

## References and Notes

- (1) To whom correspondence should be addressed.
- (2) G. W. A. Fowles in "Encyclopedia of Chemical Technology", Vol. 21, A. Standen, Ed., 2d ed, Interscience, New York, N.Y., 1970, p 175.
- (3) Gy. Varhegyi, *Nehezp. Musz. Egy., Miskolc, Idegennyelvu Kozl.*, **32**, 195 (1972); *Chem. Abstr.*, **78**, 164 730 (1973).
- (4)  $VCl_3$  cannot be recrystallized from solutions since it is soluble only in donor solvents with which it forms stable coordination compounds, nor can its solid-state texture be modified by sublimation because it decomposes to  $VCl_4$  and  $VCl_2$  (see ref 2).
- (5) H. D. Chanzy, J. F. Revol, R. H. Marchessault, and A. Lamandé, *Kolloid Z. Z. Polym.*, **251**, 563 (1973).
- (6) J. H. Simons and M. G. Powell, *J. Am. Chem. Soc.*, **67**, 75 (1945).
- (7) S. A. Shchukarev and D. V. Korol'kov, *Probl. Sovrem. Khim. Koord. Soedin.*, No. 2, 52 (1968); *Chem. Abstr.*, **70**, 51 280 (1969).
- (8) A. A. Krashennikova, A. A. Furman, and A. S. Kulyasova, *Zh. Neorg. Khim.*, **14**, 2019 (1969).
- (9) W. L. Jolly, *Adv. Chem. Ser.*, No. 80, 156 (1969).
- (10) V. Gutmann, *Monatsh. Chem.*, **86**, 765 (1955).
- (11) T. K. Ingraham, K. W. Downes, and P. Marier, *Can. J. Chem.*, **35**, 85 (1958).
- (12) R. C. Miller and R. J. Ayen, *Ind. Eng. Chem., Process Des. Dev.*, **8**, 370 (1969).

Contribution from the Department of Physical Chemistry,  
The Hebrew University of Jerusalem, Jerusalem, Israel

## Influence of Internal Hydrogen Bonding on the Kinetics of Complex Formation with Nickel(II)

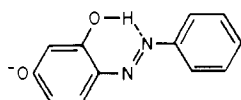
Berta Perlmutter-Hayman\* and Ruth Shinar

Received March 22, 1976

AIC60211M

We have recently become interested in the reactivity of internally hydrogen-bonded acids.<sup>1-3</sup> These substances are known to lose their proton to bases at rates far below the normal.<sup>4</sup> The rates are also abnormally low when such acids act as ligands to form labile complexes.<sup>5</sup> It seemed interesting to investigate the possible correlation between the strength of a given acid, its rate of proton loss to bases, and its rate of complex formation. For this purpose, we chose 4-(phenyl-azo)resorcinol, tropaeolin O (2,4-dihydroxy-4'-azobenzene-sulfonate), and 4-(*m*-nitrophenylazo)resorcinol, which had served in our previous investigations concerning the mechanism of proton loss.<sup>1,2</sup> Unfortunately, 4-(*p*-nitrophenylazo)resorcinol proved insufficiently soluble in the pH range suitable for the measurement of the complexation reaction.

Our substances differ from each other only in the meta or para substituent on the benzene ring and have in common the structure



The acid forms will be designated by HL, and the forms which have lost the last proton by L, omitting charges for the sake of brevity.

As cation we chose Ni(II) which has been the subject of many kinetic investigations (see, for instance, ref 5-7).

