

IV also shows a further increase in the lifetime of the 2E state of the deuterated complex in D_2O , but neither of these effects is especially significant in this context. Also, at low temperature (77 K) the lifetimes of the crystals are shorter than those of the solutions. This could be caused by exciton trapping in defect sites.

The excited states of the sar-type hexamine cage complexes of chromium(III) are potentially powerful oxidants ($E(^*Cr^{3+}/Cr^{2+}) \sim 0.8$ V), and Cr^{2+} is a powerful reductant in the ground state. In this context the very short lifetimes at room temperature are particularly undesirable for bimolecular reactions. A more thorough understanding of these usually short lifetimes at room temperature is needed, and possibilities for ligand modifications to increase the lifetimes are currently under investigation.

Photodecomposition and photoanation of chromium(III) complexes have been widely studied.³⁶⁻³⁹ A central question and point of controversy is the mechanism of relaxation of the lowest lying excited doublet states and, related to this problem, the question of whether the 2E or the usually slightly higher energy thermally equilibrated lowest quartet excited state (${}^4T_{2g}^0$) or both are responsible for photosubstitution. Table III shows that photodecomposition (ϕ_{PD}) of $Cr(\text{diamsar})^{3+}$ is very small. $Cr(\text{diamsar})^{3+}$

is, photochemically, more inert than other chromium(III) complexes³⁸ by at least 2 orders of magnitude and over $\sim 10^4$ -fold more stable than $Cr(\text{en})_3^{3+}$. This photochemical stability of the sar-type hexamine-chromium(III) cage complexes is not surprising since dissociative as well as associative substitution of the cage complexes is hindered. As with the cage complexes of other metal ions, we have found no evidence of an increased coordination number and that is very much expected from the known chemistry to date. In this respect, Endicott's recent proposal^{15,40} that such an associative species is needed for decay of the excited doublet states of chromium(III) amines is inconsistent with the current chemistry and the small cavity of the cage. Clearly, the origin of these effects needs further examination and additional spectroscopic studies; for example, studies of the temperature dependence of the infrared and Raman spectra are presently being undertaken in the hope that they will reveal information about the decay path.

Acknowledgment. We thank D. Bogsanyi for the measurement of the pK_a values and D. Wells for HPLC measurements.

Registry No. $[Cr(\text{diamsar})]Cl_3 \cdot H_2O$, 99583-52-5; $[Cr(\text{sar})]-(CF_3SO_3)_3$, 99593-38-1; $[Cr(\text{di}(\text{amH})\text{sar})]Cl_3$, 99583-53-6; D_2 , 7782-39-0.

Supplementary Material Available: Tables of thermal parameters, hydrogen atom parameters, and structure factors for $[Cr(\text{diamsar})]Cl_3 \cdot H_2O$ (18 pages). Ordering information is given on any current masthead page.

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Notes

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Nature of Intervalence Charge-Transfer Bands in Prussian Blues

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There has been considerable current interest in the electrochemistry of Prussian blue (PB)¹⁻⁴ and its related complexes.^{3,5,6}

- (1) (a) Neff, V. D. *J. Electrochem. Soc.* **1978**, *125*, 886. (b) Ellis, D.; Eckhoff, M.; Neff, V. D. *J. Phys. Chem.* **1981**, *85*, 1225. (c) Rajan, K. P.; Neff, V. D. *J. Phys. Chem.* **1982**, *86*, 4361.
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In the case of PB, it has been conclusively shown that the electron-transfer reactions observed at about 0.2 V and 1.0 V vs. SCE are due to the high-spin iron (Fe^{3+}) and the low-spin iron (Fe^{II}) ions, respectively.^{2c}

