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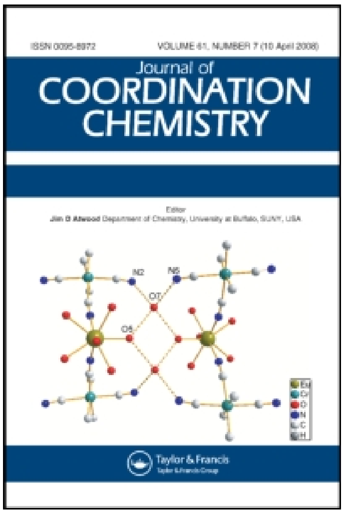

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THE SOLVENT ROLE IN THE LEWIS ACIDITY OF COBALT(I)

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The complexes, $[CoL^1An_2](B\varphi_4)_2$ and $[CoL^2An_2](B\varphi_4)_2$, where L^1 and L^2 are macrocyclic ligands containing the bis-α-diimine function, undergo spontaneous reduction to the corresponding Co^I complexes in *N,N*-dimethylformamide. These Co^I complexes act as potent Lewis acids toward a number of monodentate ligands. Equilibrium constants for adduct formation between the Co^I complexes and the donors pyridine, *N*-methylimidazole, triphenylphosphine, and Br^- have been measured spectrophotometrically and are reported herein.

Keywords: Cobalt(I), diimines, macrocycle, Lewis acids, equilibria

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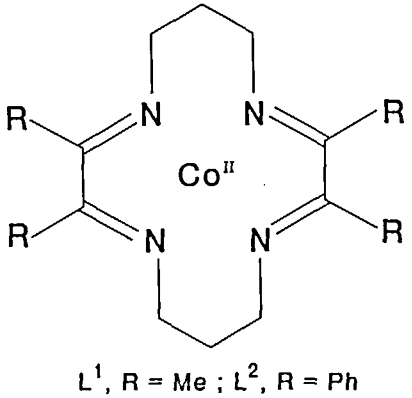
INTRODUCTION

For some time, we have been interested in complexes of Co^{II} with synthetic macrocyclic ligands containing α-diimine groups. We have shown that the complexes in Figure 1, $Co^{II}L$, undergo facile one-electron reduction to Co^IL complexes which serve as Lewis acids towards a number of donors in acetonitrile (An) solvent.[1,2] This contrasts with the tendency of Co^I complexes to behave as powerful nucleophiles.[3–7] We have explained the Lewis acidity of Co^IL as the result of π-donor-acceptor interactions between the electron-rich metal centre and empty π* molecular orbitals of the α-diimine functions in the macrocyclic ligand. This explanation is supported by the observation that the reduction potential of $Co^{II}L^2$ is 0.3 V more positive than that of $Co^{II}L^1$, consistent with the electron-withdrawing capability of the phenyl substituents of L^2.



L^1, R = Me ; L^2, R = Ph

FIGURE 1 The Co^{II} macrocyclic ligand complexes.

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An alternative explanation for the unusually positive $Co^{II,I}$ reduction potentials and marked Lewis acidity in the Co^{I} complexes is that axially bound acetonitrile, rather than the macrocyclic ligand, functions as the π acceptor for the Co^{I} centre.[8] To establish that the acidity of Co^{I} is due to π acceptance by the macrocyclic ligand, L, we have measured equilibrium constants for (*1*) for B = Br^-, pyridine, *N*-methylimidazole and triphenylphosphine, in *N*,*N*-dimethylformamide.

$$CoL^+ + B \longrightarrow CoL(B)^+ \qquad K \qquad (1)$$

Results show that CoL^+ is an effective Lewis acid even in DMF, which does not function as a π-acceptor ligand. This observation supports our proposal that the macrocyclic ligands are responsible for the Lewis acidity of the Co^{I} centre.

