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Kinetics of Exchange of 4-Picoline 1-Oxide in Nickel(II)- and Cobalt(II)-β-Diketone Complexes

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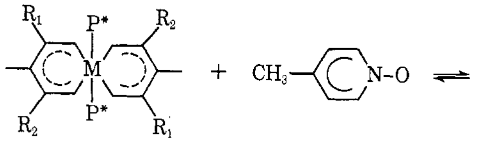
Nickel(II) and cobalt(II) complexes of β-diketones, $[M(AA)_2]_n$,[2] readily add basic ligands, L, to form hexacoordinate adducts having the stoichiometry $M(AA)_2L_2$.[3] In solutions containing an excess of L, the rate at which L exchanges between the paramagnetic complex $M(AA)_2L_2$ and the bulk solvent is in principle measurable using nmr techniques. The exchange rates of such systems where L = 4-picoline have already been studied and the slowing of the picoline exchange by electron-withdrawing substituents on the β-diketone ring has been reported.[4] In order to evaluate more fully the effect of the exchanging ligand on the rate, similar studies have also been made with 4-picoline 1-oxide, P (eq 1), and are now reported.

TABLE I
CHARACTERIZATION OF COMPLEXES

Complex	Mp, °C	% calcd C	% calcd H	% calcd Other	% found C	% found H	% found Other
$Ni(AcAc)_2P_2$	154–157[a]	55.61	5.94	12.4[b]	55.85	6.24	11.7[b]
$Ni(BzAc)_2P_2$	143–145	64.13	5.40	9.8[b]	64.19	5.59	9.8[b]
$Ni(TFAA)_2P_{1.5}$	203–205	43.16	3.53		42.83	3.48	
$Ni(TFAA)_2P_2$	142–149[a]	45.31	3.80		45.12	3.73	
$Ni(HFAA)_2P_2$		38.24	2.33		38.52	2.65	
$Co(TFAA)_2P_2$		45.30	3.80		45.41	3.74	
$Co(HFAA)_2P_2$		38.22	2.33	4.08[c]	38.65	2.65	4.01[c]

[a] Partially resolidified after melting. [b] Per cent Ni determined as ash. [c] Per cent Nitrogen.



$$M(AA)_2P^*P + P^* \quad (1)$$

The ligands 4-picoline and 4-picoline 1-oxide present an interesting contrast, for while both form hexacoordinate complexes of stoichiometry $Ni(AA)_2L_2$, 4-picoline is a moderately strong N-bonding base ($pK_a \approx 6$,[5] $\Delta_{obsd}(Ni(AA)_2L_2) = 10,200$ cm^{-1}[4,6]), but 4-picoline 1-oxide is a weak O-bonding base ($pK_a \approx 1$,[5] $\Delta_{obsd}(Ni(AA)_2L_2) = 8600$ cm^{-1}[7]). These factors tend to show that the coordination of pyridines in complexes is considerably more favorable than the bonding of the corresponding oxides.[8] Furthermore the nitrogen–metal bond and the C_2 ligand axis are approximately coincident in picoline complexes,[9,10] while the corresponding *N*-oxide complexes have metal–oxygen–nitrogen bond angles of approximately 120°.[7,11,12] Thus the steric requirements of the two ligands differ markedly. Finally although nmr studies of both ligands in solutions of $M(AA)_2$ have been interpreted in terms of a trans configuration of L in the complex,[7,12–14] X-ray structural determinations on single crystals of $Ni(AA)_2L_2$ show that the pyridine ligands are trans,[9] while in at least one crystalline modification the pyridine 1-oxide moieties are cis.[11]

Experimental Section

Preparation of Complexes.—The bis(β-diketonato)bis(4-picoline *N*-oxide)nickel(II) or -cobalt(II) complexes were prepared by heating stoichiometric amounts of the dihydrate of the complexed β-diketone with 4-picoline 1-oxide in toluene. After removal of the water by azeotropic distillation the complex $M(AA)_2P_2$ was obtained by slow crystallization. This was recrystallized from toluene saturated at room temperature with 4-picoline 1-oxide and the pure complex dried at 56° *in vacuo* for 2 hr. The infrared spectra in all cases showed the absence of the O–H stretching frequency at approximately 3400 cm^{-1} and the presence of a characteristic peak at 1210 cm^{-1} attributable to the N–O stretching frequency in a complex. Analytical data are given in Table I.