The large intervalence charge-transfer band, i.e. $Fe^{3+}-NC-Fe^{II} \rightarrow Fe^{2+}-NC-Fe^{III}$ was first discussed by Robin on the basis of the result using a colloidal form of PB prepared by adding a stoichiometric amount of $K_4Fe^{II}(CN)_6$ to an $Fe^{3+}(ClO_4)_3$ solution.⁷ In our previous spectroelectrochemical study,^{2d} it was emphasized that Berlin green, which has long been used as the conventional name for the oxidized forms of PB, is merely a partially oxidized form of PB, but that the fully oxidized form can be prepared as in the pure state by an electrochemical oxidation at SnO_2 electrodes. The color of the fully oxidized form was visually yellow-brown,^{2d,i} as has long been expected.⁸ Iron(3+) hexacyanoferrate(III), Prussian brown, had not until then been prepared chemically in the pure state. Ellis et al. reported an absorption spectrum at 1.1 V vs. SCE (saturated calomel electrode) where the absorption band due to the intervalence charge transfer persisted in the oxidized form of PB and about one-third of the ferrocyanide ions remained unoxidized.^{1b} Similar results have been recently reported by Rosseinsky et al.⁴ However, our previous paper clearly showed that no appreciable absorption band due to the intervalence charge transfer was found in the spectrum obtained at 1.4 V vs. SCE (see Figure 5 in ref 2d).

It has also been briefly described that the peak position of the intervalence charge-transfer band was remarkably shifted toward longer wavelengths not only for the partially oxidized form of PB, i.e. Berlin green, but also for the partially reduced form of PB.^{2d} On the other hand, it has been reported in a recent paper by Rosseinsky that the shift of the charge-transfer band was observed for the partially oxidized form of PB, but was not observed for the partially reduced form.^{4d}

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The purpose of the present study is to resolve the discrepancy among the literature reports. It will be shown in this paper that the remarkable shift of the peak position does occur for partially oxidized and reduced forms of PB. The results will show that the absorbance at 700 nm for the intervalence charge-transfer band is not directly proportional to the mole fraction of PB in the partially oxidized and also in the reduced forms of PB. That is, Beer's law cannot be applicable to films of PB. A careful re-determination of the molar extinction coefficients is also represented.

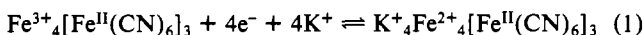
Experimental Section

SnO₂ electrodes (15–20 Ω/□) were prepared on Pyrex plates by the conventional method of chemical vapor deposition at 470 °C.⁹ The color of the SnO₂ layer was slightly blue. It has been found that the adhesion of the film was more critically important in the oxidation of PB than in the reduction as mentioned previously.^{2d} The cleaning of the electrodes should be carried out with extreme care. All the electrodes were finally immersed in hot concentrated sulfuric acid (90 °C) for at least 1 h before use. The films of PB on the electrodes were prepared in an aqueous ferric ferricyanide solution of an equal-volume mixture of 20 mM FeCl₃ in 0.01 M HCl and 20 mM K₃Fe(CN)₆ in 0.01 M HCl. The SnO₂ electrodes were cathodically polarized in the above solution galvanostatically with a current density of 10 μA/cm² as previously described.^{2d} 0.5 M K₂SO₄, 1 M KCl, and 0.05 M KBF₄ were used as supporting electrolytes. The pH was adjusted by the respective dilute acids.

Voltammograms were recorded with a PAR (Princeton Applied Research) Model 173 instrument equipped with a Model 179 digital coulometer. The absorption spectra were obtained with a Hitachi Model 330 spectrometer. An optically matched SnO₂ plate was placed in a reference cell. A saturated calomel electrode (SCE) was used as a reference electrode. Because of the catalytic activity of the reduced form of PB, Prussian white, for the reduction of molecular oxygen,^{2a,h} all measurements were carried out under a nitrogen atmosphere.

Results and Discussion

Parts A and B of Figure 1 show typical examples of cyclic voltammograms and coulometric curves of PB-modified SnO₂ electrodes in 1.0 M KCl and in 0.05 M KBF₄, respectively. The waves at about 0.2 V are due to the redox reaction of the high-spin iron ions, Fe³⁺, in PB as previously described by using the formula of the water insoluble species



where Fe³⁺, Fe^{II}, and K⁺ are the high-spin iron ions, the low-spin iron ions, and the potassium ions, respectively.