EXPERIMENTAL

Reagents

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Acetonitrile (An) (Baker, reagent grade) was refluxed over phosphorus pentoxide for 24 hours under nitrogen, distilled under nitrogen and stored over molecular sieves. Dimethylformamide (DMF) (Baker, reagent grade) was refluxed over calcium hydride for 24 hours under nitrogen, distilled under nitrogen and stored over molecular sieves. Tetra-*n*-butylammonium perchlorate (TBAP) (Alfa) and Tetra-*n*-butylammonium bromide (TBAB) (GFS) were recrystallized from hot ethanol, washed with ether, vacuum dried and stored under vacuum. *N*-methylimidazole (MeIm) (Aldrich) was refluxed over potassium hydroxide for 2 hours under reduced pressure, distilled under reduced pressure and stored over molecular sieves. Triphenylphosphine (Ph_3P) (Baker) was recrystallized from hot ethanol, washed with cold ethanol, vacuum dried and stored under vacuum. Pyridine (py) (Aldrich, gold label) was freeze thawed and stored over molecular sieves. All other chemicals were reagent grade and were used as received.

$[CoLBr_2]Br$

The dibromocobalt(III) bromide complexes were prepared by literature methods.[9,10]

$[CoL^1(An_2)](B\varphi_4)_2$

This complex was made *via* the perchlorate salt using literature methods.[1,11]

$[CoL^2(An_2)](B\varphi_4)_2$

This complex was synthesized according to the following procedure. $[CoL^2(Br_2)]Br$ (1 g) was slurried in a mixture of H_2O (25 cm^3) and An (5 cm^3), a slight stoichiometric excess of $AgClO_4 \cdot H_2O$ was added, and the mixture was stirred overnight. After filtration, the reaction yielded a grey-blue solid which was added to An (40 cm^3) and stirred for 1 hour. The solid partially dissolved to give a deep red solution and a grey residue. The mixture was filtered, and to the red-purple filtrate was added a solution of sodium tetraphenylborate ($NaB\varphi_4$) in An. After 2 hours, an initial crop of purple crystals was removed and discarded since it contained a brown contaminant. Two subsequent crops from the purple filtrate were isolated, washed with ether, and combined. The product was characterized by electronic spectroscopy (EAS), IR and cyclic voltammetry (CV).

$[CoL^{1,2}](B\varphi_4)$

These complexes were made by dissolving $[CoL^{1,2}(An)_2](B\varphi_4)_2$ (typically 1×10^{-3} g) in DMF (typically 5 cm^3) in an inert atmosphere glove box (*vide infra*). They were characterized by EAS and CV.

Physical Methods

To exclude oxygen and water, all solutions for characterization or reaction were prepared in a Vacuum Atmospheres HE-43-1 DriLab equipped with an MO-40-IV purification train, with N_2 used as the inert gas. Electronic absorption spectra were obtained using a Shimadzu UV2100U spectrophotometer system. Absorbances at fixed wavelength were measured in the inert atmosphere box using a Sequoia-Turner 340 spectrophotometer. Infrared spectra and cyclic voltammograms were obtained as previously described.[1]

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Spectrophotometric Titrations

The stoichiometries and equilibrium constants for binding of B to CoL^+ were determined by standard titration methods. Absorbance data were plotted according to (*2*),[12] where A is the absorbance of a solution containing both CoL^+ and $CoL(B)_q{}^+$, A_0 is the initial absorbance of the solution due to CoL^+, A_e is the final absorbance due to $CoL(B)_q{}^+$, q is the stoichiometry of binding, and [B] is the concentration of free base.

$$\log (A - A_0/A_e - A) = q \log [B] + \log K \qquad (2)$$

In cases where A_e was not measureable (weak binding) data were plotted according to (*3*).[12]

$$A = A_e - (A - A_0)/K[B]^q \qquad (3)$$

RESULTS AND DISCUSSION

Characterization of Complexes

Dissolution of $[CoL^{1,2}](B\varphi_4)_2$ in DMF produces intensely blue (L^1) or purple (L^2) solutions similar to those produced by reduction of $[CoL^{1,2}]^{2+}$ in An.[1] The EAS of the complexes in DMF are shown in Figure 2. Comparison of these spectra with those of $[CoL^{1,2}]^+$ in reference 1 shows that reduction of Co^{II} to Co^I is spontaneous in DMF. Absorption maxima and extinction coefficients are collected in Table I.

