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Nickel(II) Bis(phosphine) Complexes

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The synthesis, characterization, disproportionation, and dynamic ligand-exchange reactions of the complexes $[\mathrm{Ni^{II}(P\text{-}P)X_2}]$, where P-P is dppe,[1] dppey and X = Cl, Br, I, and $[\mathrm{Ni^{II}(P\text{-}P)_2}]\mathrm{X_2}$, where X = I or NO_3, are reported. For $[\mathrm{Ni^{II}(P\text{-}P)X_2}]$ the halide affinity in chloroform was determined to be Cl > Br > I by ^{31}P NMR spectroscopy, and dppey complexes were more stable than dppe complexes. Chloride and bromide ions displace P-P from $[\mathrm{Ni^{II}(P\text{-}P)_2}]^{2+}$. Disproportionation reactions, $2[\mathrm{Ni(dppe)X_2}] \rightleftharpoons [\mathrm{Ni(dppe)_2}]\mathrm{X} + \mathrm{NiX_2}$, occurred readily in methanol and less so in chloroform, followed by phosphine oxidation. In chloroform, ligand-exchange rates for the association of dppe with $[\mathrm{Ni(dppe)Br_2}]$ (4×10^4 $\mathrm{M^{-1}\ s^{-1}}$) and dppey with $[\mathrm{Ni(dppey)Br_2}]$ (10^2 $\mathrm{M^{-1}\ s^{-1}}$) were rapid. Large shielding anisotropies ($\Delta\sigma$) of up to 159 ppm were observed in solid-state ^{31}P NMR spectra and invoked to explain changes in the ^{31}P NMR spin–lattice relaxation times on complex formation by bis(phosphine) ligands. These findings are of importance for the testing and antitumor activity of Ni(II) bis(phosphine) complexes.

Introduction

Current medical interest in metal phosphine complexes ranges from the clinical use of a triethylgold(I) complex, auranofin ("Ridaura"), as an antiarthritic agent,[2,3] through the investigation of positively charged technetium complexes as heart-imaging agents,[4] to the anticancer activity of certain phosphine complexes.[5-13]

Although auranofin is potently cytotoxic to tumor cells in culture,[14] it is active only against one tumor model in vivo.[7] Bridged bis(phosphine) complexes such as XAu(dppe)AuX (X = e.g. Cl) containing linearly coordinated gold(I) exhibit a wider spectrum of activity[9] but are readily converted into four-coordinate tetrahedral gold(I) complexes by thiols and in blood plasma.[15] Tetrahedral complexes such as $[\mathrm{Au(dppe)_2}]\mathrm{Cl}$ are less reactive toward thiols and also exhibit a broad spectrum of antitumor activity.[10] The mechanism of action appears to differ from that of cisplatin. The latter cross-links intrastrand guanine bases on DNA,[16] whereas the tetrahedral gold(I) dppe complex cross-links proteins to DNA.[17] The complex $[\mathrm{Au(dppe)_2}]\mathrm{Cl}$ does not lose activity against a subline of P388 leukemia, which is resistant to cisplatin, and moreover, $[\mathrm{Au(dppe)_2}]\mathrm{Cl}$ and cisplain can be administered concurrently at their respective maximum-tolerated doses to tumor-bearing mice with no lethality. The combination is more effective against moderately advanced P388 leukemia than cisplatin alone.[10] These results indicate that the mechanism or site of action of the bis(phosphine) complex is different from that of cisplatin.

The recent work of Hoke et al.[18] suggests that the lipophilic cation $[\mathrm{Au(dppe)_2}]^+$ and related complexes belong to a novel class of inhibitors of mitochondrial function. The complex causes a rapid, dose-related collapse of the inner mitochondrial membrane potential accompanied by an efflux of calcium. It is very effective in depleting cellular ATP levels.[19] These reactions may give rise to some of the toxic side effects of the complex.

In our attempts to design more effective bis(diphosphine) complexes we have assumed that Au(I) acts as a carrier for the reactive bis(diphosphine) ligand and therefore some kinetic lability in the metal–phosphine bonds is required for activity.[12,13] Thus, tetrahedral bis(phosphine) complexes of Cu(I) and Ag(I) are also active antitumor agents.[11,20] In contrast, the complexes $[\mathrm{M(dppe)Cl_2}]$ of the group 10 metal ions M = Pd(II) and Pt(II) are inactive.[9] However, Ni(II) complexes are known to be more kinetically labile and therefore it seemed likely that Ni(II) bis(phosphine) complexes might exhibit antitumor activity.

Although the syntheses of several mono- and bischelated complexes had been reported[21-27] there seemed to be few data on their stability and ligand-exchange rates in solution. As necessary preliminary work prior to antitumor testing, which will be reported elsewhere, we have therefore studied the solid-state and solution chemistry of Ni(II) bis(phosphine) complexes by conductivity, magnetic susceptibility, infrared spectroscopy, electronic ab-

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(1) Abbreviations: CPMAS, cross polarization magic angle spinning; depe, 1,2-bis(diethylphosphino)ethane ($\mathrm{Et_2PCH_2CH_2PEt_2}$); eppe, 1-(diethylphosphino)-2-(diphenylphosphino)ethane ($\mathrm{Et_2PCH_2CH_2PPh_2}$); dppe, 1,2-bis(diphenylphosphino)ethane ($\mathrm{Ph_2PCH_2CH_2PPh_2}$); dppey, *cis*-1,2-bis(diphenylphosphino)ethylene ($\mathrm{Ph_2PCH{=}CHPPh_2}$).

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sorption, and NMR spectroscopic measurements.

Experimental Section

Solid-State NMR Spectroscopy. Solid-state ^{31}P NMR spectra were recorded by Dr. C. Groombridge of the University of London Intercollegiate Research Service on a Bruker MSL-300 at 121.5 MHz with high-power proton-decoupling, cross polarization from protons and magic angle spinning (CPMAS). Samples (0.1–0.3 g) were packed into an aluminum oxide double air-bearing rotor (6.95 mm o.d.) for spinning at 4.4–4.6 kHz. Contact times were 10 ms, except for that of $[Ni(dppe)_2](NO_3)_2$, which was 1 ms, pulse cycle repetition times were 10–30 s, and receiver dead times were 10–25 μs. The reference was H_3PO_4 (external). Spectra were analyzed to obtain the principal components of the shielding tensors by using the theory of Maricq and Waugh.[28] The components were calculated from the measured peak intensities by using the program TENSOR written by Dr. C. Groombridge. Estimates of errors were obtained by varying the intensity values by amounts equal to the baseline noise.

Solution NMR Spectroscopy. ^1H NMR spectra were recorded on a JEOL FX200 spectrometer at 199.5 MHz using 5-mm tubes, 2-kHz frequency width, 60–65° pulses, 4-s acquisition time, 2-s pulse delay, and 16k data points. The internal reference was TMS. $^{31}P\{^1H\}$ NMR spectra were recorded on either JEOL FX60, Bruker WM200, or Bruker AM500 instruments at 24.15, 81.00, or 202.4 MHz, in 8 or 10, 15, or 5-mm tubes, respectively. Typically, pulse widths were 45–90°, pulse delays 2.2–2.5 s, sweep widths 4–50 kHz, and acquisition times 0.02–1.6 s, and there were 8–16k data points. The shift reference was 85% H_3PO_4 (external, with a $CDCl_3$ or D_2O lock as appropriate for the compounds).