The electrochemical oxidations of PB can be seen as two separate waves at electrode potentials more positive than 0.8 V. The second oxidation waves are clearly seen at 1.1 V in 1.0 M KCl and 1.2 V vs. SCE in 0.05 M KBF₄, respectively. The corresponding reduction peaks do appear on the cathodic scan as shown in Figure 1, although the waves in KBF₄ are much more distinctive than those in KCl. It is found that the shape of the oxidation wave depends on the anions of supporting electrolytes used. Similar voltammograms have been previously reported in 0.5 M K₂SO₄.²ⁱ

The coulometric curves obtained at the waves of the high-spin iron ions are completely symmetric in both solutions, indicating that no side reaction is involved in the waves. On the other hand, the coulometric curve obtained at the waves of the low-spin iron ions has shown a fairly large asymmetric behavior due to the background anodic current even at SnO₂ electrodes, as described previously.^{2d} A typical example of the coulometric curve is represented in Figure 1A. We do not believe that such asymmetric behavior is due to any deterioration of PB itself. As mentioned in the Experimental Section, the adhesion was extremely important during potential scans to 1.4 V. The coulometric curve obtained in 0.05 M KBF₄ is almost completely symmetric as shown in Figure 1B because the background anodic current is very small at SnO₂ electrodes in this medium. This indicates that no side reaction is involved in the oxidation as in the reduction. It is noteworthy that the film with good adhesion was extremely stable in KBF₄ solutions. Repeated scans between 0.6 and 1.4 V at 20

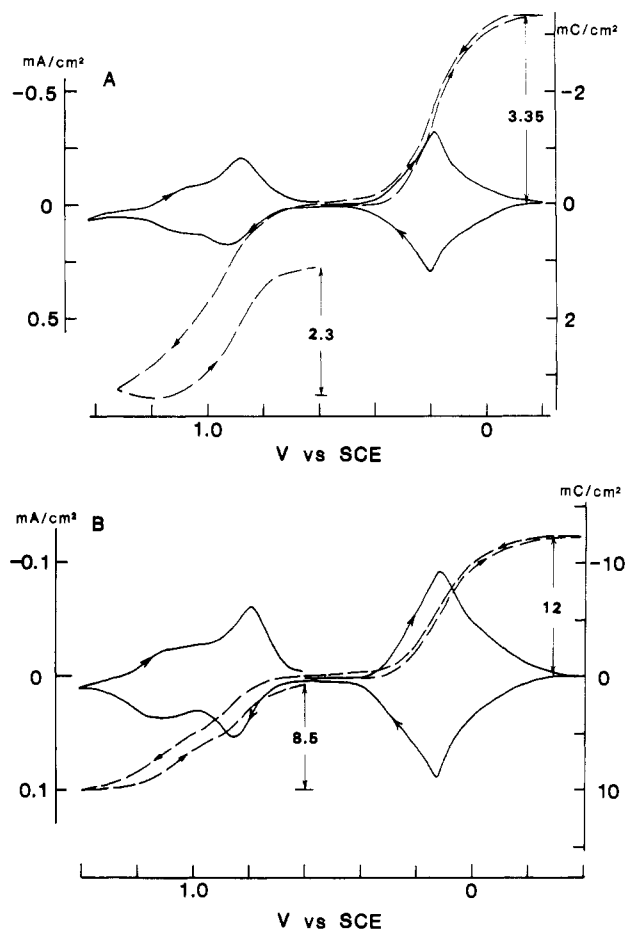


Figure 1. Cyclic voltammograms of PB-modified SnO₂ electrodes in 1.0 M KCl (pH 4.0) (A) and in 0.05 M KBF₄ (pH 3.5) (B). The charges (mC/cm²) consumed for the reduction of PB are 3.35 and 12 mC/cm² and the scan rates were 20 and 2 mV/s for curves A and B, respectively. The films of PB were prepared at a current density of 10 μA/cm². The dashed lines show the integrated current-potential curves.

mV/s showed only a 10% decrease in the coulometry after 10⁴ cycles in 0.05 M KBF₄. This high stability for the oxidation of PB encouraged us to study in detail the spectroelectrochemistry of the oxidized forms of PB.

