82, 1073 (1960); (b) D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, **6**, 1032 (1967); (c) B. Halpern, A. M. Sargeson, and K. R. Turnbull, *J. Am. Chem. Soc.*, **88**, 4630 (1966).

(30) V. Katovic, L. T. Taylor, and D. H. Busch, *Inorg. Chem.*, **10**, 458 (1971).

(31) A. L. Companion and M. A. Komarynsky, *J. Chem. Educ.*, **41**, 257 (1964).

(32) The metal-ligand distance selected for the square-planar and rectangular diagrams is 1.855 Å. The reciprocal of this value is the mean of the reciprocals of the four Ni-N distances[28] in $[Ni(AT)]^+$ and thus the centroids of the three diagrams are the same. The angles in the rectangular array were taken from single-crystal X-ray structure determinations[33] of TIM complexes.[34] In all cases a charge of 1− was used for each "ligand".

(33) L. P. Torre, Thesis, University of Washington, 1971; L. P. Torre and E. C. Lingafelter, Program and Abstracts of American Crystallographic Association Meeting, Columbia, S.C., Jan 1971; G. W. Svetich, H. W. Smith, and E. C. Lingafelter, private communication.

(34) D. A. Baldwin, R. M. Pfeiffer, D. W. Reichgott, and N. J. Rose, *J. Am. Chem. Soc.*, **95**, 5152 (1973).

(35) N. F. Curtis, *Coord. Chem. Rev.*, **3**, 3 (1968).

(36) A. B. P. Lever, "Inorganic Electronic Spectroscopy", American Elsevier, New York, N.Y., 1968, p 343.

(37) D. A. House and N. F. Curtis, *J. Am. Chem. Soc.*, **86**, 1331 (1964).

(38) The K_a of $[Ni(ATH)]^{2+}$ was estimated from data obtained by spectrophotometrically determining the $[Ni(AT)]^+$:$[Ni(ATH)]^{2+}$ ratio in aqueous solutions of known pH.

(39) The acid hydrolysis of $[Ni(CHOAT)]^+$ to $[Ni(ATH)]^{2+}$ is based on the observed changes over a period of minutes in the PMR and electronic spectra of aqueous solutions. That formic acid is also a product of this hydrolysis has been unequivocally established by the observation of peak enhancement in the PMR spectrum upon the addition of formic acid to the sample in question.

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Conformational Dissymmetry. Axial-Equatorial Isomer Distributions of *N*-Methyl Substituted Aliphatic Five-Membered Chelate Rings

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A number of (*S*)-*N*-methylpropylenediamine complexes of Pt(II) and Pt(IV) have been prepared and the equilibrium constants for the axial-equatorial distributions of the $N-CH_3$ group have been determined. It was found that, generally, there is very little free energy difference between the two internal diastereomers but that apparently very small changes in the chelate ring and/or the other groups coordinated to the platinum atom can cause sharp changes in the isomer distribution. The d-d circular dichroism spectra of the Pt(II) complexes show that the chelate ring and the asymmetrically coordinated $N-CH_3$ group contribute additively to the spectra and, consequently, provide a method for determining the diastereomer distribution.

That five-membered chelate rings formed by ethylenediamine exist in stable (chiral) conformations was first suggested by Mathieu[1] and the various nonbonding interactions associated with the ring puckering were subsequently amplified by Corey and Bailar.[2] One of the important conclusions of the quantitative analysis was that an ethylenediamine chelate ring with substituents bonded to the carbon atoms would strongly prefer the substituent groups in equatorial dispositions. A large body of data has essentially sustained[3] this prediction, although in certain systems, notably the C-substituted-ethylenediamine Schiff base complexes, axially orientated substituents are sometimes preferred. This was first suggested by circular dichroism data[4] and subsequently confirmed by single-crystal X-ray structures.[5] Despite these exceptions, where the determining factor appears to be the presence of azomethine linkages,[5] all other investigated systems have consistently confirmed the original predictions.

Were only the data derived from octahedral complexes considered, a similar conclusion might be drawn for the N-substituted ethylenediamine chelate ring, namely, that the substituent prefers an equatorial disposition.[6,7] For square-coplanar complexes, however, the experimental results indicate that a significant proportion of the axial isomer may exist at equilibrium.[8,9] Moreover, a recent conformational analysis suggests that the free energy distinction between the axial and equatorial orientations of N-substituted ethylenediamine chelates may not be large even in octahedral systems.[10]

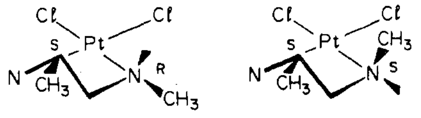
We became concerned with this problem through an interest in designing ligands suitable for metal-assisted asymmetric synthesis where the orientation of the donor atom substituents can play a major role in the diastereotopic discrimination of the substrate. This paper describes a study of the Me-*S*-pn ($CH_3NHCH_2CH(CH_3)NH_2$) ligand coordinated to platinum in both the stable square-coplanar Pt(II) and octahedral Pt(IV) oxidation states. We will show that in all cases the *C*-methyl group appears to prefer an equatorial orientation but that, in general, the *N*-methyl substituent displays an erratic preference for its two possible orientations in both the square coplanar and octahedral complexes.

1. Stereochemistry

Figure 1 shows the probable conformations of Me-*S*-pn coordinated to a square-coplanar complex. Structure I has both methyl groups equatorial and a δ conformation of the chelate ring; the same applies to structure II except that the *N*-methyl group is orientated axially. Whether the ring conformations are correct or not, the two are chemically distinct species in that they represent two internal diastereomers, namely, *R*-$[Pt(Me\text{-}S\text{-}pn)Cl_2]$ (I) and *S*-$[Pt(Me\text{-}S\text{-}pn)Cl_2]$ (II).

When $K_2[PtCl_4]$ is treated with Me-*S*-pn, the water-insoluble yellow compound $[Pt(Me\text{-}S\text{-}pn)Cl_2]$ is produced. It exists in two distinct crystalline modifications, blocks and needles, which have similar solubilities in water solution. These two forms are easily separated mechanically and, when pure, have almost enantiomorphic circular dichroism although their linear absorption spectra are nearly identical (vide infra). The two forms are quite stable in acidic media but, in neutral or basic solutions, they interconvert to a roughly equal mixture of each other. An X-ray crystal structure[11] of the blocks shows them to be the isomer *S*-$[Pt(Me\text{-}S\text{-}pn)Cl_2]$ having the δ chelate ring conformation and an axial *N*-methyl group as shown in II (Figure 1). Hence we conclude that the needles are *R*-$[Pt(Me\text{-}S\text{-}pn)Cl_2]$ with the structure I (Figure 1).