T_1 values were measured by using the inversion-recovery method with ^1H decoupling. The samples were not degassed, and Teflon plugs were used to limit vortexing. Peak heights were used for the logarithmic plots.

Magnetization Transfer. Measurements of exchange rates by magnetization transfer were carried out on a Bruker WM200 at 81 MHz. A typical sample contained $[Ni(dppe)Br_2]$ (12.3 mg, 20 μmol) and dppe (8.0 mg, 20 μmol) in ca. 5 mL of $CHCl_3$–$CDCl_3$ (1:1 v/v). Exact volumes were determined by weighing, and the NMR tube was sealed by plastic film to minimize evaporation losses.

Selective peak excitation was achieved by using a DANTE sequence:[29] $D1-(P1-D2)_n$ with the transmitter offset set to the frequency of the resonance to be inverted. The parameters were chosen, and the selectivity was checked by using $D1-(P1-D2)_{21}$–Acq with P1 adjusted such that $(P1-D2)_{21}$ resulted in a 90° pulse. This was increased to 180° and a hard pulse added to give $D1-(P1-D2)_{21}$–VD–90°–Acq. The time interval D1 was chosen to allow complete recovery of all magnetization, and D2 was sufficiently short that transmitter sidebands at 1/D2 lay outside the spectrum. VD is the variable delay or mixing time. Typical values used for Ni(II)–dppe systems were as follows: D1, 8 s; P1, 2.2 μs; D2, 100 μs; VD, 1–5 ms and 8 s. The approximate selectivity of the DANTE sequence was therefore $[n(P1 + D2)]^{-1}$ = 466 Hz. For $[Ni(dppey)Br_2]$–dppey, the relaxation delay was 14 s and the mixing times were extended up to 0.5 s.

Integrations or weighings of peaks enabled the equilibrium proportions of each species to be calculated and hence the equilibrium constants. The absolute quantities and the peak heights in the fully relaxed spectra were used to scale the other spectra in the set, and the magnetizations were expressed in micromole equivalents. From plots of magnetization against VD, the rates of change of magnetization were obtained for substitution into eqs 12–14 in the Appendix.

UV–Visible and IR Spectroscopy. UV–visible absorption spectra were recorded on a Perkin-Elmer 554 or Lambda 3 instrument using 1 cm path-length cells at ambient temperature. IR spectra were recorded on a Perkin-Elmer 597 instrument. Samples were in Nujol and placed between NaCl (4000–500 cm^{-1}) or CsI (to 250 cm^{-1}) plates.

Melting Points. These were measured on an Olympus CH microscope and a Mettler FP82 hot stage calibrated with phenacetin or a Kofler hot stage (Reichart).

Microanalyses. Elemental analyses were carried out by the Microanalysis Unit, Department of Chemistry, University College, London.

Conductivity. Conductivities on 1 mM solutions at 25 °C were measured by using a Griffin bridge with Chandos electrodes. Known salts and bis(phosphine) ligands were measured as references.

Magnetic Susceptibilities. These were measured by using a JME magnetic susceptibility balance and $Hg[Co(SCN)_4]$ as calibrant.[30] Diamagnetic corrections for the phosphine ligands were measured, and those for Ni(II) and halides were taken from Figgis and Lewis.[31]

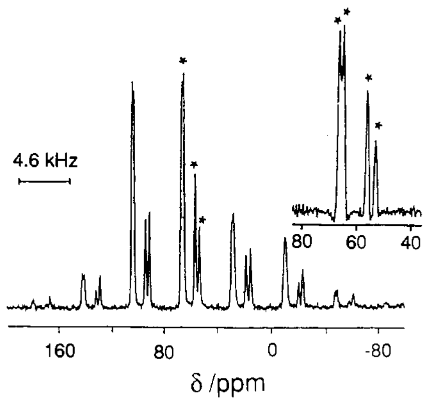

Figure 1. Solid-state CPMAS $^{31}P\{^1H\}$ NMR spectrum of $[Ni(dppe)Cl_2]$, showing the center bands (asterisks), sidebands, and sample rotation rate (4.6 kHz). The insert was resolution-enhanced.

Syntheses. The complexes $[Ni(P-P)X_2]$ and $[Ni(P-P)_2]X_2$ were prepared by using published procedures,[21–27] except that an N_2 atmosphere was not used for dppe and dppey, which are both relatively stable in air. Previous reports have rarely included mp's. The complexes are all soluble in polar solvents such as chloroform, acetone, dimethylacetamide, and acetonitrile, slightly soluble in methanol and ethanol, but insoluble in water and nonpolar organic solvents (e.g. toluene, cyclohexane). A table of elemental analyses, yields, colors, and melting points has been deposited as supplementary material (Table D1).

$[Ni(dppe)X_2]$ (X = Cl, Br, I). These were made by the method of Booth and Chatt[24] and recrystallized from $CHCl_3$ or alcoholic $CHCl_3$.

$[Ni(dppe)_2]X_2$ (X = Br, I, NO_3). These were made by a method similar to that of Chatt et al.,[23] except that dppe was dissolved in EtOH prior to the addition of the dissolved metal salt. For X = Br a better yield was obtained with dppe in excess. The complexes were recrystallized from EtOH–H_2O.

$[Ni(dppey)X_2]$ (X = Cl, Br, I). These were made by the method of McAuliffe and Meek,[26] except that the reactions were stirred for only 10 min and hydrated metal salts were used. The complexes were recrystallized from EtOH–$CHCl_3$.

$[Ni(eppe)X_2]$ (X = Cl, Br) and $[Ni(depe)Br_2]$. The metal salts were dissolved in EtOH, and after N_2 bubbling (>15 min), the liquid phosphine was added either by direct methods (eppe) or in solution with $CHCl_3$ (depe). The color formed immediately, and after stirring for ca. 10 min under N_2, the solution was concentrated under reduced pressure and the precipitate collected by filtration.

Oxidized Phosphines. Dppe and dppey were oxidized by the method of Slinkard and Meek.[32] $DepeO_2$ and $eppeO_2$ were prepared by dissolving the liquid phosphines in toluene and heating at 80 °C with a slight excess of H_2O_2. The aqueous layer was separated and freeze-dried to give viscous products.

Results

Syntheses. The monochelated complexes $[Ni(P-P)X_2]$ (P-P = dppe, dppey; X = Cl, Br, I) were easily made. $[Ni(dppe)(NO_3)_2]$ could not be prepared, and the bis complex was isolated instead. Of the bis complexes, the nitrate formed the most readily, indicative of the weakness of NO_3^- coordination compared with the halides. $[Ni(dppe)_2]Cl_2$ could not be isolated, as has been found previously,[21] suggesting that Cl^- displaces bound phosphine.

