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Nickel(II) and Cobalt(II) Perchlorate Complexes of 4-Substituted Benzamides

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Nickel(II) and cobalt(II) complexes of 4-substituted benzamides with the general formula $[M(ZC_7H_6NO)_6]$- $(ClO_4)_2$ where $Z=OCH_3$, CH_3, H, Cl, NO_2 were investigated. The magnetic and spectral data are consistent with high spin octahedral complexes. The infrared shifts of the amide I and C–N absorption bands upon complexation indicate that coordination is occuring through the carbonyl oxygen. Evidence for π-back-bonding (metal to ligand) from ligand field parameter considerations is also discussed.

Introduction

Much interest has recently been centered on studies of systematic series of transition metal complexes. Series of various transition metal complexes with 4-substituted pyridine N-oxides[2-4] as ligands have been carried out. In these instances correlations between nitrogen-oxygen stretching frequencies and the appropriate Hammet σ values or σ_{PyNO}[5] constants have been found for both the free ligand and transition metal complexes of the ligand.

Few coordination complexes of primary amides[6-19] have previously been studied. Complexes of benzamide that have been reported in the literature[13-19] are those of BCl_3, BBr_3, $TiCl_4$, $SnCl_4$, SO_3, $SbCl_5$, $AlCl_3$, $BeCl_2$, $CuCl_2$, $CdCl_2$, $CdBr_2$, $Cd(NO_3)_2$, $SbCl_3$, and

$BiCl_3$. It has been generally shown that coordination for the primary amides occurs through the carbonyl oxygen. Six coordinate complexes of benzamide with transition elements, however, have not been studied. This paper reports a study of a systematic series of octahedral nickel(II) and cobalt(II) perchlorate complexes with 4-substituted benzamides ($4-ZC_7H_6NO$) as ligands.

Experimental Section

Reagents. Benzamide (practical grade) was obtained from Matheson Coleman and Bell. The 4-nitrobenzamide and 4-toluamide were obtained from Eastman Organic Chemicals. The 4-methoxy and 4-chloro derivatives were obtained from K&K Laboratories. All, except the benzamide, were used without further purifiaction. Benzamide was purified by recrystallization from chloroform. Analytical reagent grade acetone was used as a solvent.

Synthesis. Most of the complexes were prepared by addition of the ligand to the metal salt, which had been dissolved in triethylorthoformate, so as to obtain an 8:1 molar ratio. Precipitation· of the complex occurred within 2 to 3 minutes after mixing. These complexes were filtered, washed with large quantities of ether, and dried in vacuo over phosphorous pentoxide. The 4-methoxy complexes of cobalt and nickel and the 4-nitro complex of cobalt were prepared in a similar manner with the exception that 2,2-dimethoxypropane was used as the solvent. The only complex requiring purification was the nickel complex of 4-nitrobenzamide. It was purified by recrystallization from benzene. All of the complexes were found to be slightly hygroscopic.

Elemental Analysis. Carbon, hydrogen, and nitrogen analyses were performed by Alfred Bernhardt Laboratorium in Mulheim Germany. An EDTA titrimetric method[20] was used to obtain metal analyses. The analytical data appear in Table I.

Electronic Spectra. Solution and solid state[21] spectra were run in the 350-1500 mμ region on a

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Table I. Analytical Data and Melting Points for $[M(4\text{-}ZC_7H_6NO)_6](ClO_4)_2 \cdot XH_2O$ Complexes

M	Z	X	C Found	C Calcd.	H Found	H Calcd.	N Found	N Calcd.	M Found	M Calcd.	M.P.
Ni	OCH₃	1	48.50	48.73	4.74	4.77	7.24	7.10	4.93	4.96	263-266°C
Ni	CH₃	1	53.19	53.03	5.29	5.19	7.65	7.73	5.58	5.40	264-271°C
Ni	H	0	50.90	51.24	4.58	4.30	8.38	8.54	6.07	5.96	267-271°C
Ni	Cl	0	42.12	42.36	3.21	3.05	6.95	7.06	4.70	4.93	260-262°C
Ni	NO₂	3	38.79	38.57	3.40	3.24	11.88	12.85	4.63	4.49	241-248°C
Co	OCH₃	1	48.79	48.73	4.69	4.77	7.39	7.10	4.84	4.98	235-240°C
Co	CH₃	1	53.37	53.04	5.27	5.19	7.84	7.73	5.41	5.42	235-244°C
Co	H	0	50.71	51.23	4.35	4.30	8.65	8.54	5.88	5.98	244-250°C
Co	Cl	1	42.27	41.73	3.19	3.17	6.19	6.95	4.72	4.87	234-238°C
Co	NO₂	1	39.98	39.63	3.54	3.01	13.15	13.20	4.53	4.63	233-238°C