The two isomers could not be characterized by NMR because of their insolubility, but both were converted, in acid solution, to the very soluble diaquo complexes by the action



(I) (II)

Figure 1. Structure of R-[Pt(Me-S-pn)Cl$_2$] and S-[Pt(Me-S-pn)Cl$_2$]. The former has an equatorial N–CH$_3$ group; the latter, an axial N–CH$_3$ group. Both chelate rings are δ, and the C–CH$_3$ group, in both cases, is equatorially disposed.

of AgClO$_4$. The two corresponding diaquo complexes show distinct N–CH$_3$ resonances, split by both the N–H and ^{195}Pt nuclei. The N–H split resonances occur at τ 7.60 and 7.50 for the equatorial isomer and at τ 7.48 and 7.38 for the axial isomer in D$_2$O. The C–CH$_3$ resonances of the two isomers, however, have "identical" chemical shifts, even at 100 MHz. Addition of HCl regenerates the pure starting dichloro isomers.

2. Isomer Proportions

The equilibrium constant for the reaction

$$\underset{\text{equatorial}}{R\text{-}[\mathrm{Pt(Me\text{-}}S\mathrm{\text{-}pn)Cl_2}]} \rightleftharpoons \underset{\text{axial}}{S\text{-}[\mathrm{Pt(Me\text{-}}S\mathrm{\text{-}pn)Cl_2}]}$$

has been measured by circular dichroism in aqueous solutions containing excess chloride ions to suppress standing concentrations of the aquo species. Between 29.9 and 49.8°, the equilibrium constants are the same within experimental error and have a value of 1.20 ± 0.04 ($\Delta G_{25°} = 0.1$ kcal mol^{-1}) reflecting a slight preference (55%) for the axial isomer.

The axial–equatorial N–CH$_3$ equilibrium probably depends on two main factors: the interactions between the atoms of the chelate ring and the interactions associated with the other ligands attached to the Pt(II) atom. We have investigated the second effect, which to some extent is independent of the first, by equilibrating the complexes [Pt(Me-S-pn)(NH$_3$)$_2$]Cl$_2$, [Pt(Me-S-pn)en]Cl$_2$, [Pt(Me-S-pn)phen](NO$_3$)$_2$, and [Pt(Me-S-pn)acac]ClO$_4$ in D$_2$O solutions containing sodium bicarbonate. An example of these NMR analyses is shown in Figure 2 for the [Pt(Me-S-pn)(NH$_3$)$_2$]Cl$_2$ isomeric mixture. In acid solutions, the N–CH$_3$ protons occur as multiplets due to coupling with the N–H and ^{195}Pt nuclei, but it will be seen that the main N–CH$_3$ peaks (at around τ 7.3) consist of two pairs with inner two signals nearly degenerate. As expected, in neutral D$_2$O, N–H exchange occurs and the four main N–CH$_3$ peaks collapse into two resonances. These two signals are of nearly equal area and we infer that these represent the axial and equatorial isomers which equilibrate to nearly equal proportions. As the pD is raised, the two N–CH$_3$ peaks first broaden and then coalesce, and at or above pD 13.6 at 30°, only a single sharp resonance is observed at the mean frequency (Figure 2). This last result suggests that, as the pD is increased, the axial–equatorial inversion rate increases to a stage where the two sites become indistinguishable on an NMR time scale. Moreover, as can be seen in the bottom spectrum, the ^{195}Pt coupling persists indicating that the inversion occurs without rupture of the Pt–NCH$_3$ bond. The other feature of interest is that the C–CH$_3$ resonances, which appear at higher fields, are essentially degenerate for the two isomers. This suggests that the chelate ring conformations are the same for both isomers, that is the δ conformation, where the C–CH$_3$ group is equatorial in the two cases. However, even with the same ring conformation the two equatorially disposed C–CH$_3$ groups are, in principle, environmentally different and these resonances are observed at slightly different frequencies for the two isomers of [Pt(Me-S-pn)en]$^{2+}$ and [Pt(Me-S-pn)acac]$^+$ in D$_2$O at 100 MHz. As for the dichloro and diammine complexes, these last two complexes also equilibrate to a roughly equal mixture of the axial and equatorial isomers. We have checked the reliability of the NMR method for the case of the [Pt(Me-S-pn)acac]ClO$_4$ complex by converting the equilibrated aqueous solution of the isomers into the insoluble dichloro species by the action of 1 M HCl

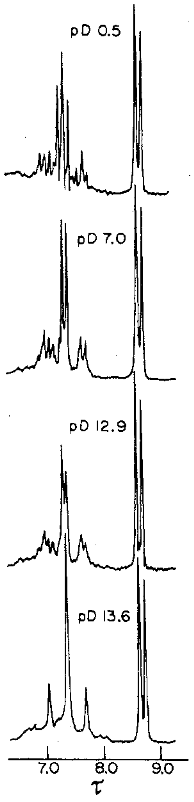


Figure 2. The 60-MHz NMR spectra of the isomeric mixture S-[Pt(Me-S-pn)(NH$_3$)$_2$]Cl$_2$ and R-[Pt(Me-S-pn)(NH$_3$)$_2$]Cl$_2$ in D$_2$O at 30° and at various pD values.

$$[\mathrm{Pt(Me\text{-}}S\mathrm{\text{-}pn)acac}]^+ + 2\mathrm{HCl} \rightarrow [\mathrm{Pt(Me\text{-}}S\mathrm{\text{-}pn)Cl_2}] + \mathrm{Hacac}$$

The quantitatively isolated dichloro complexes consist of a 55%–45% mixture of the equatorial and axial isomers, respectively, which is in excellent agreement with the NMR results. We were unsuccessful in our attempts to convert the other complexes by this method; the reactions with HCl led to the removal of the Me-S-pn ligand.