Solid-State Studies. Magnetic Measurements. The magnetic moments of the complexes $[Ni(dppe)X_2]$ (X = Cl, Br, I), $[Ni(dppe)_2]X_2$ (X = Br, I, NO_3), and $[Ni(dppey)X_2]$ (X = Cl, Br) (Table D2, supplementary material) were within the range 0.35–0.83 μ_B (lit. 0.3–0.6 μ_B)[22,26] ascribable to temperature-independent paramagnetism in predominantly square-planar complexes.

Infrared Spectroscopy. The spectra of $[Ni(dppe)X_2]$ (X = Cl, Br, I) contained many bands in the region 400–4000 cm^{-1} and were very similar to each other and also to dppe. The positions of the bands in the region 250–400 cm^{-1} are listed in the supplementary material, Table D3. The spectra of $[Ni(dppe)_2]X_2$

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Table I. Solid-State CPMAS $^{31}P\{^1H\}$ NMR Data for dppe and Ni(II) Bis(phosphine) Complexes at 121.5 MHz[a]

compd	σ_{av}/ppm	σ_{11}/ppm	σ_{22}/ppm	σ_{33}/ppm	$\Delta\nu_{1/2}$/Hz	$\Delta\sigma^d$/ppm
dppe	−12.3	*b*	*b*	*b*	100 ± 10	*b*
$[Ni(dppe)Cl_2]$	53.1	−51 ± 3	54 ± 1	156 ± 3	150 ± 40	155
	56.2	−29 ± 4	64 ± 3	134 ± 3	190 ± 40	117
	65.1	−31 ± 2	86 ± 2	140 ± 3	370 ± 40	113
	66.5	−31 ± 2	92 ± 2	138 ± 3		
$[Ni(dppe)Br_2]^c$	66.6	*b*	*b*	*b*	670 ± 40	*b*
	63.9	*b*	*b*	*b*		
$[Ni(dppe)I_2]$	75.5	−31 ± 1	93 ± 1	165 ± 2	250 ± 50	134
	82.5	−30 ± 1	86 ± 1	192 ± 1	200 ± 50	136
$[Ni(dppe)_2](NO_3)_2$	55.4	−22 ± 3	57 ± 1	132 ± 2	1000 ± 100	97
$[Ni(dppey)Cl_2]$	69.7	−42 ± 3	94 ± 7	157 ± 4	410 ± 70	131
	71.1	−39 ± 3	89 ± 7	163 ± 4		138
$[Ni(dppey)Br_2]$	72.2	−43 ± 3	82 ± 6	178 ± 4	610 ± 70	159

[a] The chemical shifts (σ_{av} in ppm relative to H_3PO_4) were measured directly, and tensor components were calculated by the method of Maricq and Waugh.[28] These are quoted according to the convention $\sigma_{33} > \sigma_{22} > \sigma_{11}$ in the chemical shift sense. The $\Delta\nu_{1/2}$ values are line widths. [b] Not calculated. [c] Resolution enhanced. [d] $\Delta\sigma = \sigma_{33} - {}^1/_2(\sigma_{22} + \sigma_{11})$.

(X = Br, I, NO_3) have fewer bands and are virtually identical with one another except for the bands at 830, 1041, and 1300–1390 cm^{-1} (overlapping with Nujol) in the nitrate complex. These were assigned as the A_2'', A_1', and E′ vibrations of NO_3^- in D_{3h} symmetry. The A_1' vibration is usually only Raman active but has been previously observed in liquid samples and ascribed to ion pairing.[33]

NMR Spectroscopy. The solid-state $^{31}P\{^1H\}$ CPMAS NMR spectrum of a representative Ni(II) bis(phosphine) complex is shown in Figure 1. From the intensity profiles of the spinning sidebands, it can be seen that the shielding in the complexes is of noncubic, nonaxial symmetry with three principal shift components. The isotropic chemical shifts (σ_{iso}), the principal components of the shielding tensor (σ_{11}, σ_{22}, σ_{33}), and $\Delta\sigma$ (=$\sigma_{33} - {}^1/_2(\sigma_{22} + \sigma_{11})$) are listed in Table I. The chemical shift anisotropy ($\Delta\sigma$) is much less for dppe, as reported previously,[34] and too few spinning sidebands were seen under the conditions used for the shift components to be calculated.

There are four bands in the solid-state spectrum of the chloride complex $[Ni(dppe)Cl_2]$ (Figure 1) whereas the analogous bromide and iodide complexes exhibit only two. A significant amount of $dppeO_2$ was detected in the spectrum of $[Ni(dppe)_2](NO_3)_2$, which took a long time to acquire (2884 scans compared to 16–256 for the other spectra), perhaps because the proton T_1's are long. The shift is almost identical with the solution value. $[Ni(dppey)Cl_2]$ had two solid-state resonances at 69.7 and 71.1 ppm, downfield of the shift in $CHCl_3$ (64.9 ppm). The average shift of $[Ni(dppey)Br_2]$, 72.2 ppm, is close to that in solution (74.0 ppm).

Solution Studies. Electronic Absorption Spectra. The absorption band positions (supplementary material, Table D4) for $CHCl_3$ solutions of the complexes $[Ni(dppe)X_2]$ (X = Cl, Br, I) and $[Ni(dppe)_2]X_2$ (X = Br, I) agree with those reported previously[21,35] for dichloromethane and nitroethane solutions. The monochelated complexes have been assigned a planar structure and the band at ca. 21 000 cm^{-1} assigned to the $^1A_1 \rightarrow {}^1B_2$ transition, with charge-transfer bands at higher energy.

The data for the dppey mono chelates agree with those of McAuliffe and Meek[26] in dichloromethane. The energies of the band maxima of both series $[Ni(dppe)X_2]$ and $[Ni(dppey)X_2]$ (X = Cl, Br, I) follow the spectrochemical series, decreasing in the order Cl > Br > I.

Data for the absorption spectra of $[Ni(dppe)X_2]$ (X = Cl, Br, I) and $[Ni(dppe)_2]X_2$ (X = Br, I NO_3) in methanol solutions are given in the supplementary material, Table D5. The most striking feature of these spectra is their similarity (major bands at ca. 230, 300, 330, and 415 nm). Initially, all solutions were pale yellow, which faded perceptibility with time, and all except $[Ni(dppe)_2]Br_2$ appeared colorless within 24 h at ambient temperature. The shoulder at ca. 415 nm may be the $^3A_{1g} \rightarrow {}^3T_{1g}(P)$ transition of aqua- or methanol-coordinated Ni(II).[36] The spectra of free ligands and their oxides were not easily distinguished, so the spectra after 24 h cannot be unambiguously assigned.