Table II. Band Assignments in Electronic Spectra of $[M(4\text{-}ZCH_6NO)_6](ClO_4)_2$ Complexes

M	OCH₃ $\nu_{max}{}^a$	OCH₃ ε_{max}	CH₃ ν_{max}	CH₃ ε_{max}	H ν_{max}	H ε_{max}	Cl ν_{max}	Cl ε_{max}	NO₂ ν_{max}	NO₂ ε_{max}	Assignment
Ni	24600	17.5	24800	17.1	24800	13.5	24900	14.2	b	—	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$
	14700	4.75	14700	4.85	14800	5.00	14900	6.75	15400	4.25	$\rightarrow {}^3T_{1g}(F)$
	13400	5.50	13400	5.50	13400	5.15	13400	6.75	13600	4.75	$\rightarrow {}^1E_g$
	8310	6.50	8260	6.50	8310	5.85	8200	6.25	8280	4.85	$\rightarrow {}^3T_{2g}$
Co	20100	22.5	20100	17.8	20400	13.5	20200	23.5	20400	14.8	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
	18900	27.8	19000	22.0	18900	19.0	19100	25.5	19200	17.8	$\rightarrow {}^4A_{2g}$
	7740	6.25	7800	4.65	7730	4.00	7830	4.70	7860	4.75	$\rightarrow {}^4T_{2g}$

^{a} All absorption maxima listed are in cm^{-1}. ^{b} This absorption was masked by a charge transfer peak.

Table III. Ligand Field Parameters, Magnetic Moments, and Conductance Data

M	Z	Dq	β	ν^a Calcd. (cm^{-1})	ν^a Obs. (cm^{-1})	T°K	$10^6\chi_m$	$10^6\chi_m$	μ_{eff} (BM)	conc., M	Λ_m cm² mho mole⁻¹
Ni	OCH₃	831	0.85	13800	14000	296	3720	4320	3.21	2×10⁻³	188
Ni	CH₃	826	0.87	13800	14100	297	4360	4920	3.43	2×10⁻¹	188
Ni	H	831	0.87	13800	14100	297	4510	4990	3.46	2×10⁻³	193
Ni	Cl	820	0.89	13700	14100	297	3800	4390	3.24	2×10⁻³	187
Ni	NO₂	828	---	---	---	296	4390	4970	3.44	2×10⁻³	109
Co	OCH₃	1010	0.94	18900	18900	297	11600	12000	5.41	2×10⁻³	181
Co	CH₃	1010	0.93	19000	19000	297	11100	11600	5.28	2×10⁻³	183
Co	H	1010	0.96	18900	18900	297	11200	11700	5.28	2×10⁻³	181
Co	Cl	1020	0.94	19100	19100	297	11000	11600	5.28	2×10⁻¹	182
Co	NO₂	1020	0.95	19200	19200	297	10800	11400	5.21	2×10⁻³	183

^{a} The values of ν_{obs} for nickel(II) are the averages of the $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ and $^3A_{2g} \rightarrow {}^1E_g$ transitions, while those for cobalt(II) are the $^4T_{1g}(F) \rightarrow {}^4A_{2g}$ transitions.

Table IV. Infrared Frequencies ^{a} for $[M(4\text{-}ZC_7H_6NO)_6](ClO_4)_2$ Complexes

M	Z	Amide I Complex	Amide I Ligand	C—N Stretch Complex	C—N Stretch Ligand
Ni	OCH₃	1650	1637	1428	1417
Co	OCH₃	1649	1637	1432	1417
Ni	CH₃	1649	1664	1417	1410
Co	CH₃	1649	1664	1419	1410
Ni	H	1648	1653	1438	1395
Co	H	1647	1653	1435	1395
Ni	Cl	1650	1652	1418	1403
Co	Cl	1651	1652	1419	1403
Ni	NO₂	1647	1672	1420	1412
Co	NO₂	1657	1672	1420	1412

^{a} Infrared absorption frequencies are listed in cm^{-1}.

solution at a concentration of $2 \times 10^{-2} M$ in 1 cm cells with a 6:1 molar ratio of excess ligand to complex to retard dissociation. The ligand field parameters Dq and β for nickel(II) and cobalt(II) were calculated as described by Drago[22] and Ballhausen,[23] respectively. These values appear in Table III.