Unlike the other ligands of this series, the atoms at the 2 and 9 positions of the complexed phen chelate extend considerably in the (complex) equatorial plane, so much so, in fact, that *trans*-phen$_2$ complexes rarely form and, when they do, the two ligands experience gross distortions due to the 2,9-atom interactions.[12] We would thus expect the phen ligand to exert a much stronger influence on the orientation of the N–CH$_3$ group than the other ligands of this series. The NMR spectrum of a D$_2$O solution containing the equilibrated [Pt(Me-S-pn)phen]$^{2+}$ ion shows only a single sharp N–CH$_3$ resonance and a sharp C–CH$_3$ doublet at 100 MHz, suggesting that one isomer predominates to at least 90%. We do not know which isomer this is, but scale molecular models indicate that the axial isomer would be least hindered. Thus for these square-coplanar complexes there is a very small energy difference between the axial and equatorial N–CH$_3$ groups except when the other ligands are capable of strongly interacting with the N–CH$_3$ group. We now turn to the problem of axial interactions in octahedral complexes where we might expect that groups coordinated perpendicularly to the mean plane of the chelate ring would have an influence on the N–CH$_3$ group's orientation.

When either of the isomers of the complex [Pt(Me-S-pn)Cl$_2$], dissolved in 1 M HCl, is oxidized with chlorine, the corresponding octahedral Pt(IV) complex is formed with the same N–CH_3 group orientation as the starting material

$$R\text{- or }S\text{-}[Pt(Me\text{-}S\text{-}pn)Cl_2] + Cl_2 \rightarrow R\text{- or }S\text{-}[Pt(Me\text{-}S\text{-}pn)Cl_4]$$

The Pt(IV) complexes are not sufficiently soluble in water to measure their NMR spectra, but the retention of stereochemistry during the oxidation has been confirmed by their reduction, with ascorbic acid, back to their Pt(II) progenitors. In both cases, the reduced complexes had circular dichroism spectra identical with those of the pure Pt(II) isomers. This reduction provided us with a method of measuring the axial–equatorial N–CH_3 distribution in the Pt(IV) species, the circular dichroism spectra of which are rather weak and not suited to precise determination of the isomer equilibrium. As with the Pt(II) species, extensive hydrolysis of the chloride ligands coordinated to the Pt(IV) complexes occurs in water solutions so that the equilibrium studies were carried out in KCl solutions of sufficient concentration to give a constant absorption spectrum over the time of equilibration. Even so, it is probable that small, temperature-dependent concentrations of the aquo species exist, and the 5% variation in the equilibrium constant that was found between 25 and 90° may be affected by small variable standing concentrations of the aquo species.[13] Within this temperature range, in neutral water solutions, the equatorial isomer predominates to the extent of 75 ± 5%.

In view of the isomer distributions found for the square-coplanar complexes, it might be inferred that the axial chloro ligands of the Pt(IV) complexes are responsible for the (small) destabilization of the axial (N–CH_3) isomer. This is probably true in part, but more subtle effects also appear to be present. Thus the *trans(Cl)*-$[Pt(Me\text{-}S\text{-}pn)(NH_3)_2Cl_2]^{2+}$ ion in D_2O displays a single sharp N(D)–CH_3 resonance at τ 7.25 and a single sharp C(H)–CH_3 doublet (τ 8.48 and 8.55) at 100 MHz after equilibration at 30°. In the unlikely event that both resonances are accidentally degenerate, the NMR spectrum indicates the presence of only one isomer at equilibrium, probably the equatorial diastereomer. This conclusion is consistent with earlier observations[6] on analogous *trans*-X_2Me-*S*-pn complexes of Co(III) which, for a variety of complexes, showed only one isomer of the N–CH_3 group. It is not immediately apparent why replacing two chloro groups in the plane of the chelate ring by two ammines should tilt the diastereomer ratio totally to one species, particularly since the two Pt(II) progenitors show the same (equal) diastereomer distribution.

3. Kinetics of Epimerization

The kinetics of epimerization of the $[Pt(Me\text{-}S\text{-}pn)Cl_2]$ isomers were followed by circular dichroism at 301 mμ in water solutions containing 0.195 *M* KCl to suppress standing concentrations of the aquo species. Raising the KCl concentration from 0.1 to 0.4 *M* caused no detectable change in either the rate constants or the absorption or circular dichroism spectra; and neither did the rate constants change detectably when the buffer was changed from *N*-ethylmorpholine hydrochloride to triethanolamine hydrochloride nor when the complex concentration was changed from 10^{-3} to 5×10^{-4} *M*. At 49.8°, the reaction was found to follow the rate law

$$k_{obsd} = k_{ep}[OH^-]$$

within experimental error between pH 5.8 and 7.6. There is probably also a first-order solvent-assisted path which contributes to k_{obsd} but its value is $\geq 1 \times 10^{-5}$ sec^{-1} at 49.8° so that, except for low pH values, its contribution can be neglected. At pH >7.8 the three isodichroic points, at 282, 332, and 363 mμ, which were sustained over 3 half-lives at lower pH's, were not maintained. These constants were therefore not included in the plot of k_{obsd} vs. $[OH^-]$ which was linear and whence k_{ep} = 402 M^{-1} sec^{-1} at 49.8° for the rate of approach to equilibrium. The equilibrium is close to unity and our data were not sufficiently precise to determine the difference in forward and backward rate constants with any accuracy. Because of this, the rate constants in Table I have been derived by treating the data as if the reaction was one of racemization.

Table I. Rate and Equilibrium Data for the Epimerization of $[Pt(Me\text{-}S\text{-}pn)Cl_2]$ in Buffered Solutions[a]

Temp, °C	pH	$10^5 k_{obsd}$, sec^{-1}	k_{ep},[b] M^{-1} sec^{-1}
49.8	5.85	1.8	402
49.8	6.34	6.3	402
49.8	6.91	22.2	402
49.8	7.23[c]	39	402
49.8	7.42	58	402
49.8	7.61	82	402
40.0	7.42	29.7	208
35.2	7.42	20.6	144
29.9	7.42	14.1	99

[a] *N*-Ethylmorpholine hydrochloride (5×10^{-3} *M*)–KCl (0.195 *M*) unless otherwise stated. [b] The values of k_{ep} = 402 were derived from the slope of k_{obsd} vs. $[OH^-]$. The values of k_{ep} at 40.0, 35.2, and 29.9° were obtained from $k_{ep} = k_{obsd}/[OH^-]$. [c] Triethanolamine buffer, 5×10^{-3} *M*.