It would have been instructive to investigate also the reaction of the much more labile Cu(II), but experiments under the same conditions of pH and concentration cannot be carried out.<sup>8</sup>

## Experimental Section

**Materials.** 4-(Phenylazo)resorcinol and 4-(*m*-nitrophenylazo)resorcinol were from Eastman Organic Chemicals, the 4-(*p*-nitrophenylazo)resorcinol was from Eastman Kodak Co., and tropaeolin O was from BDH. These substances were purified as described by previous authors.<sup>9</sup> Nickel(II) was used in the form of  $Ni(NH_2)_2 \cdot 6H_2O$ , Baker Analyzed reagent. The concentration of the Ni(II)

stock solution was determined by adding excess EDTA and back-titrating with zinc sulfate solution, using EBT as indicator.

All measurements were carried out at 25 °C and at an ionic strength of 0.2 M, regulated by the addition of potassium nitrate.

**Static Measurements.** The pH was measured with a Radiometer PHM52 pH meter having an accuracy of  $\pm 0.005$  pH unit. It was again<sup>1</sup> assumed that  $pH = -\log [H^+] \gamma_{H^+}$ , with  $\gamma_{H^+} = 0.75$ , calculated from the Davies equation<sup>10</sup> for our ionic strength.

Spectrophotometric measurements were carried out with a Hilger-Gilford spectrophotometer.

**Kinetic Experiments.** All experiments were carried out by the T-jump method, using an apparatus equipped with a reference photomultiplier (Messanlagenstudienengesellschaft m.b.H., Göttingen).

Relaxation times were again evaluated with the aid of a simple mechanical device developed in our department.<sup>11</sup>

## Results

**Formation Constants.** From our kinetic results (see below) we conclude that the phenolic group is not the active site. Furthermore, we shall make the simplifying assumption<sup>8</sup>—derived essentially from kinetic evidence<sup>8,12-14</sup>—that the phenolic hydrogen has the same  $pK$  in the complex as it has in the free ligand. When considering the formation constants of the complexes we therefore write  $[HL_T]$  for  $[HL] + [H_2L]$ , with an analogous notation for the complexes.

The determinations were carried out spectrophotometrically. At constant pH, plots of  $b/(A - \bar{\epsilon}_{HL}b - \bar{\epsilon}_{Ni}a)$  as a function of  $1/a$  should be straight lines. [See, for instance, ref 16; here,  $a$  is the total concentration of the metal ion, and  $b$  is that of the ligand, with  $a \gg b$ ;  $A$  is the absorbance, and  $\bar{\epsilon}_{HL}$ ,  $\bar{\epsilon}_{Ni}$ ,  $\bar{\epsilon}_{NiHL}$ , and  $\bar{\epsilon}_{NiL}$  are apparent molar extinction coefficients. (For example,  $\bar{\epsilon}_{HL} = (\epsilon_{HL}[HL] + \epsilon_{H_2L}[H_2L])/b$ .) The first two of these quantities were determined experimentally at each wavelength employed. They depend on pH because of the changing protonation of the phenolic hydrogen and because  $NiOH^+$ , though present in very small concentration,<sup>15</sup> has a much higher extinction coefficient than has  $Ni^{2+}$ ]. For solutions in which  $b$  was  $3 \times 10^{-5}$  M and  $a$  was varied between  $1 \times 10^{-2}$  and  $5 \times 10^{-2}$  M, this was indeed found to be the case. In the pH range between 6.8 and 7.7 (regulated by the addition of small amounts of potassium hydroxide or nitric acid solution) the ratio between the intercept and the slope of these lines showed no trend with pH. This shows that our complex cannot be  $NiL_T$ , because this would require<sup>16</sup> this ratio to be inversely proportional to  $[H^+]$ . We conclude that the proton adjacent to the azo group is retained in the complex, and the above ratio is equal to

$$K_1 = [NiHL_T]/[Ni^{2+}][HL_T] \quad (1)$$

where  $[NiOH^+]$  is neglected in comparison with  $[Ni^{2+}]$ .