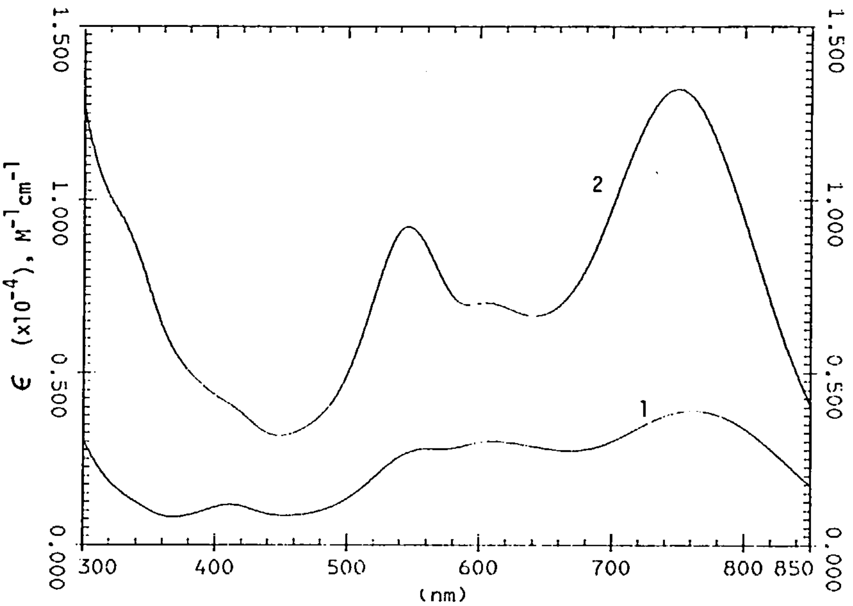

FIGURE 2 Electronic absorption spectra for [Co^{I}L]$^+$ in DMF at 25°C. Spectra 1 and 2 correspond to macrocyclic ligands L^1 and L^2, respectively.

TABLE I
Electronic spectral data.

Complex	Solvent	λ_{max}($\varepsilon \times 10^{-3}$); nm(M^{-1} cm^{-1})	Reference
(CoL^1)$^{2+}$	An	510 (2.7)	this work
		360 (1.3)	
(CoL^2)$^{2+}$		540 (5.6)	
(CoL^1)$^+$	An	750 (6.8)	1
		630 (5.2)	
		530 (3.6)	
		394 (1.7)	
	DMF	761 (3.9)	this work
		610 (3.0)	
		560 (2.8)	
		412 (1.2)	
(CoL^2)$^+$	An	750 (9.5)	1
		620 (6.4)	
		540 (5.2)	
	DMF	751 (13)	this work
		605 (7.0)	
		546 (9.2)	

Reaction of $[CoL]^+$ *with B* ($B = py, MeIm, Ph_3P, Br^-$)

Reactions of $[CoL^{1,2}]^+$ with the Lewis bases, py, MeIm, Ph_3P, and Br^- were rapid in all cases. Spectrophotometric titrations were performed in DMF containing 0.1 M