Table II. ^{31}P T_1 Data for Bis(phosphines), Bis(phosphine) Oxides, and Ni(II) Bis(phosphine) Complexes at 81 MHz, 300 ± 2 K, in $CDCl_3$–$CHCl_3$ (1:1)

compd	concn/ mM	T_1/s	compd	concn/ mM	T_1/s
dppe	9.7	8.6	dppey	5.2	20
	10.0	9.2		10.6	17
$dppeO_2$	2.4	5.0	$dppeyO_2$	1.9	7
$[Ni(dppe)Cl_2]$	10.0	0.51	$[Ni(dppey)Cl_2]$	2.1	2.8
	10.0	0.49		2.1	2.9
$[Ni(dppe)Br_2]$	6.6	0.21	$[Ni(dppey)Br_2]$	0.5	1.3
	8.7	0.15		1.7	1.7
	11.3	0.14	$[Ni(dppey)I_2]$	1.2	4.1
$[Ni(dppe)I_2]$	4.9	1.4		2.1	4.0
$[Ni(dppe)_2](NO_3)_2$	1.1	1.5			
	0.96	1.5			

Conductivity. Conductivities in acetonitrile solutions are given in the supplementary material, Table D6. $[Ni(dppe)Cl_2]$ is a nonconductor, as was shown previously for $[Ni(dppe)X_2]$ (X = Cl, Br, I) in nitrobenzene;[24] in contrast, the dibromo and diiodo complexes show much greater dissociation in acetonitrile, the latter approaching a 1:1 electrolyte after 1 day. $[Ni(dppe)_2]I_2$ is a 1:1 electrolyte in acetonitrile. The conductivities of the complexes $[Ni(dppe)_2]X_2$ (X = Br, I) have been reported to be less than for 1:1 electrolytes in nitrobenzene[24] and nitroethane;[35] in nitromethane, they are 1:1 eletrolytes.[22] Simple dissociation of one dppe ligand from the bischelated complex[21] would not account for the observed conductivities although formation of a five-coordinate complex[35] would. However, McAuliffe and Meek[26] failed to isolate $[Ni(dppe)_2X]^+$ from a variety of solvents, and there was no evidence for such species in our ^{31}P NMR spectra. $[Ni(dppe)_2](NO_3)_2$ behaved as a 1:2 electrolyte in acetonitrile as it does in nitroethane.[35] Conductivities of both dppe and dppey complexes increased in the order Cl < Br < I, the order of the rates of dissociation. The low conductivities of $[Ni(dppey)X_2]$ (X = Cl, Br, I) in acetonitrile agree with earlier measurements in nitromethane.[26] In methanol, $[Ni(dppe)Cl_2]$ was a 1:2 electrolyte consistent with the formation of $[Ni(dppe)_2]Cl_2$ and $NiCl_2$.

NMR Spectroscopy. The range of ^1H chemical shifts showed that all the complexes were diamagnetic in chloroform. ^{31}P T_1 values are listed in Table II; errors were estimated as ±5%, and ^{31}P chemical shifts are listed in Table V.

Halide Competition. These reactions were studied by ^{31}P NMR spectroscopy by adding the appropriate tetraethylammonium halide to a solution of the dppe or dppey complex $[Ni(P\text{-}P)X_2]$ in $CDCl_3$. For some samples, peaks were broadened at 81 MHz,

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Table III. $^{31}P\{^1H\}$ NMR Chemical Shifts (δ) and Coupling Constants (J) of Species Observed in Titrations and Mixed Solutions of Ni(II) Bis(phosphines)

compd	δ	J_{PP}/Hz
[Ni(dppe)ClBr]	63.1	64
	61.1	
[Ni(dppe)BrI]	72.4	48
	71.6	
[Ni(dppe)ClI]	67.3	60
	66.7	
[Ni(dppey)ClBr]	71.1	50
	68.0	
[Ni(dppey)BrI]	80.8	36
	80.3	
[Ni(dppey)ClI]	77.3	41
	73.6	
$[Ni(dppey)_2X]^+$		
X = Cl	56.4	
X = Br	53.2	
X = I	45.5	
$[Ni(dppey)(dppe)X]^+$		
X = Cl	55.7, 52.9	
X = Br	53.6	
X = I	53.5, 49.8	
$[Ni(dppey)(dppe)]^{2+}$ [a]	52.8	

[a] Tentative assignment.

Table IV. Successive Stability Constants for Ni(II) Bis(phosphine) Halides Calculated from $^{31}P\{^1H\}$ NMR Spectra at 81 MHz

(P-P)	X	Y	K_1[a]	K_2[a]
dppe	I	Br	11.6	3.6
	Br	Cl	3.6	1.1
	I	Cl	2.1	1.1
dppey	I	Br	8.9	2.5
	Br	Cl	9.4	2.0
	I	Cl	7.3	2.6

[a] K_1 = [Ni(P-P)XY][X$^-$]/[Ni(P-P)X$_2$][Y$^-$]; K_2 = [Ni(P-P)Y$_2$][X$^-$]/[Ni(P-P)XY][Y$^-$].

presumably by exchange, but were well resolved at 202 MHz. New species were identified by their ^{31}P chemical shifts and, in the case of mixed halide complexes, their $^{31}P-^{31}P$ coupling constants, which are listed in Table III. $J(^{31}P-^{31}P)$ can be seen to be smaller in the dppey complexes than the dppe complexes. Approximate equilibrium constants were calculated from peak areas, and the values are listed in Table IV. The order of halide affinities for Ni(P-P) is Cl > Br > I.

Phosphine Exchange. [Ni(dppe)X$_2$] + dppe. Addition of dppe to a solution of [Ni(dppe)Cl$_2$] caused a new peak to appear in the 202-MHz $^{31}P\{^1H\}$ NMR spectrum at 49.3 ppm, identified as $[Ni(dppe)_2]^{2+}$ (Table V). Addition of a second equivalent of dppe caused this resonance to increase in intensity. At 24 MHz, peaks were broadened and overlapped (Figure 2). From this coalescence behavior, an approximate exchange rate for dppe between mono- and bischelated species was calculated to be 460 s^{-1}. With the assumption of a second-order reaction (association of dppe with the mono chelate), this gives a second-order rate constant of ca. 5×10^4 M^{-1} s^{-1}. In contrast to [Ni(dppe)Cl$_2$], for which a peak persisted even after the addition of 2 mol equiv of dppe, addition of 1 mol equiv of dppe to the iodide complex produced wholly the bischelated species $[Ni(dppe)_2]^{2+}$, and further addition of dppe led to the appearance of a peak for free dppe (slow exchange). Intermediate behavior was observed for the bromide complex.

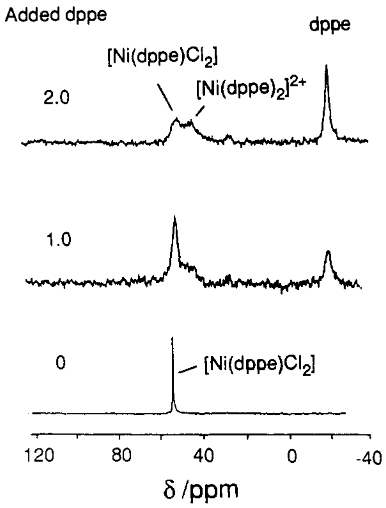

Figure 2. 24-MHz $^{31}P\{^1H\}$ NMR spectra of [Ni(dppe)Cl$_2$] (10 mM) in CDCl$_3$ in the presence of various amounts of added dppe (mol equiv).

[Ni(dppey)X$_2$] + dppey. Titrations of dppey into [Ni(dppey)X$_2$] gave sharp peaks in the region 45–57 ppm even at 24 MHz, suggesting a slower rate of exchange compared to dppe. As with dppe, 3 mol equiv of dppey did not displace all the bound chloride, whereas $[Ni(dppey)_2I]^+$ formed stoichiometrically for the iodide complex.

