Contribution From the Department of Chemistry
University of Utah, Salt Lake City, Utah 84112, U.S.A.

A Study of 4-Substituted Acetanilide Complexes of Nickel(II) and Cobalt(II) Perchlorates

R. W. Gray, M. B. Welch,[1] and R. O. Ragsdale

Received October 22, 1968

Complexes of cobalt(II) and nickel(II) perchlorates with 4-substituted acetanilides as ligands are reported for the first time. The stoichiometries of the complexes were found to be of the type $[M(4\text{-}ZC_8H_8NO)_6](ClO_4)_2$ *where M is the metal ion and* $Z = OCH_3, CH_3, H, Cl, Br, NO_2$*. The ligand-metal bond is assigned through the carbonyl oxygen on the basis of infrared spectral shifts upon complexation. The visible spectra and ligand field parameters of the complexes are also reported and discussed.*

Introduction

Systematic studies of series of substituted aromatic amine N-oxides[2-6] and benzamides[7] have been carried out. The changes in the infrared stretching frequencies for the nitrogen-oxygen and carbon-oxygen bonds in a series of complexes which is brought about by the various substituents have proven to be of considerable interest. The effect of the substituents upon the ligand field parameter, Dq, has also been investigated. Studies of the donor properties of primary[8] and secondary[9] amides have also been of interest since amides have two possible sites, the carbonyl oxygen and the amide nitrogen, through which coordination may occur. Most workers have assigned coordination as occuring through the carbonyl oxygen on the basis of infrared spectral shifts.

Several complexes with acetanilide as the ligand have been characterized with a wide range of Lewis acid to ligand molar ratios. These complexes include the following (where L represents acetanilide): $SO_3 . L$,[10] $AlCl_3 . L$,[10,11] $BCl_3 . L$,[8] $SbCl_5 . 2L$,[10] $SnCl_4 . 2L$,[10,11] $TiCl_4 . 2L$,[10] $SnBr_4 . 2L$,[12] $SbCl_5 . 3L$,[10] $SnCl_4 . 4L$,[10] $TiCl_4 . 4L$,[10] $WOCl_4 . 4L$,[13] $TiBr_4 . 4L$,[14] $WBr_5 . 5L$,[15] $WCl_6 . 6L$.[16] A few complexes of 4-substituted acetanilides have also been reported: WCl_6 . 6-(4-aminoacetanilide),[16] WBr_5 . 5(4-aminoacetanilide),[15] $WOCl_4$. 4(4-aminoacetanilide),[13] and BCl_3 . 1(4-methoxyacetanilide).[8] However, six coordinate complexes of nickel(II) and cobalt(II) perchlorates with acetanilide and 4-substituted acetanilides as ligands have not been described. This paper reports the preparation and characterization of octahedral complexes of these transition metal salts with a series of 4-substituted acetanilides.

Experimental Section

Reagents. Acetanilide, *p*-aceto(toluidine (4-methylacetanilide), and 4-bromoacetanilide were obtained from Matheson Coleman and Bell, 4-chloroacetanilide and *p*-acetanisidine (4-methoxyacetanilide) from Eastman Organic Chemicals and 4-nitroacetanilide from Fisher Chemical Company. The ligands were used without further purification. Solvents used were analytical reagent grade acetone, and Matheson Coleman and Bell spectroquality nitromethane.

Preparation of Complexes. Hexaquonickel(II) and cobalt(II) perchlorates were stirred in triethylorthoformate to remove the water of hydration. Solid ligand was then added in 8:1, 7:1, and 6:1 molar ratios of ligand to metal salt. These molar ratios were varied according to the ease of washing the unreacted ligand out of the product. The product was washed with chloroform and/or ether, then dried in vacuo over phosphorus pentoxide. The yields varied from 30% to 86%. All of the complexes were found to be slightly hygroscopic. Analyses were obtained as previously described.[5]

Electronic Spectra. Visible and near infrared spectra (330 to 1500 mμ) were measured with a Cary 14 recording spectrophotometer. The spectra of the complexes with the exception of the 4-nitroacetanilide complex of nickel(II) were taken using acetone solutions, 0·02 molar in the complex with a 0.12 molar excess of the appropriate ligand. The purpose of

---

(1) National Defense Education Trainee, 1967-1970.
(2) R. Whyman, W. E. Hatfield, and J. S. Paschal, *Inorg. Chim. Acta*, *1*, 113 (1967).
(3) F. E. Dickson, E. W. Gowling, and F. F. Bentley, *Inorg. Chem.* 6, 1099 (1967).
(4) D. W. Herlocker, R. S. Drago, and V. I. Meek, *ibid.*, *5*, 2009 (1966).
(5) J. H. Nelson, L. C. Nathan, and R. O. Ragsdale, *ibid.*, *7*, 1840 (1968).
(6) J. H. Nelson and R. O. Ragsdale, *Inorg. Chim. Acta*, *2*, 439 (1968).
(7) M. B. Welch, R. S. Stephens, and R. O. Ragsdale, *ibid.*, *2*, 367 (1968).
(8) W. Gerrard, M. F. Lappert, H. Pyszora, and J. W. Wallis, *J. Chem. Soc.*, 2144 (1960).
(9) R. A. Mackay and E. J. Poziomek, *Inorg. Chem.*, *7*, 1454 (1968).
(10) R. C. Paul, B. R. Sreenathan, and S. L. Chadha, *J. Inorg. Nucl. Chem.*, *28*, 1225 (1966).
(11) R. C. Aggarwal and P. P. Singh, *Z. Anorg. Allgem. Chem.*, *332*, 103 (1964).
(12) R. C. Aggarwal and P. P. Singh, *J. Inorg. Nucl. Chem.*, *28*, 1655 (1966).
(13) S. Prasad and K. S. R. Krishnaiah, *J. Ind. Chem. Soc.*, *38*, 757 (1961).
(14) S. Prasad and R. C. Srivastava, *ibid.*, *39*, 11 (1962).
(15) S. Prasad and R. Swarup, *ibid.*, *42*, 789 (1965).
(16) S. Prasad and K. S. R. Krishnaiah, *ibid.*, *38*, 177 (1961).