Table II. Activation Parameters

	E_a, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
$[Pt(Me\text{-}S\text{-}pn)Cl_2]$	14.4	−4
$[Pt(Meen)en]Cl_2$[a,c]	18.1	+12
$[Pt(Meen)(NH_3)_2]Cl_2$[b]	19.8	+17
$[Pt(Meen)phen]Cl_2$[b]	17.3	+17

[a] D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *J. Am. Chem. Soc.*, 91, 5227 (1969). [b] J. B. Goddard and F. Basolo, *Inorg. Chem.*, 8, 2223 (1969). [c] Meen = *N*-methylethylenediamine.

Table II shows the activation parameters (ln k_{ep} vs. $1/T$) for these reactions together with analogous data for similar systems. In the absence of proton-exchange studies, which we were unable to do because of the low solubilities of the complexes, it is difficult to contrast the present results with those obtained for the other systems. One significant difference, however, resides in the $\Delta S^{\ddagger}$ which is slightly negative for the present system and substantially positive for the others. This may be related to the charges of the complexes. The neutral complexes become negatively charged on forming the conjugate base whereas the others change from dipositive to unipositive species upon forming their respective conjugate bases. Thus the slight negative entropy may indicate that the solvation order is only marginally affected in going from a neutral ground state to a negatively charged transition state, but the substantial positive $\Delta S^{\ddagger}$ suggests that the dipositive to unipositive change results in the production of considerable solvation disorder. The other notable difference is that the rates of racemization are one to two orders of magnitude slower for the present systems. The temptation to ascribe this to the greater stabilization of the conjugate base for the positively charged complexes is restrained by the fact that the neutral species have a lower activation energy; the determining factors appear to be connected with the activation entropies. It seems probable, therefore, that the important factor contributing to the rates of racemization is the structure and strength of association of the immediate solvation sphere, which will affect not only the rates of proton exchange but more particularly the retention ratios of the nitrogen inversion.

4. Absorption and Circular Dichroism Spectra

Figure 3 shows the absorption and circular dichroism of the two isomers of $[Pt(Me\text{-}S\text{-}pn)Cl_2]$ in aqueous acidic KCl solutions. As expected, the linear absorptions are nearly identical; but the circular dichroism is almost enantiomorphic

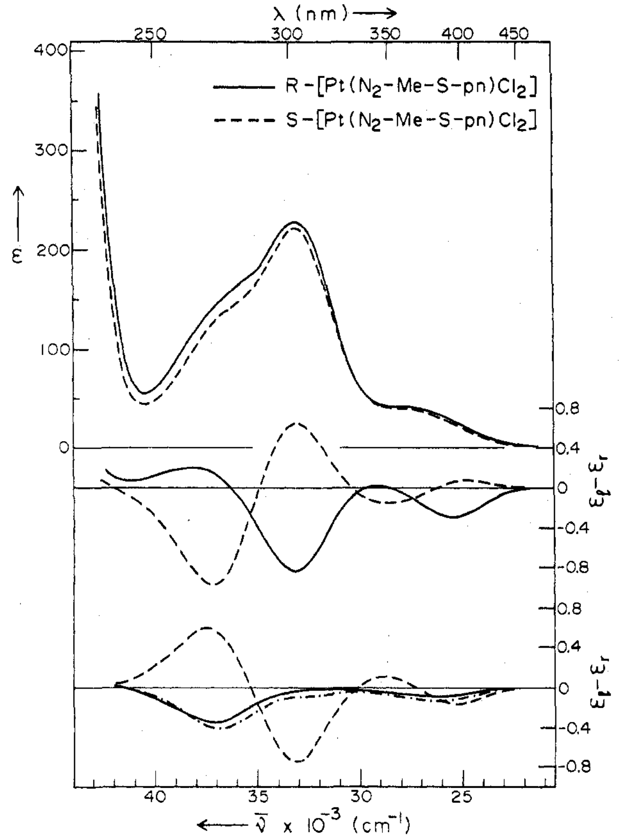


Figure 3. Absorption and circular dichroism spectra of *R*-[Pt(Me-*S*-pn)Cl$_2$] (equatorial isomer) and *S*-[Pt(Me-*S*-pn)Cl$_2$] (axial isomer) dissolved in aqueous KCl (0.2 *M*), at pH 1.0. Bottom circular dichroism curves: - - -, calculated contribution to the circular dichroism of the *R* N–CH$_3$ center; - · - ·, calculated circular dichroism contribution of the δ chelate ring; ——, observed circular dichroism of [Pt(*S*-pn)Cl$_2$] which also has a δ chelate ring.

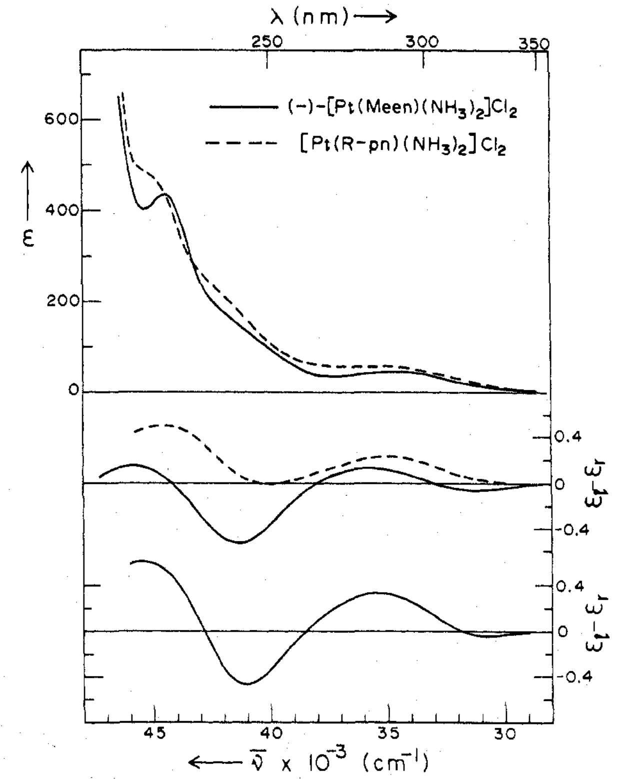


Figure 4. Absorption and circular dichroism spectra of (−)-[Pt(Meen)(NH$_3$)$_2$]Cl$_2$ and [Pt(*R*-pn)(NH$_3$)$_2$]Cl$_2$ in water solutions. The bottom curve is the calculated circular dichroism for the *R* N–CH$_3$ center derived from the two spectra above it.