The results are shown in Table I, together with the acid dissociation constants for the last proton which we determined earlier.<sup>1,2</sup>

**Kinetic Results.** The value of  $b$  was kept constant at  $10^{-4}$  M and  $a$  was varied between  $4 \times 10^{-2}$  and  $7 \times 10^{-2}$  M. (At lower values of  $a$  the relaxation amplitude was too small for reliable results to be obtained, whereas at higher values  $Ni(OH)_2$  precipitated.) The reciprocal relaxation time  $1/\tau$  increased linearly with increasing  $a$ . Furthermore,  $1/\tau$  increased with increasing pH. A reaction scheme compatible with these findings is



The vertical reactions involve the phenolic hydrogen and the

**Table I.** Acid Dissociation Constants, and Equilibrium and Rate Constants, for the Formation of Ni(II) Complexes with Some Internally Hydrogen-Bonded Ligands

Substance	$10^{12}K_a, M$	$K_1, M$	$10^{-2}\vec{k}_{Ni}, M^{-1}s^{-1}$	$10^{-4}\vec{k}_{NiOH}, M^{-1}s^{-1}$	$\overleftarrow{k}_{Ni}, s^{-1}$	$10^{-8}\overleftarrow{k}_{NiOH}, M^{-1}s^{-1}$
4-(Phenylazo)resorcinol	1.0 <sup>b</sup>	17 ± 2	0.69 ± 0.10	9.21	4.12	2.75
Tropaeolin O	1.5 <sup>c</sup>	43 ± 3	1.45 ± 0.17	12.1	3.36	1.41
4-( <i>p</i> -Nitrophenylazo)resorcinol	2.0 <sup>b</sup>	50 ± 12				
4-( <i>m</i> -Nitrophenylazo)resorcinol	2.9 <sup>b</sup>	90 ± 11	2.67 ± 0.15	8.73	2.96	0.485

<sup>a</sup> The errors given are the standard deviations from the mean of results obtained at two to three values of pH and two to three different wavelengths at each pH. The mean value at different wavelengths and the same pH did not differ significantly from the mean value at different values of pH and the same wavelength. Furthermore, for each substance the standard deviations *within* a given pH did not differ significantly from those *between* different values of pH. <sup>b</sup> Reference 2;  $I = 0.1 M$ . <sup>c</sup> Reference 1;  $I = 0.1 M$ .

equilibrium between  $Ni^{2+}$  and  $NiOH^+$  and are very fast in comparison with the process we are studying. We therefore see only one relaxation time.

An additional reaction, namely, that between  $Ni^{2+}$  and L, would have exactly the same pH dependence as reaction 2a but can be ruled out because the concentration of L is at most  $10^{-5}$  times the total ligand concentration. For this reaction to contribute to the observed rate it would have to have a rate constant of  $\sim 10^7 M^{-1} s^{-1}$ , much higher than any value reported for  $Ni^{2+}$ .

Our assumption that the pK of the phenolic hydrogen in the complex is similar to that in the ligand leads to the further assumption that this hydrogen has little influence on the reaction rate. This is in accordance with previous findings<sup>8,12-14</sup> concerning negative charges far removed from the reaction site. Assuming the rate constants of reactions 1a and 1b and 2a and 2b, respectively, to be actually identical, we can write the reciprocal relaxation time<sup>17-19</sup>