Magnetic Moments. The magnetic moments were determined by the Gouy technique using a Varian e.p.r. magnet. The compound used as a calibrant was $Hg[Co(SCN)_4]$.[24] Pascal's constants[25] were used to calculate the diamagnetic corrections. The calculated magnetic moments are presented in Table III.

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Cary Model 14 recording spectrophotometer. All spectra listed in Table II were obtained in acetone

Infrared Spectra. Infrared spectra of the ligands and their complexes were obtained for nujol mulls of the samples, using a Perkin-Elmer Model 421 with 521 interchange or a Beckman IR 5A recording spectrophotometer. Calibration on the IR 5A was achieved with known frequency bands of polystyrene. The data obtained are listed in Table IV.

Conductance Data. Conductance measurements were made on an Industrial Instruments conductance bridge model RC16B2 at 25°C using acetone as a solvent. These data appear in Table III.

Results and Discussion

The conductance data suggest the presence of 2:1 electrolytes in acetone for all of the complexes except the nickel complex of 4-nitrobenzamide. The conductance data on this complex suggest that it is a 1:1 electrolyte in acetone. However, with a six-fold excess of 4-nitrobenzamide in acetone the value of the molar conductance for the complex was found to be 180 cm^2 mho mole^{-1} which indicates that under these conditions this complex is also behaving as a 2:1 electrolyte. Similar results were obtained in this laboratory for the 4-nitroacetanilide complex of nickel(II) perchlorate.[26] The fact that this occurred with only the 4-nitro-substituted ligands is reasonable since they are the weaker bases, thus making it possible for the perchlorate ion to compete for a coordination site. The occurance of these phenomena in the case of the nickel(II) complexes and not the cobalt(II) complexes implies that cobalt(II) is a stronger Lewis acid than nickel(II).

Most of the calculated magnetic moments are within the allowed range for nickel(II) and cobalt(II) high spin octahedral complexes. The values are larger than those usually reported for similar nickel(II) (2.80-3.50 BM)[25] and cobalt(II) (4.30-5.20 BM)[25] complexes. This suggests that these complexes have a large orbital contribution to the magnetic moment.

Primary amides are usually characterized by the following absorption bands in the solid state infrared spectra:[27] N–H stretching vibrations found near 3350 and 3180 cm^{-1}, amide I (due mainly to the carbonyl group) absorption band near 1650 cm^{-1}, amide II peak (N–H deformation believed to be predominate factor) around 1650-1620 cm^{-1}, and an absorption band (assignable to C–N stretching mode) in the 1418-1399 cm^{-1} region. All of these absorption bands were assignable in the infrared spectra of the ligands. However, the amide II absorption band changed upon complex formation in frequency and intensity such that it could not be assigned.

Two absorption bands, appearing around 3370 and 3180 cm^{-1}, in the solid state infrared spectra of all the free ligands except that of 4-nitrobenzamide were assigned to N–H stretching frequencies. Upon complexation three bands appeared in this region around 3400, 3350, and 3250 cm^{-1}. Gerrard, *et al.*,[16] have

proposed that the third peak could possibly indicate two geometrical isomers, while Penland, *et al.*,[28] point out that this third peak often appears in the infrared spectra of free amides. It was found that solution spectra of the free ligands in dioxane showed several (4-5) peaks in this region. In the case of 4-nitrobenzamide several absorption bands were found in this region in both the solid state and solution spectra. The fact that the number and the frequencies of the absorption bands in this region for the free ligands vary from solid to liquid state spectra indicates that different degrees of hydrogen bonding are occurring. Therefore, the third band observed in the spectra of the complexes is probably assignable to a form of hydrogen bonding. The amide I and C–N absorption frequencies are reported in Table IV. In all the spectra of the complexes the amide I peak shows up as a distinct doublet, but with only 5-10 cm^{-1} separating the two peaks. The C–N stretching mode appeared, usually, as a shoulder on the nujol peak at 1460 cm^{-1}.