Nmr Spectra and Kinetics.—All experiments were carried out in deuteriochloroform with tetramethylsilane as an internal standard in a manner described in more detail elsewhere.[4]

The ratio P_m of the coordinated picoline *N*-oxide to the total concentration of this ligand in the system was varied from 0.01 to 0.08 for a total ligand concentration in the range of 1–2 *M*.

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[2] The following abbreviations will be used in this note: AA, a general β-diketonate anion; AcAc, 2,4-pentanedionate (acetylacetonate); BzAc, benzoylacetonate; TFAA, 1,1,1-trifluoro-2,4-pentanedionate; HFAA, 1,1,1,-5,5,5-hexafluoro-2,4-pentanedionate; DPM, 2,2,6,6-tetramethyl-3,5-heptanedionate (dipivaloylmethide); P, 4-picoline 1-oxide.

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TABLE II

KINETIC DATA FOR LIGAND EXCHANGE

R_1	R_2	M	$k_1(25°)$,[a] sec^{-1}	$\Delta H^{\ddagger}$,[b] kcal	$\Delta S^{\ddagger}$,[c] eu
tert-C_4H_9	*tert*-C_4H_9	Ni	$(6 \pm 2) \times 10^6$ (1.1×10^5)		
CH_3	CH_3	Ni	7.5×10^5 (1.0×10^5)	11.2	5.4
CH_3	C_6H_5	Ni	6.3×10^5 (3.8×10^4)	11.4	6.5
CH_3	CF_3	Ni	2.2×10^4 (1.4×10^3)	12.4	3.0
CF_3	CF_3	Ni	$(5 \pm 2) \times 10^2$		
CH_3	CF_3	Co	7.1×10^5	10.1	0.5
CF_3	CF_3	Co	9.4×10^3	11.4	−1.9

[a] Rate constants for eq 1 are twice the values reported here. Rates in parentheses are those for 4-picoline exchange.[4] The errors are estimated to be ±10% unless otherwise indicated. [b] ±1 kcal. [c] ±5 eu.