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TBAP in order to determine equilibrium constants for adduct formation according to (*1*). Use of 0.1 M electrolyte in the solutions allowed direct comparison of the equilibrium constants with those from our previous study, in which electrolyte was mandatory. Spectra obtained during the titration of $[CoL^1]^+$ with MeIm are shown in Figure 3. Isosbestic points at 417, 432, and 544 nm indicate 1:1 stoichiometry. A plot of the data from Figure 3 according to (*2*) is shown in Figure 4. The slope of the plot is 1.03 and the intercept yields log K = 2.86. Titrations for the other bases with both complexes were similar. The binding of Br^- to $[CoL^1]^+$ was so weak that a limiting final spectrum could not be attained. The value of log K for this system was estimated using (*3*). Equilibrium constants for binding of B to $[CoL^{1,2}]^+$ in DMF (0.1 M TBAP) at 25°C are collected in Table II. For $[CoL^1]^+$, log K increases in the order $Br^- < py < MeIm < Ph_3P$. For $[CoL^2]^+$, log K increases in the order $py \approx Br^- < Ph_3P < MeIm$.

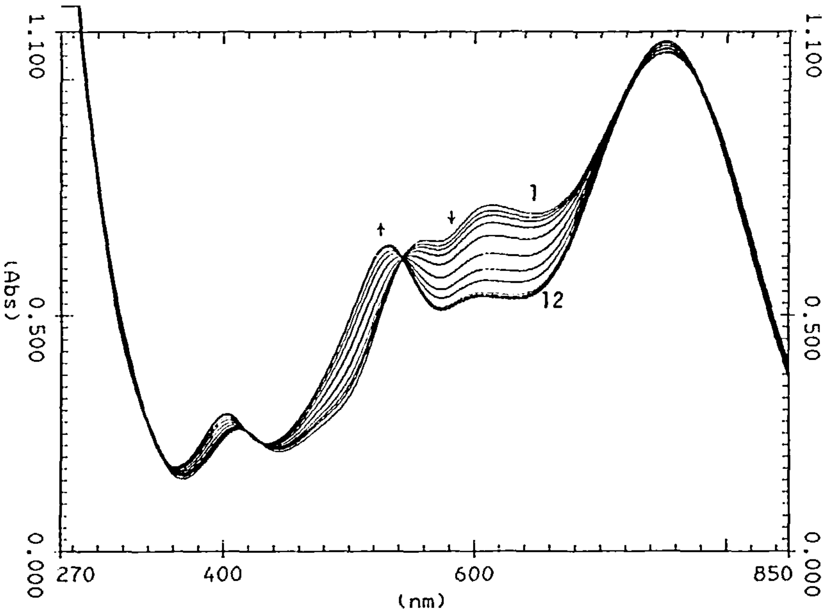

FIGURE 3 Spectrophotometric titration of $[Co^IL^1]^+$ with MeIm in DMF containing 0.1 M TBAP at 25°C. Scan ($[MeIm] \times 10^3$): 1(0), 2(0.10), 3(0.20), 4(0.40), 5(0.80), 6(1.80), 7(3.78), 8(7.71), 9(56.9), 10(106), 11(154), 12(202).

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To assess the effect of electrolyte on the equilibrium constant for adduct formation, $[CoL^2]^+$ was titrated with each base in DMF without added TBAP. Stoichiometry and log K values are reported in Table II. Within the limits of error, electrolyte has no effect on the adduct formation equilibrium constants.

The ordering of base strength toward $[CoL^1]^+$ is the same in DMF and An (Table II),[1] though the stronger donor ability of DMF is reflected in uniformly smaller log K values. Equilibrium constants for binding of Br^- and MeIm are about an order of magnitude larger for $[CoL^2]^+$ than for $[CoL^1]^+$ in both An and DMF, whereas pyridine does not discriminate between $[CoL^2]^+$ and $[CoL^1]^+$ in either solvent. Ph_3P binds more strongly than expected, as based on σ-donor ability. Of the four donors,