$$1/\tau = (\vec{k}_{Ni} + \vec{k}_{NiOH}K_{NiOH}K_w/[H^+])B \quad (II)$$

where  $B$  is (to a very good approximation) given by

$$B = [Ni^{2+}] + 1/K_1 \quad (III)$$

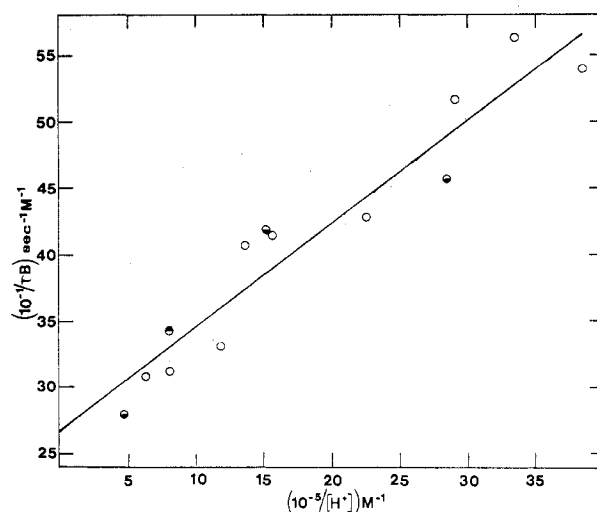
and  $K_{NiOH}$  is defined as  $[NiOH^+]/[OH^-][Ni^{2+}]$ . In a pH range of 5.7–6.7, regulated as before, plots of  $1/\tau B$  against  $1/[H^+]$  were straight lines. (An example is presented in Figure 1.) This shows the validity of eq II. In particular, the total absence of a term proportional to  $[H^+]$  corroborates our spectrophotometric result according to which a reaction  $Ni^{2+} + HL \rightleftharpoons NiL + H^+$  should take place to a negligibly small extent. The intercepts of these lines gives  $\vec{k}_{Ni}$ . From their slopes we calculate  $\vec{k}_{NiOH}$ , using<sup>15</sup>  $K_{NiOH} = 5 \times 10^4 M^{-1}$  and<sup>20</sup>  $K_w = 1.79 \times 10^{-14} M$ . The results are also shown in Table I, together with the rate constants for the reverse reactions, calculated from the formation constants.

## Discussion

**Influence of the Internal Hydrogen Bond.** According to the Eigen mechanism<sup>6</sup> the rate of complex formation is equal to  $K_{IP}$ , the formation constant of an outer-sphere ion pair, multiplied by  $k_w$ , the rate at which water from the inner coordination sphere changes places with the ligand. This mechanism has been found to be applicable to the reaction of  $Ni^{2+}$  with a variety of ligands (see, e.g., ref 5 and 7).

Our ligands are clearly among the exceptions. Even though we neglect the influence of negative charges which are far removed from the reaction site and therefore use the value of  $K_{IP}$  of 0.3 M which corresponds to an uncharged ligand<sup>7</sup> and even if we introduce an—often omitted—statistical factor<sup>21</sup> of 0.75 to obtain  $k_w$  from  $2.7 \times 10^4 s^{-1}$ ,<sup>22</sup> the rate of water exchange between inner shell and bulk water, we should expect  $\vec{k}_{Ni} \approx 6 \times 10^3 M^{-1} s^{-1}$ , higher than our values by a factor of 20–100.

This effect lies in the direction expected for ligands in which the reaction site is blocked by a proton,<sup>5,12-14,23,27</sup> especially



**Figure 1.** Dependence of  $1/\tau B$  on  $1/[H^+]$ , for Ni(II) and 4-(*m*-nitrophenylazo)resorcinol:  $\circ$ ,  $a = 6 \times 10^{-2} M$ ;  $\bullet$ ,  $a = 5 \times 10^{-2} M$ ;  $\bullet$ ,  $a = 4 \times 10^{-2} M$ .

when the proton has formed an internal hydrogen bond. (This, together with the pH effect, excludes the phenolic group as the reactive site.)

Just as in the case of proton transfer to bases, we see, in principle, two mechanisms which can explain the low values of  $k_{Ni}$ . In the first of these,  $Ni^{2+}$  reacts by the Eigen mechanism<sup>6</sup> but only with *that* fraction of  $HL_T$ —let us call it again<sup>1-3</sup>  $HL^*$ —in which the internal hydrogen bond has been broken. For this mechanism to be operative, the equilibrium between  $HL^*$  and  $HL$  has to be rapid in comparison with the observed rate. The rate constants we have found previously<sup>1,2</sup> show that this condition is fulfilled in the present case—in contradistinction with the much faster reaction of proton transfer to hydroxyl ions.<sup>1,2</sup> However, for alizarin yellow G we estimated<sup>3</sup> that  $[HL^*_T]/[HL_T]$  is  $\sim 3 \times 10^{-3}$ ; for our present ligands we should expect the ratio to be even lower. Therefore, this mechanism predicts  $\vec{k}_{Ni}$  to be lowered even more drastically than we have found.