Shifts in the absorption frequencies of the amide I to lower energy and the C–N to higher energy upon complex formation are consistent with bonding through the carbonyl oxygen.[13,29-30] All of the complexes reported here show a shift of the amide I to lower frequencies by 0-20 cm^{-1} with the exception of the 4-methoxybenzamide complexes, and an increase in frequency of the C–N stretching mode. These shifts indicate that the ligands are coordinated to the metal through the carbonyl oxygen. It should be noted that all of the amide I absorption bands come at approximately the same frequency (1647-1657 cm^{-1}) in the complexes while the range in the free ligands is from 1637-1672 cm^{-1}. No correlation between Hammett σ values and amide I stretching frequencies was found. This is not unreasonable since the amide I band is not a pure carbonyl stretching mode[27] but is coupled with other vibrations.

The assumption of octahedral symmetry was based on the similarity of the visible spectra to other known octahedral complexes. The ligand field parameter, Dq, was found to vary with the concentration of excess ligand in the solution spectra. In going from a 0:1 molar excess of ligand to the nickel complex of benzamide to a 10:1 molar ratio in chloroacetonitrile, Dq was found to vary from 895 to 822 cm^{-1}. A similar variation of Dq with amount of added excess ligand was observed for the solvents acetonitrile and nitromethane. With acetone as a solvent the amount of excess ligand was varied from a 0:1 to a 15:1 molar ratio with a resulting variation of Dq from 831 to 819 cm^{-1}. The Dq value found for the solid state was 846 cm^{-1}. The variation in Dq with the amount of added excess ligand indicates that varying degrees of dissociation of the complexes are occurring in the solvents. Upon dissociation of the complexes, solvent molecules or perchlorate anions must enter the coordination sphere of the metal ion to replace

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the ligand molecules lost. Thus, complexes with ligand, solvent molecules, and perchlorate anions in varying ratios according to the degree of dissociation can exist in solution resulting in the observed variation of Dq. Because of solubility problems and the effect of excess ligand on Dq in the various solvents tried, all spectra were run in acetone at a 6:1 molar ratio of excess ligand to metal complex. Based upon the molar conductance for $Ni(NO_2C_7H_6NO)_6(ClO_4)_2$ in acetone with a 6:1 ratio of excess ligand and the close agreement between the calculated spectra and observed spectra (Table III), it appears that the reported spectra are for the six coordinate complexes of benzamide.

There are four factors which contribute to Dq: steric effects, $p\pi-d\pi$ ligand to metal bonding, π-back-bonding (metal to ligand), and the relative basicities of the ligands. Based on structural models of the nickel(II) and cobalt(II) octahedral complexes of 4-substituted benzamides, quinoline N-oxides, and pyridine N-oxides, the benzamide complexes are more sterically hindered. This means that on this consideration alone the Dq values for the pyridine and quinoline N-oxide complexes should be greater than those of the benzamides. The amount of $p\pi-d\pi$ bonding should be negligible in all cases since the π-bonding d orbitals involved are already filled. The pKa's of all the 4-substituted benzamides (−1.80 for

the p-methoxy to −3.23 for the p-nitro)[31] are much lower than those of the 4-substituted pyridine N-oxides (2.05 for the p-methoxy to −1.7 for the p-nitro)[32] and the 4-substituted quinoline N-oxides (1.62 for the p-methoxy to −1.39 for the p-nitro).[32] The basicities, therefore, also favor higher Dq values for the pyridine and quinoline N-oxides since they are much stronger bases than the benzamides. The Dq values reported here, however, are of the same magnitude or larger than those reported for nickel(II) and cobalt(II) complexes of the above mentioned ligands. This suggests that the contribution of π-back-bonding to the Dq values of the benzamide complexes must be very large. If this is the case, varying amounts of π-back-bonding might be expected as the 4-substituent on benzamide is changed. This is indeed substantiated by two factors: first, all the Dq values are approximately the same for complexes of the different metals; and secondly, all the infrared carbonyl absorption bands for all the complexes appear at about the same frequency. These factors suggest that π-back-bonding is counteracting the electron donating and withdrawing effects of the various 4-substituents on the benzamide molecules.

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