for the two isomers. The polarized crystal spectra and the magnetic circular dichroism of the [PtCl$_4$]$^{2-}$ ion,[14] together with the linear relationship that exists[15] between crystal field strength and the individual transitions of the series [Pt(NH$_3$)$_n$Cl$_{4-n}$]$^{(n-2)+}$, leave little doubt about the general electronic provenance of the absorption bands arising within the d-electron manifold. Thus the central (linear) absorption band at 33,000 cm^{-1} is the $d_{xy} \rightarrow d_{x^2-y^2}$ magnetic dipole and spin-allowed excitation, while the other magnetic dipole allowed transition, d_{xz}, $d_{yz} \rightarrow d_{x^2-y^2}$, is seen as the shoulder centered at 36,500 cm^{-1}. The weak, broad feature seen between 29,000 and 23,000 cm^{-1} represents the singlet–triplet state transitions derived from the d-electron manifold. The two circular dichroism spectra reveal that this spin-forbidden absorption consists of at least two transitions and we ascribe the circular dichroism at 25,000 cm^{-1} to the $d_{xy} \rightarrow d_{x^2-y^2}$ (singlet–triplet) transition and the weaker circular dichroism centered at 29,000 cm^{-1} to the spin-forbidden d_{xz}, $d_{yz} \rightarrow d_{x^2-y^2}$ excitation. These latter assignments are based on the supposition that energy ordering of the spin-forbidden excited states will roughly parallel that of their spin-allowed counterparts. The circular dichroism associated with two (observed) singlet–singlet state transitions could be interpreted in either of two ways: either the bands centered at 33,000 cm^{-1} are the $d_{xy} \rightarrow d_{x^2-y^2}$ transitions and those at 37,500 cm^{-1} represent the d_{xz}, $d_{yz} \rightarrow d_{x^2-y^2}$ transitions, or these couplets actually originate from the split d_{xz}, $d_{yz} \rightarrow d_{x^2-y^2}$ excitations. If this latter assignment is adopted, the circular dichroism associated with the $d_{xy} \rightarrow d_{x^2-y^2}$ absorption would lie under the 33,000-cm^{-1} bands. In view of the circular dichroism shown by analogous d–d transitions in Co(III) complexes,[16] where the d_{xz}, $d_{yz} \rightarrow d_{x^2-y^2}$ transition generally shows a couplet for tetragonal N-substituted polyamine complexes, this less obvious assignment cannot be dismissed and we are inclined to interpret the spectra in this way. We, however, have no strong evidence to support this except to note that a gaussian analysis of the 33,000-cm^{-1} bands is consistent with the presence of two bands in this region. There is, as usual, no evidence in either the linear or circular dichroic absorption for the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition. If it lies under the d–d absorption manifold, its presence may not distort the circular dichroism spectra sufficiently to be detected because it is magnetic dipole forbidden in zero order (D_{4h}) and thus is expected to carry the weakest circular dichroism.

Because both of the [Pt(Me-*S*-pn)Cl$_2$] isomers have a δ ring and are structurally distinguished by the chirality of the asymmetric nitrogen center, the observation that the circular dichroism is nearly enantiomorphic for the two isomers suggests that the chiral nitrogen center has a dominating influence on the d–d circular dichroism. We assume that the ring conformation and the chiral nitrogen center make additive contributions to the d–d circular dichroism. There is no a priori justification for this but, as we shall show, the systems behave as if this were the case and it provides a method for the determination of the conformations of related systems. Thus half the sum and half the differences of the two observed circular dichroism spectra should give the contributions due to the δ ring and the nitrogen centers, respectively. Figure 3 shows the results obtained for the δ ring and the *R* nitrogen center; the *S* center, by assumption, is exactly opposite. Also shown is the circular dichroism of [Pt(*S*-pn)Cl$_2$], where the propylenediamine ring is in a δ conformation. It will be seen that, within experimental error, the calculated and observed spectra are identical. This remarkable result suggests that it might be possible to assign the conformations and absolute configurations of *N*-CH$_3$ substituted ethylenediamine complexes of Pt(II).

Table III. Isomer Distributions of the N–CH_3 Group

	Axial %	Equatorial %
$[Pt(Me\text{-}S\text{-}pn)Cl_2]$	55	45
$[Pt(Me\text{-}S\text{-}pn)(NH_3)_2]^{2+}$	50	50
$[Pt(Me\text{-}S\text{-}pn)en]^{2+}$	50	50
$[Pt(Me\text{-}S\text{-}pn)acac]^{+}$	45	55
$[Pt(Me\text{-}S\text{-}pn)phen]^{2+}$	100[a]	0
$[Pt(Meen)(NH_3)_2]^{2+}$	0	100
$[Pt(Me\text{-}S\text{-}pn)Cl_4]$	25	75
trans-(*Cl*)-$[Pt(Me\text{-}S\text{-}pn)(NH_3)_2Cl_2]^{2+}$	0	100[a]

[a] Both complexes have only one stable isomer; the one designated is probable but has not been proven.

