples in 0.1 M TBAH/CH_3CN (TBAH is tetra-*n*-butylammonium hexafluorophosphate) with peak-to-peak splittings of 60–80 mV. The half-wave potential ($E_{1/2}$)[13] for the $[Ru(bpp)_2]^{3+/2+}$ couple was observed at 1.25 V vs SSCE (saturated sodium calomel electrode), which is only 40 mV cathodic of the $[Ru(tpy)_2]^{3+/2+}$ couple. As such, bpp is a reasonably good redox mimic for tpy in these complexes.

Scheme II



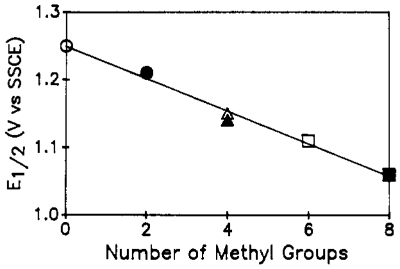


Figure 1. Graph of the $Ru^{III/II}$ couple vs total number of methyl groups in the complex: (○) $[Ru(bpp)_2]^{2+}$; (●) $[Ru(bpp)(Me_2\text{-}bpp)]^{2+}$; (△) $[Ru(bpp)(Me_4\text{-}bpp)]^{2+}$; (▲) $[Ru(Me_2\text{-}bpp)_2]^{2+}$; (□) $[Ru(Me_2\text{-}bpp)(Me_4\text{-}bpp)]^{2+}$; (■) $[Ru(Me_4\text{-}bpp)_2]^{2+}$. The $Ru^{III/II}$ couples were determined by cyclic voltammetry at a platinum disk electrode in 0.1 M TBAH/CH_3CN vs SSCE at a scan rate of 100 mV·s^{-1}.

Increasing the total number of methyl groups on the bis-chelated complexes from zero (for $[Ru(bpp)_2]^{2+}$) to eight (for $[Ru(Me_4\text{-}bpp)_2]^{2+}$) results in a steady decrease in the $Ru^{III/II}$ couple from 1.25 to 1.06 V vs SSCE. A graph of $E_{1/2}(Ru^{III/II})$ vs the total number of methyl groups is shown in Figure 1, illustrating the fine control of redox potential that is possible with these ligands. An average potential step size of 24 mV/methyl group is obtained from the slope of the graph. The decrease in the $Ru^{III/II}$ couple is consistent with the electron-donating nature of the methyl groups.

The electronic spectra of $[Ru(tpy)_2]^{2+}$ and $[Ru(bpp)_2]^{2+}$ reveal significant differences between 2,2′:6′,2″-terpyridine and the parent 2,6-bis(*N*-pyrazolyl)pyridine ligand. For both complexes, the UV region consists primarily of a manifold of intense ligand-localized π–π^* transitions, while the visible region is dominated by a single metal-to-ligand charge transfer (MLCT) band. The MLCT bands for $[Ru(bpp)_2]^{2+}$ and $[Ru(tpy)_2]^{2+}$ are observed in acetonitrile at 377 and 476 nm, respectively, which corresponds to an energy difference of 5500 cm^{-1}. Since the $Ru^{III/II}$ couples for these complexes differ by only 0.04 V (roughly 300 cm^{-1}), the difference in MLCT band energy must be due to differences in the energies of the ligand π^* orbitals. The relative energies of the π^*(bpp) and π^*(tpy) orbitals are reflected in the $[Ru(bpp)_2]^{2+/+}$ and $[Ru(tpy)_2]^{2+/+}$ reduction potentials. $[Ru(tpy)_2]^{2+}$ is reversibly reduced at −1.25 V ($E_{p,c} = -1.28$ V) while $[Ru(bpp)_2]^{2+}$ is irreversibly reduced at $E_{p,c} = -1.66$ V,[14] indicating that the π^*(bpp) orbitals are significantly higher in energy than the π^*(tpy) orbitals.[15]

Given the substantial difference in energy between the π^*(bpp) and π^*(tpy) orbitals, bpp should be a poorer π-acceptor than tpy

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[12] The pyrazolate salts were formed by treating the pyrazole with potassium metal in diglyme.

[13] The half-wave potential is defined as $E_{1/2} = (E_{p,a} + E_{p,c})/2$, where $E_{p,a}$ and $E_{p,c}$ are the peak anodic and peak cathodic currents, respectively.

[14] Determined by cyclic voltammetry in an inert-atmosphere box at a platinum disk electrode in 0.1 M TBAH/CH_3CN vs SSCE at a scan rate of 100 mV·s^{-1}.