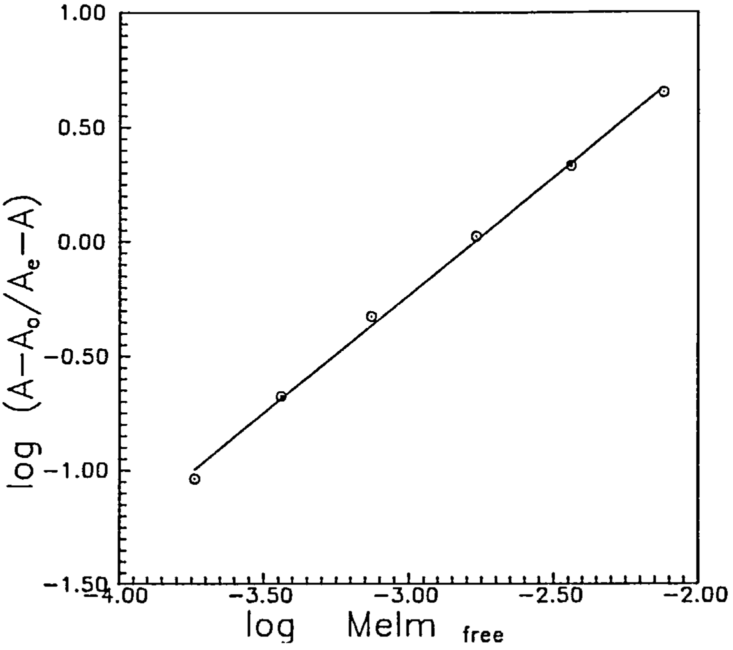

FIGURE 4 Plot of the data from Figure 3 at λ = 650 nm according to (*2*); see text.

TABLE II
Equilibrium constants for formation of CoL(B)$^+$ (charge omitted for clarity in table entries).

Adduct	Solvent	Electrolyte	q	log K	Reference
CoL^1 (MeIm)	An	0.1 M TBAP	1.0	4.0 ± 0.1	1
CoL^1 (py)			1.0	3.36 ± 0.08	
CoL^1 (Br)			1.0	2.36 ± 0.08	
CoL^2 (MeIm)			1.10	5.10 ± 0.02	
CoL^2 (py)			1.01	3.65 ± 0.01	
CoL^2 (Br)			1.04	3.26 ± 0.05	
CoL^1 (Ph_3P)	DMF		0.98	3.2 ± 0.3	this work
CoL^1 (MeIm)			0.98	2.7 ± 0.2	
CoL^1 (py)			1.0	2.43 ± 0.05	
CoL^1 (Br)				≈1.5	
CoL^2 (MeIm)			0.95	3.60 ± 0.04	
CoL^2 (Ph_3P)			1.0	3.2 ± 0.1	
CoL^2 (Br)			1.2	2.93 ± 0.02	
CoL^2 (py)			0.91	2.36 ± 0.02	
CoL^2 (MeIm)		none	0.88	3.4 ± 0.1	
CoL^2 (Ph_3P)			0.95	3.08 ± 0.07	
CoL^2 (Br)			0.96	2.85 ± 0.06	
CoL^2 (py)			0.89	2.20 ± 0.05	

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it forms the strongest adduct with $[CoL^1]^+$, and is unusual in binding relatively more strongly to $[CoL^1]^+$ than to $[CoL^2]^+$. Preference of this ligand for $[CoL^1]^+$ can be understood in terms of two factors. First, Ph_3P forms stable complexes with electron-rich metals by functioning as a π-acceptor. There is more electron density on the Co^I centre in $[CoL^1]^+$ than in $[CoL^2]^+$ because L^2 is a better π-acceptor than L^1. Synergic σ–π bonding between Co^I and Ph_3P is thus more effective for $[CoL^1]^+$. Secondly, binding of Ph_3P is readily influenced by steric factors. Approach to the Co^I centre in $[CoL^2]^+$ may be restricted by the bulky phenyl substituents of the macrocyclic ligand.

Finally, the possibility that the Lewis acidity of these complexes is due to the π-acidity of axially-coordinated An rather than to that of the macrocycle is ruled out, since both complexes act as effective Lewis acids in the non-backbonding solvent DMF.

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