The total charges required for the reduction and oxidation of PB are 12 and 8.5 mC/cm² in 0.05 M KBF₄, respectively. The ratio of the charges above is 0.708, which gives a fairly accurate proof that the formula of PB is the water-insoluble species, i.e. Fe³⁺₄[Fe^{II}(CN)₆]₃. The same value has been obtained by a photoelectrochemical study of PB on *n*-TiO₂ semiconductor.²ⁱ Mortimer and Rosseinsky have suggested that the initial deposit, the insoluble species, is converted into the soluble species, K⁺Fe³⁺Fe^{II}(CN)₆, under cyclic voltammetric conditions, on the basis of a spectroelectrochemical investigation.^{4d} While we do not discount the possibility of the existence of the soluble form, the coulometric data in Figure 1B suggests that one-fourth of the sites for the low-spin iron ions per unit cell is vacant on the average, as proposed by Ludi et al.¹⁰

Note that the voltammogram obtained in a 0.05 M KBF₄ solution was shifted negatively relative to that obtained in 1 M KCl. Ellis et al. reported^{1b} that the midpeak potential for both the oxidation and reduction reactions was shifted negatively with decreasing mean ionic activity of KCl and the behavior was Nernstian with a slope of 59 mV per decade of activity for both reactions. We found a similar slope of ca. 50 mV per decade for the reduction reaction, yielding evidence for the diffusion of the potassium ions into or out of the films. However, the oxidation

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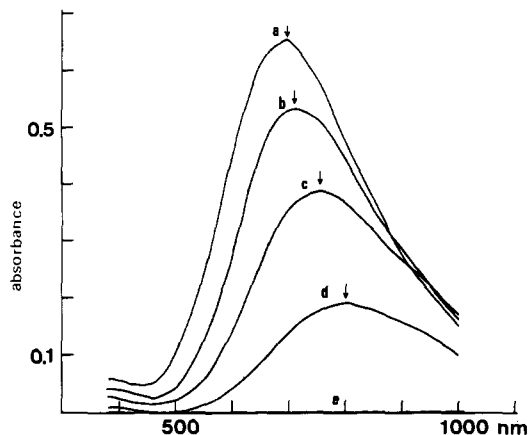


Figure 2. Absorption spectra obtained on an SnO_2 electrode with 8.6 mC/cm^2 of PB at different degrees of reduction in 0.05 M KBF_4 . The degrees of reduction of PB are $1/4$, $1/2$, $3/4$, and 1 for lines b–e. The line labeled a is for PB obtained at 0.6 V vs. SCE.

reaction should be much more complicated than the reduction. Two separate waves for the oxidation reaction seemed to be shifted toward the opposite direction. That is, it can be seen in Figure 1 that the second oxidation wave was shifted slightly toward the positive potentials in 0.05 M KBF_4 . This behavior might be an indication that both cations and anions would be involved in the oxidation reactions. A more detailed investigation of this behavior is currently under way.

Figure 2 shows the absorption spectra of PB, partially reduced PB, and fully reduced PB, Prussian white (Everitt's salt). The absorption spectrum of Prussian white does not show any distinct band in the visible region as shown in Figure 2 (the line labeled e). The value of the absorbance is almost equal to zero in the visible region, indicating that the SnO_2 electrodes used here have a similar refractive index to that of the films of Prussian white. In our previous study, it was found that there were some scattering effects in the spectrum of Prussian white. For example, an absorbance of 0.06 was observed through the visible region for the film of Prussian white with 10.5 mC/cm^2 (see Figure 5 in ref 2d), which was linearly dependent on the thickness of the films. This behavior seemed to be due to the mismatch of the refractive indices of the SnO_2 previously used and Prussian white. The molar extinction coefficients have been reported as 7880 and $10500 \text{ L mol}^{-1} \text{ cm}^{-1}$ with respect to Fe^{3+} and Fe^{II} , respectively, assuming the formula $\text{Fe}^{3+}_4[\text{Fe}^{\text{II}}(\text{CN})_6]_3$. These values were calculated without taking into account the mismatching in the refractivity.