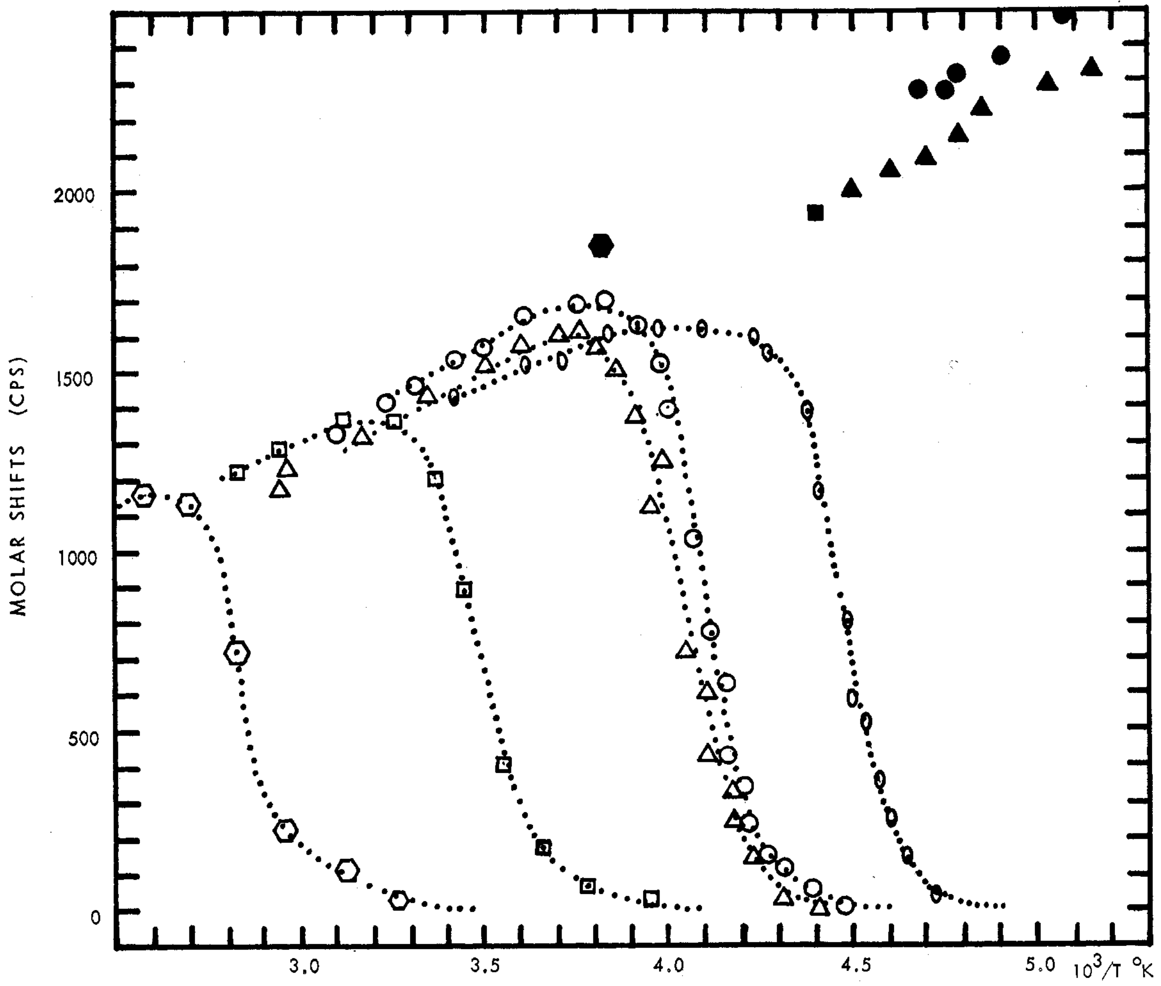

Figure 1.—Plot of the molar shift of the 4-methyl resonance of 4-picoline 1-oxide (observed shift divided by the mole fraction of coordinated ligand) with respect to reciprocal absolute temperature: 0, $Ni(DPM)_2P_2$; O, $Ni(AcAc)_2P_2$; Δ, $Ni(BzAc)_2P_2$; □, $Ni(TFAA)_2P_2$; ⬡, $Ni(HFAA)_2P_2$. The solid points represent data for the resonance shifts observed in the pure paramagnetic complexes. For clarity, only about 20% of the useful data obtained at various concentrations are presented. The dotted lines represent the weighted average of all the points.

The $Ni(DPM)_2$ data were obtained using pure $Ni(DPM)_2$ rather than preformed $Ni(DPM)_2P_2$, while those involving $Ni(TFAA)_2$ were carried out using $Ni(TFAA)_2P_{1.5}$ as the starting complex. Spectra of $Ni(HFAA)_2P_2$ solutions showed peaks indicative of a second component.

Results

The exchange of 4-picoline 1-oxide in the bulk solution with that coordinated in the bis(β-diketonato)-nickel(II) adducts, Ni $(AA)_2L_2$, while generally rapid at room temperature, is sufficiently slow at lower temperatures to allow measurement of the exchange kinetics by nmr spectroscopy. First-order rate constants, k_1 (Table II), were obtained principally from the frequency shifts of the 4-CH_3 and 3-H resonances of the 4-picoline 1-oxide in solution (Figure 1). The 2-H resonance was used where possible. The data were analyzed using the equations of Swift and Connick,[15] the details of which are similar to those reported elsewhere.[4] The exchange rates so derived are independent (to within experimental error) of the concentration of excess ligand in solution indicating a dissociative ligand-exchange mechanism as was found for the corresponding picoline systems.[4]

[15] T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962).

The stoichiometry of the complexes was determined at −64° where separate resonances are observed for the 4-picoline 1-oxide protons in the paramagnetic and diamagnetic environments (slow exchange). For the $Ni(AcAc)_2P_2$ complex, the integrated areas under the paramagnetic and diamagnetic 3-H and $4-CH_3$ peaks (P_m = 0.35–0.61) give a 4-picoline 1-oxide, P, to $Ni(AcAc)_2$ ratio of (1.9 ± 0.2):1. The area under the acetylacetonate methyl resonance (a broad peak centered at −4.90 ppm) also indicates a $P:Ni(AcAc)_2$ ratio of (2.0 ± 0.2):1.