Figure 4 shows the absorption and circular dichroism spectra of (–)-$[Pt(Meen)(NH_3)_2]Cl_2$ and $[Pt(R\text{-}pn)(NH_3)_2]Cl_2$ in water solution; the latter has a λ ring. As expected, these spectra occur at higher energies compared to the dichloro analogs, and we assign these absorption bands in a similar way, since it is clear that all that has occurred is a simple shift to higher energies and some variations in intensity. The circular dichroism spectrum of (–)-$[Pt(Meen)(NH_3)_2]^{2+}$ is very similar to that of the *R*-$[Pt(Me\text{-}S\text{-}pn)Cl_2]$ complex, the corresponding transitions carry identical signs, and the relative intensities are similar. This implies that the two probably have the same absolute configurations, specified by a δ ring and an *R* equatorial N–CH_3 group. If the ring conformation and the chiral nitrogen center contribute additively to the circular dichroism and if we assume that the chiral carbon center's contribution is small, then it is possible to check this assignment by calculating the contribution due to the chiral nitrogen center. The two complexes in Figure 4 are assigned opposite ring conformations and thus a simple addition of the two circular dichroism spectra should give the contribution of the presumed *R* nitrogen center in the (–)-$[Pt(Meen)(NH_3)_2]^{2+}$ species. The result is shown in Figure 4 and it will be seen that, apart from the energy displacement, the calculated spectrum is very similar to that calculated for the *R* nitrogen center in the *R*-$[Pt(Me\text{-}S\text{-}pn)Cl_2]$ complexes (Figure 3). This supports our initial structural assignment and leads to the surprising conclusion that the $[Pt(Meen)(NH_3)_2]^{2+}$ ion exists largely with an equatorially disposed methyl group. Moreover, the circular dichroism of the $[Pt(Me\text{-}S\text{-}pn)(NH_3)_2]^{2+}$ ion, which consists of a nearly equal mixture of axial and equatorial isomers in water solutions (Figure 2), is nearly identical throughout the d–d region with that shown by $[Pt(S\text{-}pn)(NH_3)_2]^{2+}$, which would be expected if the additivity rule obtains. Thus, it is probable that for the $[Pt(Meen)(NH_3)_2]^{2+}$ ion, the equatorial disposition is preferred to at least 90%. While it is true that the calculated and observed vicinal and conformational effects do not match exactly in going from the dichloro to diammine complexes, the internal consistency is such as to make this conclusion difficult to ignore. The wonder to us is not that additivity is imprecise but that it works at all.

5. Discussion

Table III summarizes the diastereomer distributions for both the square-coplanar and octahedral complexes. The fact that the $[Pt(Me\text{-}S\text{-}pn)(NH_3)_2Cl_2]^{2+}$ ion with trans chloride ligands and $[Pt(Me\text{-}S\text{-}pn)Cl_4]$ give different results, as do the slightly different pair $[Pt(Me\text{-}S\text{-}pn)(NH_3)_2]^{2+}$ and $[Pt(Meen)(NH_3)_2]^{2+}$ suggests that very small effects can shift the preference to either the axial or equatorial isomers. Because these changes need involve only about 1 kcal mol^{-1} in free energy, the sharp changes in proportions that are observed accompanying small structural variations is perhaps not unexpected. The conformational calculations[10] suggest that a small flattening in the puckering of the chelate ring, changes in bond lengths, and small differences in interaction between the various atoms could result in change in conformational interaction of about 1 kcal mol^{-1}. It seems, therefore, that any proportion of the two isomers is possible in these N–CH_3-substituted ethylenediamine chelate rings and that it is difficult to predict the outcome for any given case, except, perhaps, by a complete conformational analysis.

6. Experimental Section

Absorption spectra were measured on a Unicam 800A spectrometer and the circular dichroism spectra were obtained with a Roussel-Jouan Dichrographe II. Varian T-60 and HA-100 spectrometers were used.

Kinetics and Equilibration. The kinetics of epimerization of $[Pt(Me\text{-}S\text{-}pn)Cl_2]$ were followed by circular dichroism at 301 mμ, using 5-cm quartz cells. A series of buffer solutions was made up containing *N*-ethylmorpholine hydrochloride (5×10^{-3} *M*) together with KCl sufficient to bring the total Cl^- concentration to 0.2 *M*. The pH of the solution was measured at the appropriate temperature.

Generally the $[Pt(Me\text{-}S\text{-}pn)Cl_2]$ was finely ground and dissolved in the thermostated buffer solution. Usually 1×10^{-3} *M* complex concentrations were used. The flask containing the reaction mixture was wrapped in tin foil and placed in the thermostated bath. Samples were quenched in ice and analyzed at 12°. After a suitable period of time the equilibrium spectrum was measured. The circular dichroism spectra at "zero time" were obtained from the complexes dissolved in 0.2 *M* HCl. Using the "zero time" and "infinity" spectra, the equilibrium constants were derived by an obvious procedure. Plots of ln $(d_\infty - d_t)$ vs. time (where d_∞ is the circular dichroism deflection at equilibrium and d_t is the deflection at any time) were linear for 3 half-lives of reaction and gave the constants for approach to equilibrium (Table I).

The $[Pt(Me\text{-}S\text{-}pn)Cl_4]$ complexes were equilibrated as follows. The Pt(IV) complex (0.0213 g) was dissolved in 25 ml of a 1 *M* KCl water solution. Sodium hydroxide (10^{-2} *M*; 0.5 ml) and water (15 ml) were then added. The resulting solution was allowed to equilibrate at the appropriate temperature for 2 hr, after which time HCl (3 *M*; 0.2 ml) followed by ascorbic acid (0.1 g) was added. After this solution was heated on a steam bath for about 30 min, the reduction was complete; the cooled solution was made up to 50 ml and analyzed. The resultant circular dichroism spectra are totally accounted for in terms of the $[Pt(Me\text{-}S\text{-}pn)Cl_2]$ species.

Preparations. $[Pt(Me\text{-}S\text{-}pn)Cl_2]$. $K_2[PtCl_4]$ (8.30 g) and (*S*)-N^2-methylpropylenediamine dihydrochloride[6] (3.22 g) were dissolved in water (70 ml). The solution was stirred and brought to 80°, and, then, solid sodium bicarbonate (3.36 g) was added in small portions at such a rate that after each successive addition the effervescence had subsided. An orange-yellow precipitate was formed almost immediately. After the addition was complete, LiCl (2 g) was added and the hot solution was stirred for 0.5 hr. The solution was allowed to cool and the now yellow precipitate was collected, washed first with cold water, and then washed with acetone (5.5 g; 78%).

Separation of the Isomers. The yellow solid derived from the above reaction mixture consists of a mixture of isomers which were purified and separated as follows. The solid (4.8 g) was dissolved in boiling water (800 ml) and the mixture was filtered while hot into lithium chloride (4 g) in water (20 ml). The resultant solution was brought to the boil and allowed to cool slowly to room temperature. After 2 days, crystallization was complete and resulted in the formation of two distinct types of crystals, blocks and feathery needles. The much lighter needles were partially separated by agitating the mixture and simultaneously decanting the mother liquor. The remaining solid was collected and suspended in acetone and the remaining lighter needles were again removed from the blocks by decantation. In this way the nearly pure isomers were obtained (blocks, 2.23 g; needles, 1.25 g). (The inequality of the proportions reflects the slightly different solubilities of the two isomers.)