Mixed Titrations. Careful consideration of relative peak heights, concentrations, and T_1 values allowed assignment of resonances to mixed bis chelates, as shown in Table III.

Phosphine-Exchange Rates by Magnetization Transfer. Since many of the systems above exhibited separate NMR resonances from magnetically distinct species (i.e. slow exchange), exchange rates were studied by magnetization transfer with the equations described in the Appendix. A set of spectra from a typical magnetization-transfer experiment is shown in Figure 3, together with magnetization against time plots.

The equilibrium constant (K) for the reaction of [Ni(dppe)Br$_2$] with dppe

$$[Ni(dppe)Br_2] + dppe \rightleftharpoons [Ni(dppe)_2]^{2+} + 2Br^-$$

was calculated to be 0.05 ± 0.02 M. Six inversion experiments were carried out and sixteen values of k_b calculated. The mean and standard deviation (σ_{n-1}) were (8.2 ± 3.2) × 10^5 M^{-2} s^{-1}, yielding k_f = (4.1 ± 1.6) × 10^4 M^{-1} s^{-1}.

For the dppey complex, the equilibrium constant for the reaction

$$[Ni(dppey)Br_2] + dppey \rightleftharpoons [Ni(dppey)_2Br]^+ + Br^-$$

was about 6.0, and the exchange rate was much less favorable for magnetization-transfer experiments. From two experiments, k_f appeared to be ca. 10^2 M^{-1} s^{-1} and k_b 10–10^2 M^{-2} s^{-1}.

Discussion

Nickel(II) Bis(phosphine) Complexes in the Solid State. Very few solid-state ^{31}P NMR studies of phosphines[34,37] or coordinated

Table V. $^{31}P\{^1H\}$ NMR Data at 81 MHz for Ni(II) Bis(phosphine) Complexes in CDCl$_3$–CHCl$_3$ (1:1)

complex	δ_P	Δ_{obs}[a]	complex	δ_P	Δ_{obs}	J_{PP}/Hz
[Ni(dppe)Cl$_2$]	58.2	70.0	[Ni(dppey)Cl$_2$]	64.9	87.4	
[Ni(dppe)Br$_2$]	66.4	78.2	[Ni(dppey)Br$_2$]	74.0	96.5	
[Ni(dppe)I$_2$]	78.2	90.0	[Ni(dppey)I$_2$]	87.5	110.0	
[Ni(dppe)$_2$]Br$_2$	49.6	61.4	[Ni(eppe)Cl$_2$]	74.4	90.5	*b*
				60.7	72.2	
[Ni(dppe)$_2$]I$_2$	49.3	61.1	[Ni(eppe)Br$_2$][c]	79.7	95.8	59
				67.8	79.3	
[Ni(dppe)$_2$](NO$_3$)$_2$	55.7	67.5	[Ni(depe)Br$_2$]	83.5	100.6	

[a] Coordination chemical shift Δ_{obs} = δ(complex) − δ(ligand). [b] Not resolved. [c] 24.25 MHz in CHCl$_3$.

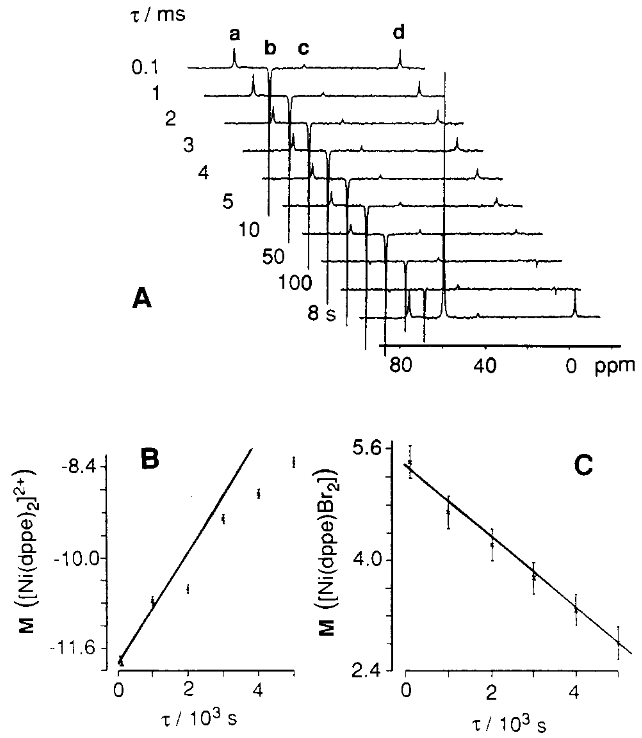

Figure 3. (A) 81-MHz $^{31}P\{^1H\}$ NMR spectra of [Ni(dppe)Br$_2$] in the presence of added dppe (1 mol equiv) in chloroform solution. The magnetization of $[Ni(dppe)_2]^{2+}$ was inverted, and spectra were acquired after a delay of τ. Assignments: (a) [Ni(dppe)Br$_2$]; (b) $[Ni(dppe)_2]^{2+}$; (c) dppeO$_2$; (d) dppe. (B,C) Changes in magnetization (M/μmol equiv) of $[Ni(dppe)_2]^{2+}$ and [Ni(dppe)Br$_2$], respectively, at times τ following inversion of the magnetization of $[Ni(dppe)_2]^{2+}$. Solid lines are best fits, weighted toward earlier points.

phosphines[38-40] have been reported, although extensive use is made of solution ^{31}P NMR chemical shifts, δ, to characterize such compounds. Solution chemical shifts are averages, corresponding to σ_{iso} in the solid state, and it might be expected that the principal components of the shift tensor, σ_{11}, σ_{22}, and σ_{33}, would show better correlations with structural parameters than would σ_{iso} or δ. This has been shown to be the case for a series of phosphido-bridged diiron complexes.[39] The data in Table I appear to be the first reported for a series of mononuclear phosphine complexes. It is apparent that relatively small changes in σ_{iso} mask larger changes in the components, especially σ_{22} and σ_{33}. The chemical shift anisotropy, $\Delta\sigma$, for dppe was much less for the free ligand than for the complexes. Several phosphines PR^{1}R^{2}R^3 have been studied recently by Penner and Wasylishen,[37] and from their data $\Delta\sigma$ values of 0–48 ppm may be calculated. When $R^1 = R^2 = R^3$ most of the compounds gave rise to spectra which were axially symmetric or nearly so. Complexation reduces the symmetry, and the complexes studied here exhibited shielding anisotropies of 97–159 ppm (Table I). Such large values have implications for the mechanisms of spin–lattice relaxation (vide infra).