As shown in Figure 2, the absorbance obtained on an SnO_2 electrode with 8.6 mC/cm^2 is 0.65 at 700 nm . Three different amounts of PB, 5.5 , 7.5 , and 11.5 mC/cm^2 , deposited on SnO_2 electrodes gave 0.41 , 0.58 , and 0.865 for the absorbances at 700 nm . The above observation shows a perfect straight line with a zero intercept. On the basis of these values, the molar extinction coefficients have been recalculated as 7300 and $9800 \text{ L mol}^{-1} \text{ cm}^{-1}$ with respect to Fe^{3+} and Fe^{II} , respectively. Note that exactly the same extinction coefficients can be obtained from the data previously reported from our laboratory by taking into account the scattering effect. The extinction coefficient of 9800 obtained here with respect to the number of $\text{Fe}^{\text{II}}(\text{CN})_6$ moieties in the film is consistent with the value reported by Robin⁷ using a colloidal form of PB prepared by adding a stoichiometric amount of $\text{K}_4\text{Fe}(\text{CN})_6$ to a $\text{Fe}(\text{ClO}_4)_3$ solution.

The lines labeled b, c, and d in Figure 2 are the spectra of the partially reduced forms of PB. The degrees of the reduction of PB are one-fourth, one-half, and three-fourths, respectively. It is remarkable that the maximum position of the spectra is shifted toward longer wavelengths with an increase in the degree of the reduction of PB. Maxima near 1000 nm can be seen for further reduced films. The same behavior has been obtained for different amounts of PB on SnO_2 electrodes. The result is that the peak positions shown in Figure 2 are independent of the amount of PB, but do depend on the degree of the reduction of PB.

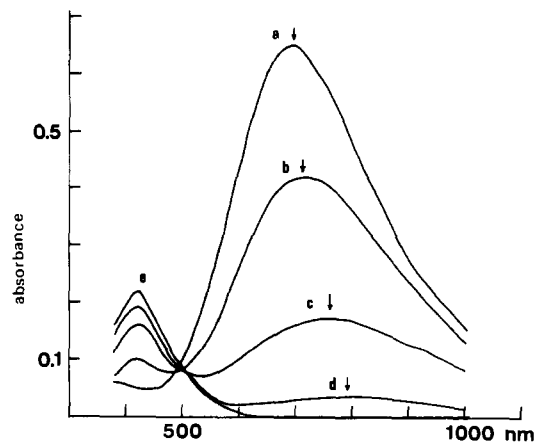


Figure 3. Absorption spectra obtained on the same SnO_2 electrode with PB at different degrees of oxidation in 0.05 M KBF_4 . The degrees of oxidation of PB are $1/3$, $2/3$, $5/6$, and 1 for lines b–e. The lines labeled a and e are obtained at 0.6 and 1.4 V vs. SCE, respectively.

Figure 3 shows the spectra obtained at the potentials for the oxidation of PB with the same SnO_2 electrode. It is obvious that the intervalence charge-transfer band does not persist in the spectrum obtained at 1.4 V vs. SCE (the spectrum labeled e). This spectrum should be attributed to the fully oxidized form of PB, Prussian brown. The spectra labeled b, c, and d in Figure 3 are for the partially oxidized forms of PB. Again, the peak position of the charge-transfer bands is remarkably shifted toward longer wavelengths just as for the reduced forms of PB. The spectra in Figure 3 were reproducible during repeated measurements due to the high stability of the films discussed above. Three independent experiments have been carried out, yielding the fact that the peak positions do depend only on the degree of the oxidation of PB.

Similar spectra for the partially oxidized form of PB have been recently reported by Mortimer et al.^{4d} However, they found a very broad flat band centered at about 790 nm in the spectrum obtained at 1.2 V vs. SCE. From the present work, it is very clear that the potential of 1.2 V is not enough to oxidize PB completely. From the voltammogram shown in Figure 1B, potentials more positive than 1.3 V should be applied for complete oxidation in this medium. It can be seen in Figures 2 and 3 that the absorbance obtained at 700 nm for the intervalence charge-transfer band is not directly proportional to the mole fraction of PB in both the partially oxidized and reduced forms of PB. This is the reason for the isosbestic point not being defined in the spectra shown in Figure 3. The isosbestic point should be rigorously held if the spectral changes involve only a two-species equilibrium. However, it is clear from the present study that Beer's law cannot be applicable to the films of PB.