[15] In spite of the substantial energy difference between the π^* orbitals of bpp and tpy, the mixed-ligand complex $[Ru(bpp)(tpy)]^{2+}$ shows a single MLCT band at 430 nm in acetonitrile, indicating strong coupling between the π^* orbitals in the mixed-ligand complex.[16]

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and hence less effective in stabilizing Ru^{II}. The reduced π-acidity of pyrazole-containing ligands relative to polypyridine ligands has been noted previously.[17-19] Therefore, it is interesting that the $[Ru(bpp)_2]^{3+/2+}$ and $[Ru(tpy)_2]^{3+/2+}$ couples differ by only 40 mV. The similarity in the $Ru^{III/II}$ redox potentials suggests that, in addition to being a weaker π-acceptor, bpp is also a weaker σ-donor than tpy. Pyrazole-containing ligands are expected to be weaker donors than the analogous pyridine-containing ligands, given the difference in ligand basicities for pyridine and pyrazole ring systems.[20,21] The dimethyl-substituted pyrazoles are more basic than pyrazole and hence are expected to be better donors. As such, Me_2-bpp and Me_4-bpp are better able to stabilize the Ru^{III} oxidation state, which is reflected in the $Ru^{III/II}$ couples of complexes containing these ligands.

In conclusion, the 2,6-bis(*N*-pyrazolyl)pyridine ligands described here are structural and redox analogues of 2,2′:6′,2″-terpyridine, with the added feature that the ligand superstructure can be conveniently varied, providing an opportunity for rational ligand design. The methyl-substituted ligands demonstrate the potential for gradually regulating the driving force for electron transfer over a relatively broad range (200 mV). The synthetic methodologies described here can be easily extended to prepare a wide array ligands with the possibility of optimizing both steric and electronic effects, which may be of great importance in the design of redox catalysts based on these ligands.

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Supplementary Material Available: Elemental analyses for the new ligands (Table I) and complexes (Table II) (1 page). Ordering information is given on any current masthead page.

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(21) The reduced donor ability of bpp relative to tpy may also be a result of the geometric constraints on the chelate bite of a planar tridentate ligand containing two five-membered heterocycles.[19]

(22) See paragraph at end of paper regarding supplementary material.

Articles

Contribution from the Institute for Inorganic Chemistry, University of Witten/Herdecke, Stockumer Strasse 10, 5810 Witten, FRG, and Institute for Inorganic Chemistry, University of Regensburg, 8400 Regensburg, FRG

Kinetics and Mechanism of the Anation of Aquocobalamin (Vitamin B_{12a}) by Cyanoferrates. Isolation and Identification of a Cyano-Bridged Product and Mechanistic Information from Pressure Effects

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Aquocobalamin and $Fe(CN)_6^{4-}$ react to produce the binuclear anion $[\text{cobalamin}-\mu\text{-NC}-Fe(CN)_5]^{3-}$, which could be isolated and identified as the zinc salt. The anation reactions of aquocobalamin by N_3^-, $Fe(CN)_5NO^{2-}$, $Fe(CN)_5H_2O^{2-}$ and $Fe(CN)_6^{4-}$ were studied as a function of ligand concentration, pH, temperature, and pressure. The observed second-order rate constants vary between 930 and 3600 $M^{-1}\,s^{-1}$ at pH $\approx$ 6 and 25 °C. The activation entropies and activation volumes are significantly positive and thus support the operation of a dissociative mechanism. Solvational effects caused by changes in electrostriction can account for the variation in the volume of activation with the charge on the anating ligand. The results are discussed in reference to earlier data reported in the literature.

Introduction

Recent reports in the literature dealing with the interaction of aquocobalamin with cyanide and cyanoferrate complexes[2-7] have stimulated our interest in the intimate mechanism of anation reactions of aquocobalamin (hereafter referred to as B_{12}–H_2O^+). Although B_{12}–H_2O^+ was originally recommended for use as an effective antidote for potential cyanide poisoning induced by the hypotensive agent nitroprusside, later studies revealed qualitatively that B_{12}–H_2O^+ reacts much faster with nitroprusside itself than with free cyanide.[5,8] This interaction was recently studied in detail by employing ^{13}C NMR,[6] from which it follows that nitroprusside forms 1:1 and 1:2 complexes with B_{12}–H_2O^+, containing Fe–C–N–Co fragments including the axial cyano ligand in the 1:1 complex and a trans pair of equatorial cyano ligands in the 1:2 complex. This interaction drastically affects the pharmacology of nitroprusside, such that B_{12}–H_2O^+ cannot be regarded as a satisfactory antidote.[5,9] Other cyanoferrate species produce similar

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