We conclude that the pathway via  $HL^*$  makes only a small contribution to the observed rate, and the reaction takes place mainly via a second mechanism: attack on the blocked binding site by  $Ni^{2+}$ , either after the ion pair has been formed or by a concerted mechanism. Not surprisingly, in this attack  $Ni^{2+}$  is less efficient than are even weak bases. (For example,<sup>3</sup> the rate constant between tropaeolin O and triethanolamine is  $\sim 10^3 M^{-1} s^{-1}$ .)

Our spectrophotometric and kinetic results concur in showing that the last proton is retained in the complexes. This is somewhat unusual, but not without precedent.<sup>8,14,28,29</sup> In the present case, again, it is not surprising that at a pH  $\sim 5$  units below the pK, the metal ion should be unable to dislodge the proton. At higher values of pH, much stronger, chelate, complexes may well be formed. We cannot investigate the

kinetics of their formation, because nickel(II) hydroxide would precipitate.

**Comparison between the Three Ligands.** We see from Table I that  $\bar{k}_{\text{Ni}}$  increases with increasing acid strength of the ligand. This trend is in the expected direction, since it is reasonable to assume that the stronger the acid, the weaker the internal hydrogen bond.

On the other hand, the values of  $\bar{k}_{\text{Ni}}$  differ only little from each other, whereas usually it is the rate of dissociation that is characteristic for the ligand<sup>6</sup> and thus determines the strength of the complex. In the present case, the opposite is true, and we get the somewhat unusual situation<sup>30</sup> where the formation constant is higher the stronger the acid.

**Reaction between NiOH<sup>+</sup> and Ligands.** Table I shows that  $\bar{k}_{\text{NiOH}}$  is much higher than  $\bar{k}_{\text{Ni}}$  and is almost uninfluenced by the acid strength of the ligand.

The reaction via HL\* can be ruled out on the same grounds as before; it would require the rate constant for NiOH<sup>+</sup> to be several powers of 10 above the "normal" value for Ni<sup>2+</sup>. There is no corroborating evidence for such a behavior. To our knowledge, the only paper where a kinetic influence of NiOH<sup>+</sup> is reported at all is that by Funahashi and Tanaka<sup>13</sup> which pertains to 4-(2-pyridylazo)resorcinol. There,  $\bar{k}_{\text{NiOH}}$  is higher than  $\bar{k}_{\text{Ni}}$  by a factor of not much more than 4. The authors ascribe the enhanced reactivity of NiOH<sup>+</sup> to the influence of OH<sup>-</sup> on the rate of water loss from the inner hydration sphere, an effect which has been found to be very pronounced<sup>6</sup> in ions of the type of Fe(III).

We believe that, in the present case, the explanation must lie elsewhere; if the "normal" value of  $\bar{k}_{\text{NiOH}}$  were really above that of  $\bar{k}_{\text{Ni}}$ , the contribution of NiOH<sup>+</sup> to the observed rate of complexation should have made itself felt in other investigations carried out in a pH range similar to, or higher than, ours (see, e.g., ref 28). We suggest that it is only in those cases where the reaction site is blocked by a proton (internally hydrogen bonded or not; Funahashi and Tanaka concluded that there is little effect of hydrogen bonding in their case) that the reactivity of NiOH<sup>+</sup> exceeds that of the unhydrolyzed Ni<sup>2+</sup>. The basic properties of the former substance will enable it to assist in the breakage of the hydrogen bond or in the total displacement of the proton. This would explain why the reactivity of NiOH<sup>+</sup> has so far almost universally escaped notice. As we have already noted, its reaction with a protonated ligand HL has the same pH dependence as that of Ni<sup>2+</sup> with L<sup>-</sup>. Except when HL is an extremely weak acid—such as the ligands employed in this work—the latter reaction path is dominant and may completely mask the contribution of NiOH<sup>+</sup>.