The two crystals were dissolved in hot HCl (0.1 *M*), 350 ml for 2.23 g of the blocks and 250 ml for 1.25 g of the needles, and the solutions were set aside to crystallize. The *S*-$[Pt(Me\text{-}S\text{-}pn)Cl_2]$ isomer deposited as yellow blocks (1.95 g) and the *R*-$[Pt(Me\text{-}S\text{-}pn)Cl_2]$ isomer formed light yellow feathery needles (1.0 g). These were collected, were washed first with water and then with acetone, and were allowed to dry at 100° for 12 hr.

Anal. Calcd for $[Pt(C_4H_{12}N_2)Cl_2]$: C, 13.6; H, 3.4; N, 7.9; Cl, 20.0. Found for *S*-$[Pt(Me\text{-}S\text{-}pn)Cl_2]$: C, 13.3; H, 3.6; N, 7.8; Cl, 20.1. Found for *R*-$[Pt(Me\text{-}S\text{-}pn)Cl_2]$: C, 13.4; H, 3.3; N, 7.8; Cl, 19.6.

$[Pt(Me\text{-}S\text{-}pn)(NH_3)_2]Cl_2$. An isomeric mixture of [Pt(Me-*S*-

pn)Cl$_2$] (6.3 g) was suspended in an evaporating dish with aqueous ammonia (concentrated; 30 ml) and the mixture was allowed to evaporate to dryness. The process was repeated with the residue using 20 ml of aqueous ammonia and then once more with a further 10 ml of aqueous ammonia. The almost white residue was taken up in hot methanol (50 ml) and filtered. Acetone (~100 ml) was added to the filtrate and after a few minutes a clear oil began to deposit. The oil was induced to crystallize by adding methanol dropwise and scratching the beaker with a glass rod. When all the oil was converted to crystals, the solution was brought to the boil and acetone (300 ml) was added to the boiling mixture. The mixture was allowed to cool and ether (50 ml) was then added. After the mixture was allowed to stand at 0° for 12 hr, the crystals were collected and washed with acetone and then with ether (6.3 g).

The white crystals (5 g) were dissolved in warm water (5 ml) and the solution was slowly diluted with absolute ethanol. After 3 days at 0° the solution deposited large colorless blocks, together with some fine white needles. These were collected, washed with acetone, and dried at 100° (2.6 g). (Despite the well-formed crystals, no separation of the isomers was achieved; both the blocks and needles are a nearly equal mixture of isomers.)

Anal. Calcd for [Pt(C$_4$H$_{12}$N$_2$)(NH$_3$)$_2$]Cl$_2$: C, 12.4; H, 4.7; N, 14.4; Cl, 18.3. Found: C, 12.5; H, 4.7; N, 14.5; Cl, 18.2.

[Pt(Me-*S*-pn)en]Cl$_2$. Anhydrous (BaO) ethylenediamine (0.225 g) was added to a suspension of an isomeric mixture of [Pt(Me-*S*-pn)Cl$_2$] (1 g) in water (25 ml). The mixture was stirred and held at 80° for 30 min, whereafter all of the solid had dissolved and a colorless solution was formed. The solution was evaporated to dryness and the residue was taken up in 98% ethanol (20 ml). Excess acetone was then slowly added to the solution to deposit a white, hygroscopic powder which was filtered and immediately dissolved in boiling absolute ethanol (45 ml). To the hot solution was added acetone (40 ml) and then ether (10 ml); the cloudiness of the resultant mixture was removed by the addition of a few drops of 95% ethanol. The solution was allowed to stand at 25° for 3 days and the fine white crystals were collected. The filtrate was brought to the boil, ether (25 ml) was added, and the mixture was set aside. The crystals were collected, the filtrate was brought to the boil, and ether was added. This procedure was repeated a number of times to give finally 0.5 g of white crystals of an isomeric mixture of [Pt(Me-*S*-pn)en]Cl$_2$. The above, somewhat elaborate crystallization procedure was the only one we found that avoided the production of an intractable gel.

Anal. Calcd for [Pt(C$_6$H$_{20}$N$_4$)]Cl$_2$: C, 17.4; H, 4.9; N, 13.5; Cl, 17.1. Found: C, 17.3; H, 5.0; N, 13.4; Cl, 17.0.

[Pt(Me-*S*-pn)(phen)](NO$_3$)$_2$. A solution of silver nitrate (1.419 g) in water (25 ml) was slowly added to a hot, stirred suspension of the isomeric mixture of [Pt(Me-*S*-pn)Cl$_2$] (1.478 g) in water (25 ml). The mixture was then heated on a steam bath for 20 min and then the coagulated silver chloride was filtered off. The filtrate was pumped to dryness and the residue was dissolved in hot water (20 ml) and filtered. The yellowish filtrate was diluted with water (150 ml) and brought to the boil. Solid *o*-phenanthroline monohydrate (1.2 g) was added to the hot, stirred solution. After the mixture was heated at 80° for 30 min, it was filtered and then evaporated to dryness, leaving a yellow solid. The residue was slurried with a 1:1 acetone–ether mixture and collected. It was taken up in hot water (10 ml), and after the solution was filtered, it was left for 1 day at 25°. The solid was collected and finally recrystallized from hot water (10 ml) by the addition of ethanol (10 ml). The pure product formed bright yellow blocks (0.75 g).

Anal. Calcd for [Pt(C$_{16}$H$_{20}$N$_4$)](NO$_3$)$_2$: C, 32.7; H, 3.4; N, 14.3. Found: C, 32.6; H, 3.5; N, 14.2.

[Pt(Me-*S*-pn)(acac)]ClO$_4$. Silver perchlorate (1.625 g) in water (25 ml) was added slowly to a hot, stirred suspension of [Pt(Me-*S*-pn)Cl$_2$] (1.388 g) in water (25 ml). The mixture was stirred at 80° for 30 min and filtered. To the filtrate were added acetylacetone (0.58 g) and lithium carbonate (0.21 g) and the resulting mixture was stirred and refluxed for 20 min. The metal that had formed was removed and the solution was evaporated to dryness. The residue was extracted with ether and then dissolved in hot water (5 ml). After 2 days at 25° the crystals were collected and finally recrystallized from water (5 ml). The yellow needles were collected and washed with 1:1 acetone–ether and then with ether (0.75 g).