Each of the complexes exhibited an isotropic solid-state shift which was within 5 ppm of the chloroform solution value, implying that the molecular structures were the same in both phases. Additional resonances occurred in the spectra of the solids due to ^{31}P occupying crystallographically inequivalent sites, e.g. [Ni(dppe)X$_2$], X = Cl gave rise to four bands, X = Br, I gave rise to two bands. A crystal structure of [Ni(dppe)Cl$_2$]·CH$_2$Cl$_2$ has been published.[41] The complex crystallized in space group $P2_1/c$ with $Z = 4$, thus there were two inequivalent ^{31}P sites in the unit cell. IR spectral studies have distinguished two forms of [Ni(dppe)Cl$_2$], A and B,[42] and the form used in this work was identifiable from the IR spectrum as form A. Form B was said to be of higher symmetry than form A and isomorphous with [Ni(dppe)X$_2$] (X = Br, I). This suggested that the crystal structure was of form B and the two resonances observed in the spectra of [Ni(dppe)X$_2$] (X = Br, I) were due to crystallization in space group $P2_1/c$ with $Z = 4$.[43] This has been shown to be the case for [Ni(dppe)Br$_2$]·CH$_2$Cl$_2$.[44] The lower symmetry of form A could be due to the same crystallographic asymmetry (i.e. ^{31}P atoms of the ligand on crystallographically inequivalent sites) with some disorder, such as cis and gauche conformations of the five-membered ring, or to crystallization with two molecules per asymmetric unit.

Nickel(II) Bis(phosphine) Complexes in Solution. $^{31}P\{^1H\}$ NMR was used to characterize solutions of the complexes and mixtures of the complexes with added halide or ligand. In order to determine whether true signal intensities were being observed under normal pulsing conditions, some spin–lattice relaxation times (T_1) were measured. Since the results were required to aid the interpretation of routine spectra, they were measured under routine conditions using nondegassed solutions. Considering the widespread use of ^{31}P NMR in inorganic chemistry, remarkably few T_1 measurements have been reported for transition-metal complexes.[45-48] In some Au(I) and Ir(I) complexes of arylphosphines, the dipolar interaction ($1/T_{1DD}$) was found not to be the major contributer to the overall relaxation rate.[46] For a series of compounds of similar structure, the effect of molecular tumbling is to make T_{1DD} decrease with increasing molecular weight. The variation observed for the complexes [Ni(dppe)X$_2$] and [Ni(dppey)X$_2$] (Table II), T_1 increasing in the order X = Br < Cl < I, suggests that the dipolar mechanism probably does not dominate the spin–lattice relaxation of these complexes either. The decrease in T_1 upon coordination of monodentate arylphosphines[46] has been attributed to increased shielding anisotropy.[45] Measurements show that $\Delta\sigma$ for triphenylphosphine increases from 50 ppm when free[40] to 121–222 ppm when complexed.[38,45] Our measurements on free and complexed dppe show this also to be the case for the bidentate phosphine, so the decreased T_1 of the complexes (Table II) is probably a consequence of increased shielding anisotropy.

The T_1 values of the compounds studied cover 2 orders of magnitude. This would be expected to lead to problems in choice of a pulse delay time. However, it was found that in solutions of mixtures of Ni(II), dppe, and halides, where comparisons of peak intensities were required to estimate relative concentrations, the ligands were exchanging at a rate fast relative to T_1^{-1}. Thus determinations of T_1 for a mixture of dppe–[Ni(dppe)Br$_2$] (1:1 mol/mol) in chloroform returned averaged values of 0.8 s (±0.1 s), and the peak heights at any pulse delay were proportional to concentration. The only exception was oxidized dppe, i.e. dppeO$_2$. This did not exchange, and its T_1 remained long. In contrast, measurements of T_1 in a chloroform solution of dppey–[Ni(dppey)Br$_2$] (1:1 mol/mol) gave values very close to those for the isolated species, and the rate of exchange must have been slower than the shortest T_1 observed (1.4 s), which puts an approximate upper limit of 0.7 s^{-1} on the rate, and gives a second-order rate constant of <350 M^{-1} s^{-1}. Bearing in mind the above results, it was possible to interpret and assign the spectra from the competition and exchange experiments. The order of halide affinities for Ni(P-P) was Cl > Br > I, and the tendency for bis chelation

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in the presence of halide or NO_3^- increased in the order Cl < Br < I < NO_3^-. This behavior is typical of a class "a" metal ion and contrasts with the usual behavior of Pd(II) and Pt(II) which are class "b" ions.[49] Both the mono- and bischelated dppey complexes were more stable than their dppe counterparts. These trends were also evident in solutions of pure complexes, as $[Ni(dppe)_2]^{2+}$ resonances were observed in spectra of $[Ni(dppe)I_2]$ and resonances due to $[Ni(dppe)Br_2]$ in spectra of $[Ni(dppe)_2]Br_2$. The former must have arisen from equilibrium 1. It is almost certainly

$$2[Ni(dppe)X_2] \rightleftharpoons [Ni(dppe)_2]X_2 + NiX_2 \qquad (1)$$

this equilibrium which gave rise to the unexpected conductivities of these compounds in polar, nonprotic solvents and not simple dissociation[21] or formation of a five-coordinate complex.[35] It is consistent with the increasing conductivities of the monochelated complexes as the halide was changed Cl < Br < I (supplementary material, Table D6). Ligand-exchange rates in chloroform solution were measured as 4×10^4 M^{-1} s^{-1} for association of dppe with $[Ni(dppe)Br_2]$ and ca. 10^2 M^{-1} s^{-1} for association of dppey with $[Ni(dppey)Br_2]$. The values bear our estimates of 5×10^4 M^{-1} s^{-1} for the association of dppe with $[Ni(dppe)Cl_2]$ from the phosphine-exchange experiment and $<3 \times 10^2$ M^{-1} s^{-1} for the association of dppey with $[Ni(dppey)Br_2]$ from the measurements of T_1 on a mixture. This implies that association proceeds at similar rates for the bromide and chloride complexes, although the equilibrium constants are different. The only related measurements which appear to have been previously reported are for phosphine exchange:

$$NiL_2X_2 + L' \rightleftharpoons NiLL'X_2 + L$$

where L = L′ = triphenylphosphine or tri-*p*-tolylphosphine and X = Cl, Br, I,[50] where second-order rate constants of 6.2×10^2 to 3.2×10^5 M^{-1} s^{-1} were found.

The rate constants determined here for bischelating phosphines correspond to slow exchange on the NMR time scale: sharp resonances were observed for individual species, and magnetization-transfer experiments were possible. However, they are fast on the preparative time scale in that even for dppey millimolar concentrations of Ni(II)–bis(phosphine) complexes come into equilibrium with ligands such as halides within a few seconds. In biological systems there are many potential ligands for Ni(II), notably H_2O, Cl^-, and N-containing bases. Thus it must be expected that a Ni(II)–bis(phosphine) complex introduced into a biological milieu would rapidly come into equilibrium with the available ligands, giving rise to a number of species which might or might not include the original species.