The absorption spectrum of PB has been first discussed by Robin⁷ and in more detail by Braterman.¹¹ Equation 2 has been proposed by Robin based on ligand field theory for the energy of the intervalence charge-transfer band, i.e. $(t_{2g})_C \rightarrow (t_{2g})_N$, in PB,⁷ where the difference in the intraatomic electrostatic energies

$$h\nu (\text{cm}^{-1}) = 13400 - E_{\text{one}} + E_{\text{cryst}} \quad (2)$$

of the $(t_{2g})_C^6(t_{2g})_N^3(e_g)_N^2$ and $(t_{2g})_C^5(t_{2g})_N^4(e_g)_N^2$ configurations is 13400 cm^{-1} .¹² E_{one} is the difference in the one-electron energies of a $(t_{2g})_N$ electron in an iron ion in a nitrogen hole and in a carbon hole, $(t_{2g})_C$, and E_{cryst} is the Coulombic destabilization energy expended in transferring the electron from the carbon hole to the nitrogen hole in the electrostatic field of all the ions in the crystal.

The first two terms, i.e. the intraatomic electrostatic energies and E_{one} , must be assumed to be constant for the partially oxidized and reduced PB within the theory. Only the last term, E_{cryst} , in eq 2 can be responsible for the shift of the peak position of the charge-transfer band. As discussed above, the peak position was

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(12) Tanabe, Y.; Sugano, S. *J. Phys. Soc. Jpn.* **1954**, *9*, 753, 766.

shifted toward wavelengths longer than 700 nm by both the reduction and oxidation of the high-spin iron ions and low-spin iron ions, respectively. This result can possibly predict that the crystal destabilization energy, E_{cryst} , should be decreased by the reduction and oxidation of the iron ions in the film. The calculation of E_{cryst} for the partially oxidized and reduced forms of PB would be of special interest. This electrostatic (Coulombic) energy seems to be more acceptable for the explanation of the band shift than the mixed-valence delocalization energies proposed by Mortimer and Rosseinsky.^{4d} Finally, it is noteworthy that the peak positions of the intervalence charge transfer bands for the iron ruthenium cyanide, $\text{Fe}^{3+}_4[\text{Ru}^{\text{II}}(\text{CN})_6]_3$,^{3a} and the iron osmium cyanide, $\text{Fe}^{3+}_4[\text{Os}^{\text{II}}(\text{CN})_6]_3$,^{3b} are also considerably shifted to longer wavelengths. This behavior is basically the same as observed in the PB films.

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Registry No. PB, 12240-15-2; SnO_2 , 18282-10-5.

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Reactions of Metal Complexes with Carbohydrates: Nickel(II) Complexes Containing *N*-Glycosides Derived from a Sugar and β -Alanine

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It is an interesting subject to clarify the interactions between the transition-metal complexes of amino acids and sugars in coordination chemistry and in bioinorganic chemistry. Recently we have studied the nickel(II) complexes containing the *N*-glycosides derived from the reaction of a diamine and a monosaccharide, including X-ray crystallography.¹⁻⁵ It is well-known that sugars react with an amine center of amino acids as well as amines to yield *N*-glycosides.⁶ Accordingly, the coordination behavior of the *N*-glycosides derived from aldoses and amino acids are expected to be similar to that of *N*-glycosides from diamines and aldoses. Weitzel et al. reported in 1957 that they isolated several metal complexes of the *N*-glycosides derived from an aldose and an amino acid.⁷ They confirmed the composition of the compounds by elemental analyses, but made no comment upon the spectral and stereochemical features. We reinvestigated to obtain such complexes according to their methods. However it was difficult to isolate analytically pure metal complexes containing a series of monosaccharides.⁸

We found that the metal complexes having sugar and amino acid residues can be easily obtained from the reaction of aldoses with $[\text{Ni}(\beta\text{-ala})_2(\text{H}_2\text{O})_2]$, which is unusually soluble in methanol

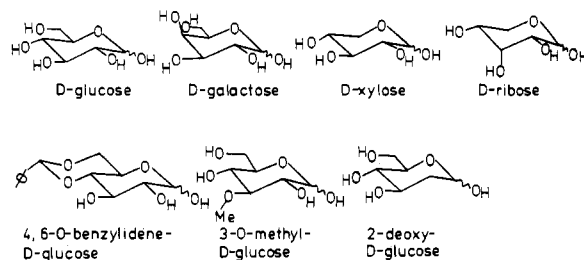


Figure 1. Structures of starting sugars.

for bis(amino acidato)nickel(II) complexes, where β -ala is β -alaninato. The structures of these complexes were assigned by using several analogous of D-glucose in relation to their spectral features.