**Registry No.** 4-(Phenylazo)resorcinol, 2051-85-6; tropaeolin O acid, 2050-34-2; 4-(*p*-nitrophenylazo)resorcinol, 74-39-5; 4-(*m*-nitrophenylazo)resorcinol, 2243-74-5; Ni<sup>2+</sup>, 14701-22-5.

## References and Notes

- (1) B. Perlmutter-Hayman and R. Shinar, *Int. J. Chem. Kinet.*, **7**, 453, 798 (1975).
- (2) B. Perlmutter-Hayman, R. Sarfaty, and R. Shinar, *Int. J. Chem. Kinet.*, in press.
- (3) B. Perlmutter-Hayman and R. Shinar, *Int. J. Chem. Kinet.*, in press.
- (4) M. Eigen, *Angew. Chem.*, **75**, 489 (1963); *Angew. Chem., Int. Ed. Engl.*, **3**, 1 (1964).
- (5) R. G. Wilkins, *Acc. Chem. Res.*, **3**, 408 (1970).
- (6) M. Eigen and G. Wilkins, *Adv. Chem. Ser.*, No. **49**, 55 (1965).
- (7) K. Kustin and J. Swinehart, *Prog. Inorg. Chem.*, **13**, 107 (1970).
- (8) B. Perlmutter-Hayman and R. Shinar, *Isr. J. Chem.*, in press.
- (9) M. C. Rose and J. E. Stuehr, *J. Am. Chem. Soc.*, **93**, 4350 (1971).
- (10) C. W. Davies, "Ion Association", Butterworths, London, 1962, p 41.
- (11) H. J. G. Hayman, *Isr. J. Chem.*, **8**, 603 (1970).
- (12) J. C. Cassatt and R. G. Wilkins, *J. Am. Chem. Soc.*, **90**, 6045 (1968).
- (13) S. Funahashi and M. Tanaka, *Inorg. Chem.*, **8**, 2159 (1969).
- (14) W. A. Johnson and R. G. Wilkins, *Inorg. Chem.*, **9**, 1917 (1970).
- (15) L. G. Sillen and A. E. Martell, *Chem. Soc., Spec. Publ.*, No. **17** (1964); No. **25** (1971).
- (16) R. Koren, B. Perlmutter-Hayman, and R. Shinar, *Int. J. Chem. Kinet.*, **6**, 39 (1974).

- (17) F. P. Cavasino, *Ric. Sci., Parte 2: Sez. A*, **8**, 1120 (1965).
- (18) F. P. Cavasino, *J. Phys. Chem.*, **69**, 4380 (1965).
- (19) B. Perlmutter-Hayman, *Adv. Mol. Relaxation Processes*, in press.
- (20) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions", 2d ed, Reinhold, New York, N.Y., 1950, p 485.
- (21) J. Neely and R. Connick, *J. Am. Chem. Soc.*, **92**, 3476 (1970).
- (22) T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962); see also R. E. Connick and D. Fiat, *ibid.*, **44**, 4103 (1966).
- (23) T. S. Turan and D. B. Rorabacher, *Inorg. Chem.*, **11**, 288 (1972).
- (24) J. C. Cassatt, W. A. Johnson, L. M. Smith, and R. G. Wilkins, *J. Am. Chem. Soc.*, **94**, 8399 (1972).
- (25) B. Perlmutter-Hayman and F. Secco, *Isr. J. Chem.*, **11**, 623 (1973).
- (26) T. S. Roche and R. G. Wilkins, *J. Am. Chem. Soc.*, **96**, 5082 (1974).
- (27) R. W. Taylor, H. K. Stepien, and D. B. Rorabacher, *Inorg. Chem.*, **13**, 1282 (1974).
- (28) D. W. Margerum, D. B. Rorabacher, and J. F. G. Clarke, Jr., *Inorg. Chem.*, **2**, 667 (1963).
- (29) P. H. Tedesco and J. A. Gonzalez Quintana, *J. Inorg. Nucl. Chem.*, **37**, 1798 (1975).
- (30) F. P. Cavasino and E. diDio, *J. Chem. Soc. A*, 1151 (1970).