Some work was also carried out on methanol solutions of the complexes, since it is a protic solvent and therefore a better model for parts of biological systems. The solubilities in methanol were very low, so it was difficult to obtain NMR spectra and long accumulation times were required. However, the results may be interpreted in conjunction with the electronic absorption spectra as showing the rapid formation of $[Ni(dppe)_2]^{2+}$ in solutions of all the dppe complexes followed by slow oxidation of the ligand to $dppeO_2$ over several hours or days. It would seem therefore that equilibrium (1) is shifted wholly to the right-hand side in methanol, presumably due to better solvation of the ions by methanol compared to chloroform. Resonances due to semioxidized ligands (dppeO, dppeyO) and completely oxidized ligands ($dppeO_2$, $dppeyO_2$) were also observed in spectra of the phosphine-exchange experiments. They were not present in spectra of pure compounds in chloroform and were not a simple consequence of the presence of free bis(phosphine) in solution since autoxidation of such compounds in chloroform takes place over several days.[51] Rather the oxidation seems to be related to ligand exchange on Ni(II). PPh_3 is known to be oxidized in the presence of $[Pt(PPh_3)_3]$, and a mechanism analogous to that proposed for the latter reaction[52,53] can be considered in the present case, although this would require the involvement of Ni(0) intermediates, which may be unlikely.

Conclusions

^{31}P NMR spectroscopy in particular has provided a deeper insight into the structures and reactivity of Ni(II) bis(phosphine) complexes in solution and the solid state. Ni(II) in solution exchanges rapidly with bis(phosphine) and halide ligands and can promote catalytic oxidation of the bis(phosphine). Since $dppeO_2$ is not cytotoxic,[9] Ni(II) bis(phosphines) must be stabilized if they are to be of biological use.

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Appendix

Magnetization loss from a particular site is due to spin–lattice relaxation at that site and to chemical exchange with other sites as described by the Bloch equations modified by McConnell[54] and generalized for *N* equivalent sites by Forsên and Hoffman.[55] The generalization is

$$\mathrm{d}M_A/\mathrm{d}t = -(\rho_A + \sum_{i \neq A} \lambda_{A,i})M_A + \rho_A M^0{}_A + \sum_{i \neq A} \lambda_{i,A} M_i \qquad (A1)$$

where M_A is the instantaneous *z* magnetization of nucleus Y at site A, $M^0{}_A$ the equilibrium *z* magnetization of nucleus Y at site A, $\lambda_{A,B}$ the probability per unit time for a nucleus Y at site A to be transferred to site B, $\rho_A = 1/T_{1A}$, T_{1A} the spin–lattice relaxation time of nucleus Y at site A. The lifetime of Y at site A is τ_A with $1/\tau_A = \sum \lambda_{A,i}$. This assumes no dipolar coupling between the sites,[56] which is true in the present case since they are on different molecules.

The following equilibrium was assumed for the Ni(II)–dppe system:

$$[Ni(dppe)X_2] + dppe \underset{k_b}{\overset{k_f}{\rightleftharpoons}} [Ni(dppe)_2]^{2+} + 2X^-$$

From eq 1, it follows that

$$\mathrm{d}M_L/\mathrm{d}t = -(\rho_L + \lambda_{L,ML_2})M_L + \rho_L M^0{}_L + \lambda_{ML_2,L} M_{ML_2} \qquad (A2)$$

$$\mathrm{d}M_{ML}/\mathrm{d}t = -(\rho_{ML} + \lambda_{ML,ML_2})M_{ML} + \rho_{ML} M^0{}_{ML} + \lambda_{ML_2,ML} M_{ML_2} \qquad (A3)$$

$$\mathrm{d}M_{ML_2}/\mathrm{d}t = -(\rho_{ML_2} + \lambda_{ML_2,ML} + \lambda_{ML_2,L})M_{ML_2} + \rho_{ML_2} M^0{}_{ML_2} + \lambda_{ML,ML_2} M_{ML} + \lambda_{L,ML_2} M_L \qquad (A4)$$

where L, ML, and ML_2 denote nuclei in the free ligand, mono chelate, and bis chelate, respectively. These all give singlet $^{31}P\{^1H\}$ resonances. The $\lambda_{A,B}$ terms may be rewritten as pseudo-first-order rate constants in terms of the second- and third-order rate constants k_f and k_b:

$$\lambda_{L,ML_2} = k_f[ML] \qquad (A5)$$

$$\lambda_{ML,ML_2} = k_f[L] \qquad (A6)$$

$$\lambda_{ML_2,ML} + \lambda_{ML_2,L} = k_b[X]^2 \qquad (A7)$$

In addition, since $ML_2 \rightarrow ML + L$ is a dissociation, $\lambda_{ML_2,ML}$ must be equal to $\lambda_{ML_2,L}$, so

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$$2\lambda_{\mathrm{ML_2,ML}} = 2\lambda_{\mathrm{ML_2,L}} = k_b[\mathrm{X}]^2 \quad \text{(A8)}$$

$$\mathrm{d}M_{\mathrm{L}}/\mathrm{d}t = -(\rho_{\mathrm{L}} + k_f[\mathrm{ML}])M_{\mathrm{L}} + \rho_{\mathrm{L}}M^0{}_{\mathrm{L}} + 0.5k_b[\mathrm{X}]^2M_{\mathrm{ML_2}} \quad \text{(A9)}$$

$$\mathrm{d}M_{\mathrm{ML}}/\mathrm{d}t = -(\rho_{\mathrm{ML}} + k_f[\mathrm{L}])M_{\mathrm{ML}} + \rho_{\mathrm{ML}}M^0{}_{\mathrm{ML}} + 0.5k_b[\mathrm{X}]^2M_{\mathrm{ML_2}} \quad \text{(A10)}$$

$$\mathrm{d}M_{\mathrm{ML_2}}/\mathrm{d}t = -(\rho_{\mathrm{ML_2}} + k_b[\mathrm{X}]^2)M_{\mathrm{ML_2}} + \rho_{\mathrm{ML_2}}M^0{}_{\mathrm{ML_2}} + k_f[\mathrm{L}]M_{\mathrm{ML}} + k_f[\mathrm{ML}]M_{\mathrm{L}} \quad \text{(A11)}$$

In the inversion-transfer experiment, magnetization at one site is selectively inverted and after some time *t* the magnetization at all the sites is nonselectively detected. For example, if the $\mathrm{ML_2}$ magnetization is inverted then initially

$$M_{\mathrm{ML_2}} = -M^0{}_{\mathrm{ML_2}} \qquad M_{\mathrm{L}} = M^0{}_{\mathrm{L}} \qquad M_{\mathrm{ML}} = M^0{}_{\mathrm{ML}}$$

assuming perfect selectivity and inversion. Thus eqs A9-11 give the initial rates of change:

$$[\mathrm{d}M_{\mathrm{L}}/\mathrm{d}t]_{t=0} = -k_f[\mathrm{ML}]M^0{}_{\mathrm{L}} - 0.5k_b[\mathrm{X}]^2M^0{}_{\mathrm{ML_2}} \quad \text{(A12)}$$

$$[\mathrm{d}M_{\mathrm{ML}}/\mathrm{d}t]_{t=0} = -k_f[\mathrm{L}]M^0{}_{\mathrm{ML}} - 0.5k_b[\mathrm{X}]^2M^0{}_{\mathrm{ML_2}} \quad \text{(A13)}$$

$$[\mathrm{d}M_{\mathrm{ML_2}}/\mathrm{d}t]_{t=0} = 2\rho_{\mathrm{ML_2}}M^0{}_{\mathrm{ML_2}} + k_b[\mathrm{X}]^2M^0{}_{\mathrm{ML_2}} + k_f[\mathrm{L}]M^0{}_{\mathrm{ML}} + k_f[\mathrm{ML}]M^0{}_{\mathrm{L}} \quad \text{(A14)}$$

Similar equations apply to the inversion of the magnetization of the other two resonances.