Anal. Calcd for [Pt(C$_9$H$_{19}$N$_2$O$_2$)]ClO$_4$: C, 22.4; H, 4.0; N, 5.8; Cl, 7.4. Found: C, 22.5; H, 4.0; N, 5.9; Cl, 7.4.

***S*-[Pt(Me-*S*-pn)Cl$_4$].** The following procedure can be applied to the preparation of either the axial or equatorial *N*-methyl–platinum(IV) compounds. We give the preparation of axial isomer. *S*-[Pt(Me-*S*-pn)Cl$_2$] (0.5 g) was dissolved in hot hydrochloric acid (200 ml; 1 *M*) and chlorine was bubbled through the hot solution for 5 min. The resulting light canary yellow solution was allowed to stand for 1 hr, and then it was purged with a stream of air to remove the excess chlorine. The solution was pumped down to a volume of 10 ml, and the bright yellow crystals were collected and washed with a little water, then with 1:1 acetone–ether, and finally with ether (0.4 g).

Anal. Calcd for [Pt(C$_4$H$_{12}$N$_2$)Cl$_4$]: C, 11.3; H, 2.9; N, 6.6; Cl, 33.4. Found: C, 11.5; H, 3.0; N, 6.5; Cl, 33.1.

***trans*(*Cl*)-*R*-[Pt(Me-*S*-pn)(NH$_3$)$_2$Cl$_2$]Cl$_2$·0.5H$_2$O.** The isomeric mixture [Pt(Me-*S*-pn)(NH$_3$)$_2$]Cl$_2$ (0.5 g) was dissolved in hydrochloric acid (25 ml; 0.1 *M*) and chlorine was bubbled through the solution for 5 min. The resulting bright yellow solution was allowed to stand for 1 hr, and then the dissolved chlorine was purged with a strong current of air. The solution was pumped to dryness, the residue was taken up in water (10 ml), and the product was precipitated with a large volume of acetone. It was finally recrystallized from hot saturated methanol solution by the very slow addition of ether. The product crystallized as very pale yellow blocks (0.2 g).

Anal. Calcd for [Pt(C$_4$H$_{12}$N$_2$)(NH$_3$)$_2$Cl$_2$]Cl$_2$·0.5H$_2$O: C, 10.3; H, 4.1; N, 12.0; Cl, 30.3. Found: C, 10.2; H, 4.5; N, 12.0; Cl, 30.6.

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Registry No. *R*-[Pt(Me-*S*-pn)Cl$_2$], 56258-73-2; *S*-[Pt(Me-*S*-pn)Cl$_2$], 56323-56-9; *R*-[Pt(Me-*S*-pn)(NH$_3$)$_2$]Cl$_2$, 56258-74-3; *S*-[Pt(Me-*S*-pn)(NH$_3$)$_2$]Cl$_2$, 56297-99-5; [Pt(Me-*S*-pn)en]Cl$_2$, 56258-75-4; [Pt(Me-*S*-pn)(phen)](NO$_3$)$_2$, 56258-77-6; [Pt(Me-*S*-pn)(acac)]ClO$_4$, 56258-79-8; *S*-[Pt(Me-*S*-pn)Cl$_4$], 56258-80-1; *trans*(*Cl*)-*R*-[Pt(Me-*S*-pn)(NH$_3$)$_2$Cl$_2$]Cl$_2$, 56258-81-2; (−)-[Pt(Meen)(NH$_3$)$_2$]Cl$_2$, 25956-86-9; [Pt(*R*-pn)(NH$_3$)$_2$]Cl$_2$, 17787-81-4; [Pt(*S*-pn)Cl$_2$], 56298-00-1; *R*-[Pt(Me-*S*-pn)(H$_2$O)$_2$]$^{2+}$, 56258-82-3; *S*-[Pt(Me-*S*-pn)(H$_2$O)$_2$]$^{2+}$, 56298-01-2; ethylenediamine, 107-15-3; acetylacetone, 123-54-6.

References and Notes

(1) J. P. Mathieu, *Bull. Soc. Chim. Fr.*, **5**, 725 (1938); *Ann. Phys.* (*Leipzig*), **19**, 335 (1944).

(2) E. J. Corey and J. C. Bailar, *J. Am. Chem. Soc.*, **81**, 2620 (1959).

(3) S. Yano, S. Ito, Y. Koike, J. Fujita, and K. Saito, *Bull. Chem. Soc. Jpn.*, **42**, 3184 (1969).

(4) B. Bosnich, *J. Am. Chem. Soc.*, **90**, 627 (1968).

(5) C. Busetto, F. Cariati, A. Fusi, M. Gullotti, F. Morazzoni, A. Pasini, R. Ugo, and V. Valenti, *J. Chem. Soc., Dalton Trans.*, 754 (1973), and references therein.

(6) M. Saburi, Y. Tsujito, and S. Yoshikawa, *Inorg. Chem.*, **9**, 1476 (1970).

(7) D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, **7**, 915 (1968), and references therein.

(8) P. Haake and P. C. Turley, *J. Am. Chem. Soc.*, **90**, 2293 (1968).

(9) L. E. Erickson, M. D. Erickson, and B. L. Smith, *Inorg. Chem.*, **12**, 412 (1973).

(10) L. J. DeHayes and D. H. Busch, *Inorg. Chem.*, **12**, 1505 (1973).

(11) N. C. Payne, private communication.

(12) E. D. McKenzie, *Coord. Chem. Rev.*, **6**, 187 (1971).

(13) We have observed that the ascorbic acid reduction occurs "instantaneously" if the complexes are first allowed to hydrolyze, but at high Cl$^-$ concentrations the reduction is slow. This suggests that the ascorbic acid reduction may proceed via an aquo complex.

(14) D. S. Martin, M. A. Tucker, and A. J. Kassman, *Inorg. Chem.*, **4**, 1682 (1965); **5**, 1298 (1966); D. S. Martin, J. G. Foss, M. E. McCarville, M. A. Tucker, and A. J. Kassman, *ibid.*, **5**, 491 (1966).

(15) J. Chatt, G. A. Gamlen, and L. E. Orgel, *J. Chem. Soc.*, 486 (1958).

(16) B. Bosnich and J. MacB. Harrowfield, *J. Am. Chem. Soc.*, **94**, 3425 (1972).