Contribution from the Department of Chemistry,  
University of Manchester Institute of Science and Technology,  
Manchester M60 1QD, England

## Platinum(II) Thiocyanate Complexes of Some Bidentate Group 5B Donor Ligands

R. J. Dickinson, W. Levason, C. A. McAuliffe,\*  
and R. V. Parish\*

Received July 22, 1975

AIC50529Z

The thiocyanate ion is one of the most intensively studied ambidentate ligands,<sup>1</sup> but in spite of this a comprehensive explanation of the effects of neutral ligands on the nature of the M-CNS bond is still not possible (-CNS, coordination atom unspecified; -NCS, N bonded; -SCN, S bonded). Palladium(II) thiocyanate complexes of bidentate group 5B donor ligands have been thoroughly investigated,<sup>2-7</sup> and the type of thiocyanate coordination has been shown to depend both upon the ligand backbone "bite" and the nature of the group 5B donor atoms. Platinum(II) complexes have received less attention, but, since the covalent radii of Pd(II) and Pt(II) are the same (1.31 Å),<sup>8</sup> on steric grounds alone the same ligand should promote identical thiocyanate coordination to both metals. We have recently shown<sup>5,6</sup> that in the cases of (*o*-diphenylphosphinophenyl)diphenylstibine, *o*-C<sub>6</sub>H<sub>4</sub>(PPh<sub>2</sub>)-(SbPh<sub>2</sub>) (sbp), and *o*-phenylenebis(diphenylarsine), *o*-C<sub>6</sub>H<sub>4</sub>(AsPh<sub>2</sub>)<sub>2</sub> (aa), the palladium(II) complexes are of the type PdL(NCS)(SCN), but the platinum analogues are PtL(SCN)<sub>2</sub>. Here we report the results of a study of the platinum(II) complexes of group 5B donor bidentates with ethylene and alkane backbones.

## Experimental Section

Physical measurements were made as described previously.<sup>5</sup> The following ligands were prepared by literature methods: bis(diphenylphosphino)methane (dpm),<sup>9</sup> 1,2-bis(diphenylphosphino)ethane (dpe),<sup>9</sup> 1,3-bis(diphenylphosphino)propane (dpp),<sup>10</sup> *cis*-1,2-bis(diphenylphosphino)ethylene (vpp),<sup>11</sup> 1,2-bis(diphenylarsino)ethane (dae),<sup>12</sup> *cis*-1,2-bis(diphenylarsino)ethylene (vaa),<sup>13</sup> 1-diphenylarsino-2-diphenylphosphinoethane (pae),<sup>14</sup> *cis*-1-diphenylarsino-2-diphenylphosphinoethylene (vpa).<sup>14</sup>

**Pt(dpe)(NCS)(SCN).** Sodium tetrachloroplatinate(II) (0.38 g, 1 mmol) and potassium thiocyanate (0.5 g, ~5 mmol) were stirred together in aqueous solution (20 cm<sup>3</sup>) for 3 h. A solution of dpe (0.396 g, 1 mmol) in dichloromethane (10 cm<sup>3</sup>) was added, followed by sufficient ethanol to produce a homogeneous solution, and the mixture was refluxed for 1 h. The solution was evaporated to dryness, and