The resonances for uncomplexed 4-picoline 1-oxide show concentration and temperature variations indicating some changes in orientation in the solvent. For example at 37° the 2-H, 3-H, and $4-CH_3$ resonances are found at −8.11, −7.12, and −2.36 ppm while at −53° they are found at −8.22, −7.24, and −2.44 ppm. However, under slow exchange conditions these diamagnetic resonance positions are found to be unaffected by the added paramagnetic complex. It was therefore assumed that the presence of the nickel complex in the intermediate and fast-exchange regions also has no effect on the diamagnetic resonance positions and the isotropic shifts were calculated using the proton resonance positions of the ligand in the absence of complex. The ratios of the spin densities at the various ligand nuclei were also observed to shift with temperature. For $Ni(AcAc)_2P_2$ at −64° (slow-exchange region) the isotropic shifts (ppm) are as follows: 2-H, +27.5; 3-H, −14.4; $4-CH_3$, −39.2. These yield ratios (normalized to the 3-H resonance) of +1.9:1.0:−2.8 while at 37° the corresponding ratios are +1.8:−1.0:−2.35. The latter (fast-exchange ratios) are in agreement with those previously reported[7] and when compared with the low-temperature data may reflect a contribution to the isotropic shifts of a second geometrical isomer or a more subtle change in structure of the 2:1 complexes. The formation of adducts having less than 2:1 stoichiometry is also a possibility. However, since for a given complex the rates calculated from the shifts of the different ligand protons are all the same within experimental error, this complication does not affect the semiquantitative interpretation of the present data.

Discussion

Previous studies have shown that, all other factors being equal, the rate of ligand exchange in octahedrally coordinated nickel(II) chelates decreases as the substituents on the chelate rings become more electronegative.[4,16] This electron withdrawal from the central metal atom can be interpreted in terms of an incremental increase in its effective oxidation number. The resulting increased binding of the ligand in the ground state relative to the transition state produces the observed decrease in exchange rate. The relative magnitudes of this effect have been correlated with substituent parameters of the Hammett or Taft variety thus confirming its electronic origin.

While results of the present study support this general conclusion, they also suggest that steric factors play a more significant role in the 4-picoline 1-oxide–$Ni(AA)_2$ systems than in the 4-picoline–$Ni(AA)_2$ systems. Faster than expected rates of 4-picoline 1-oxide exchange are observed for both $Ni(BzAc)_2P_2$ and $Ni(DMP)_2P_2$, both of which contain bulky groups (R = phenyl or *tert*-butyl). The difference in behavior between these and the corresponding 4-picoline complexes can be accounted for by the angular structure[11] of coordinated 4-picoline 1-oxide. The Ni–O–N bond angle of approximately 120° allows the ligand ring to extend laterally in space and interact sterically with the chelate ring substituents R_1 and R_2. Such steric destabilization of the ground state relative to the transition state increases the exchange rate. On the other hand, the cylinder of steric influence generated by coordinated 4-picoline in $Ni(AA)_2L_2$ does not extend as far as the R_1, R_2 groups and mere variation in their size apparently has negligible effect on the exchange rate except as it may inhibit solvation in the ground and/or transition state. A second factor which may affect the rate of exchange, a variation in the ratio of trans to cis isomers in solution with the change in R_1 and R_2, cannot be evaluated at this time.

Two additional generalizations become apparent from this study. (a) The rates of the 4-picoline 1-oxide exchange are greater than those for the comparable 4-picoline systems. This is probably due to a combination of factors including the lower basicity and the greater steric interaction of 4-picoline 1-oxide with the chelate ring. (b) The rates of exchange in the cobalt(II) complexes are faster than those of the corresponding nickel(II) complexes. This order of lability for hexacoordinate complexes of Ni^{2+} and Co^{2+} has been observed in many other cases and is in agreement with simple ligand field stabilization arguments.[17]

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Infrared and Mass Spectral Studies on Azaferrocene (π-Cyclopentadienyl-π-pyrrolyliron)

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After the synthesis of azaferrocene,[1,2] little attention has been devoted to its physicochemical properties.

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