Experimental Section

Preparation of $[\text{Ni}(\beta\text{-ala})_2(\text{H}_2\text{O})_2]$. A 0.05-mol sample of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ followed by 0.1 mol of β -alanine was dissolved in 150 mL of water. To this solution was added an aqueous solution of NaOH (0.1 mol in 50 mL) gradually. The blue precipitates formed were collected and washed with cold water and dried. Analytical data of this complex agreed with the proposed formula (C, H, N); the IR spectral data correspond to the reported value⁹ in the range 4000–200 cm^{-1} .

Reaction of Monosaccharides with $[\text{Ni}(\beta\text{-ala})_2(\text{H}_2\text{O})_2]$. The following monosaccharides (Figure 1) were used in this study; D-glucose (D-Glc), D-galactose (D-Gal), D-xylose (D-Xyl), D-ribose (D-Rib), 4,6-*O*-benzylidene-D-glucose (4,6-Bn-D-Glc),¹⁰ 3-*O*-methyl-D-glucose (3-Me-D-Glc), and 2-deoxy-D-glucose (2-De-D-Glc). Methanol was dried over 3-Å molecular sieves before use. A 10-mmol sample of monosaccharide was added to a solution of $[\text{Ni}(\beta\text{-ala})_2(\text{H}_2\text{O})_2]$ (5 mmol) in 60 mL of warm methanol (to dissolve D-Gal, 120 mL of methanol was used) and then heated to reflux. Blue precipitates were formed in the midst of refluxing in the cases of D-Gal and D-Rib. For the case of D-Glc, the solution was refluxed for 1 h and allowed to stand at room temperature; then a green complex crystallized. The blue compounds containing D-Xyl, 4,6-Bn-D-Glc, and 3-Me-D-Glc were formed when the solution was refluxed for 1 h and concentrated to about 30 mL. Of these complexes, the D-Gal, 3-*O*-Me-D-Glc, and 4,6-*O*-Bn-D-Glc complexes were obtained as gel-like solids. The aldose residues contained in these complexes were analyzed as follows. The complexes were dissolved in water, and then the solution was passed through ion-exchange resins (Dowex 50W, H^+ form, and Dowex 2, HCO_3^- form). By this process, the complexes were hydrolyzed and the free aldoses were separated. The aldoses in this solution were analyzed by HPLC system.¹¹

Measurements. Visible and near-infrared absorption spectra, diffusion reflectance spectra, circular dichroism spectra, and magnetic susceptibility were measured as previously described.^{4b}

Results and Discussion

Blue or green compounds were obtained from the reaction between $[\text{Ni}(\beta\text{-ala})_2(\text{H}_2\text{O})_2]$ and aldoses except in the case of 2-De-D-Glc. They are scarcely soluble in methanol except for the 3-Me-D-Glc complex. Analytical data indicated that they have two *N*-glycoside ligands, which are made from a β -alanine and an aldose, except for the 3-Me-D-Glc complex (Table I).¹² The 3-Me-D-Glc complex was found to have an *N*-glycoside ligand, a β -ala ligand, an aqua ligand, and a solvated methanol. HPLC analysis indicated that all these complexes contain the starting aldose residue. All these compound are hydrolyzed gradually in water.

The effective magnetic moments of the isolated complexes are also listed in table I, and the near-infrared and visible absorption spectra and the CD spectra of these complexes are shown in Figure

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(12) The following abbreviations are used: *N*-D-glucosyl-3-aminopropionate anion, D-Glc- β -ala; *N*-D-galactosyl-3-aminopropionate anion, D-Gal- β -ala; *N*-D-xylosyl-3-aminopropionate anion, D-Xyl- β -ala; *N*-D-ribosyl-3-aminopropionate anion, D-Rib- β -ala; *N*-(4,6-*O*-benzylidene-D-glucosyl)-3-aminopropionate anion, 4,6-Bn-D-Glc- β -ala; *N*-(3-*O*-methyl-D-glucosyl)-3-aminopropionate anion, 3-Me-D-Glc- β -ala.