Exchange of Ni(II) and dppey was assumed to obey the following stoichiometry:

$$[\mathrm{Ni(dppey)X_2}] + \mathrm{dppey} \rightleftharpoons [\mathrm{Ni(dppey)_2X}]^+ + \mathrm{X}^-$$

The initial rate equations are the same as eqs A12-14, except that the concentration of X is not squared.

The experiment measures the initial rates of change of magnetization. The values of ρ_{A} $(=1/T_{1\mathrm{A}})$ were measured independently, and signal intensities in the fully relaxed spectra gave $M^0{}_{\mathrm{A}}$ and also enabled the equilibrium constant, *K*, to be determined. Thus the concentrations of the various species could be calculated from the total amounts added. Since $K = k_f/k_b$ at equilibrium, k_f and k_b could be calculated from eqs A12-14. When the magnetization of ML or L is inverted, two terms cancel in the expression for $(\mathrm{d}M_{\mathrm{ML_2}}/\mathrm{d}t)_{t=0}$ and k_b can be calculated without using the equilibrium constant.

Supplementary Material Available: Tabulations of the elemental analyses, magnetic data, IR data, electronic absorption data, and molar conductivities (6 pages). Ordering information is given on any current masthead page.

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Reactions of $[\mathrm{Ni(1,4,7\text{-}triazacyclononane)_2}]^{3+/2+}$ with the Components of Nitrous Acid

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The reactions of $[\mathrm{Ni(tacn)_2}]^{3+}$ with some of the components of nitrous acid have been studied in aqueous solution at 25 °C. $\mathrm{NO_2}^-$ reacts to form $[\mathrm{Ni(tacn)_2}]^{2+}$ and $\mathrm{NO_3}^-$, and the rate law is $-\mathrm{d}[\mathrm{Ni(tacn)_2}^{3+}]/\mathrm{d}t = k[\mathrm{Ni(tacn)_2}^{3+}][\mathrm{N(III)}]/(1 + [\mathrm{H}^+]/K_a)$ with $k = 212 \pm 7\ \mathrm{M^{-1}\,s^{-1}}$ and $K_a = (9.6 \pm 1.1) \times 10^{-4}$ M at $\mu = 0.1$ M ($\mathrm{LiClO_4}$). Electron transfer from $\mathrm{NO_2}^-$ to $[\mathrm{Ni(tacn)_2}]^{3+}$ is proposed as the rate-limiting step. In 0.79 mM NO, $[\mathrm{Ni(tacn)_2}]^{3+}$ reacts with the rate law $-\mathrm{d}[\mathrm{Ni(tacn)_2}^{3+}]/\mathrm{d}t = k'[\mathrm{Ni(tacn)_2}^{3+}] + k''[\mathrm{Ni(tacn)_2}^{3+}]/[\mathrm{H}^+]$ where $k' = (1.02 \pm 0.06) \times 10^{-3}\ \mathrm{s^{-1}}$ and $k'' = (1.36 \pm 0.07) \times 10^{-4}\ \mathrm{M\,s^{-1}}$ at $\mu = 1.0$ M ($\mathrm{LiClO_4}$). The k'' pathway leads to destruction of the complex, presumably through nitrosation of the N-deprotonated conjugate base form of the Ni(III) reactant. The k' pathway is interpreted as an outer-sphere electron-transfer reaction between NO and $[\mathrm{Ni(tacn)_2}]^{3+}$.

Introduction

Rapid acid/base equilibria cause solutions of nitrous acid to contain $\mathrm{HNO_2}$, $\mathrm{NO_2}^-$, and NO^+, the relative concentrations depending on pH. Moreover, such solutions are unstable and soon contain significant quantities of NO, $\mathrm{NO_2}$, $\mathrm{NO_3}^-$, and other species. Many of these components of nitrous acid are quite reactive, so that the study of nitrous acid chemistry remains a fertile endeavor. Of interest in this paper are reactions in which the components of nitrous acid react by an outer-sphere electron-transfer mechanism, specifically, reactions in which the $\mathrm{NO_2}/\mathrm{NO_2}^-$ and $\mathrm{NO}^+/\mathrm{NO}$ redox couples participate.

Electron-transfer reactions involving the $\mathrm{NO_2}/\mathrm{NO_2}^-$ couple have been investigated previously, and they serve as important examples of the class of triatomic redox couples. An effective self-exchange rate constant of $2 \times 10^{-2}\ \mathrm{M^{-1}\,s^{-1}}$ was derived by applying the cross relationship of Marcus' theory to a series of reactions with substitution-inert coordination compounds.[1] Although there was good consistency between the results for the various metal complexes, there was some basis for concern that the reactions were not truly outer sphere in that all the complexes had exposed lone pairs or π-systems that might interact specifically with the $\mathrm{NO_2}$. More recently, a value of 580 $\mathrm{M^{-1}\,s^{-1}}$ was measured for the actual electron-transfer rate constant between $\mathrm{NO_2}$ and $\mathrm{NO_2}^-$.[2] The significant discrepancy between the effective and actual self-exchange rate constants, combined with the reservations expressed above regarding the nature of the cross-reactions, suggested the need for further study.

Electron-transfer reactions involving the $\mathrm{NO}^+/\mathrm{NO}$ couple have not been studied as often as those of the $\mathrm{NO_2}/\mathrm{NO_2}^-$ couple. Potentially, the system is of great interest because of the substantial difference in bond length between NO^+ and NO and because of the high force constants of those bonds. These factors could lead to a high degree of nuclear tunneling in electron-transfer reactions. We reported that the reaction of NO^+ with $\mathrm{IrCl_6}^{3-}$ was diffusion-controlled and that this high rate required an inner-sphere mechanism.[3] In that paper, we reviewed the literature evidence for outer-sphere electron transfer involving the $\mathrm{NO}^+/\mathrm{NO}$ couple and concluded that it was lacking. To our knowledge, the only subsequent report pertains to the reaction of NO^+ with $\mathrm{Re_2(CO)_{10}}$ in $\mathrm{CH_3CN}$, but this reaction is complicated by Re-Re bond cleavage.[4] Thus there is considerable motivation for investigating reactions of the $\mathrm{NO}^+/\mathrm{NO}$ couple that are truly outer sphere.

To investigate genuine outer-sphere electron-transfer reactions of the $\mathrm{NO_2}/\mathrm{NO_2}^-$ and $\mathrm{NO}^+/\mathrm{NO}$ couples requires special properties of the redox partner. It must be substitution-inert, a strong oxidant, and a species with a strictly saturated ligand system. The $[\mathrm{Ni(tacn)_2}]^{3+/2+}$ system (tacn = 1,4,7-triazacyclononane) meets these requirements. An added benefit is its low self-exchange rate, which makes the cross-reaction rate constants quite sensitive to the intrinsic barriers of the $\mathrm{NO_2}/\mathrm{NO_2}^-$ and $\mathrm{NO}^+/\mathrm{NO}$ couples.

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