Table I. Elemental analyses for Hexakis (4-Z-Acetanilide) Complexes of Nickel(II) and Cobalt(II) Perchlorates.

Z	% C Found	% C Calcd.	% H Found	% H Calcd.	% N Found	% N Calcd.	% Metal Found	% Metal Calcd.
				Nickel(II) Perchlorate Complexes				
OCH_3	51.69	51.97	5.35	5.33	6.11	6.73	4.70	4.70
CH_3 [a]	55.21	55.43	5.88	5.86	6.99	7.18	5.30	5.02
H [a]	53.11	53.06	5.20	5.19	7.60	7.73	5.65	5.40
Br	38.46	37.39	3.64	3.14	5.67	5.45	3.59	3.81
Cl [b]	44.15	43.97	3.98	4.00	6.09	6.41	5.00	4.48
NO_2	43.91	43.05	4.44	3.61	13.68	12.55	4.34	4.39
				Cobalt(II) Perchlorate Complexes				
OCH_3 [a]	50.93	51.23	5.25	5.41	6.61	6.64	4.69	4.65
CH_3	56.44	56.30	5.45	5.78	7.16	7.30	4.76	5.11
H [a]	53.03	53.06	5.07	5.19	7.85	7.73	5.48	5.45
Br [a]	37.00	36.95	3.40	3.23	5.25	5.37	3.74	3.78
Cl	44.40	45.21	3.60	3.79	7.19	6.59	4.26	4.62
NO_2	44.60	43.05	4.11	3.61	12.61	12.55	4.24	4.40

[a] Calculations for monohydrate. [b] Calculations for dihydrate.

Table II. Infrared Mull Spectra of the Free Ligands and Their Metal Perchlorate Complexes.

Compound	N-H Stretch	Amide I	Amide II	Amide III	C-N[12] Stretch	C-N[21] Stretch
4-Methoxy-acetanilide	3257	1664	1524	1285	1031	1245
Ni^{2+} Complex	3344	1634	[a]	1285	1032	1250
Co^{2+} Complex	3356	1637	[a]	1289	1032	1250
4-Methyl-acetanilide	3311	1667	1534	1319	1015	1267
Ni^{2+} Complex	3333	1637	1536	1324	1022	1271
Co^{2+} Complex	3333	1637	1541	1324	1016	1274
Acetanilide	3300	1664	1538	1323	1013	1263
Ni^{2+} Complex	3356	1634	[a]	1332	1017	1274
Co^{2+} Complex	3344	1634	1541	1332	1017	1274
4-Bromo-acetanilide	3322	1669	1534	1309	1008	1256
Ni^{2+} Complex	3322	1637	1538	1321	1012	1255
Co^{2+} Complex	3322	1634	1538	1319	1012	1269
4-Chloro-acetanilide	3311	1669	1538	1314	1011	1261
Ni^{2+} Complex	3322	1634	1536	1318	1016	1264
Co^{2+} Complex	3322	1634	1536	1318	1014	1267
4-Nitro-acetanilide	3329	1684	1541	1302	1006	1267
Ni^{2+} Complex	3333	1645	[b]	[c]	1008	1256
Co^{2+} Complex	3356	1650	[b]	1314	1013	1272

[a] Band masked by ring absorption. [b] Band masked by nitro group absorption. [c] Band too weak to distinguish.

Table III. Magnetic Moments, Melting Points, and Conductance Data for Complexes of the Type $[M(4\text{-}ZC_8H_8NO)_6](ClO_4)_2$.

M	Z	m.p. (°C)	Λ_m ($cm^2ohm^{-1}mole^{-1}$)	$10^6\chi_m$	$10^6\chi_m'$	T(°K)	μ_{eff} (BM)
Ni	OCH_3	140-145	167 [a]	4510	5150	297	3.51
Co	OCH_3	119-121	173	12700	13400	297	5.66
Ni	CH_3	169-172	163	4990	5620	297	3.67
Co	CH_3	149-152	183	11900	12500	297	5.48
Ni	H	179-182	164	4340	4900	297	3.43
Co	H	164-167	172	11900	12400	298	5.46
Ni	Br	188-195	146	3480	4190	297	3.17
Co	Br	186-190	174	11800	12500	298	5.49
Ni	Cl	206-210	165	4970	5640	297	3.68
Co	Cl	194-197	175	11700	12300	297	5.43
Ni	NO_2	208-217	122	4230	4840	297	3.40
Co	NO_2	213-217	172	12300	12900	298	5.57

[a] Conductance values were taken at 2×10^{-3} molar concentrations.

Table IV. Visible Spectra of $[M(4\text{-}ZC_8H_8NO)_6](ClO_4)_2$ in Acetone Solution.[a]

M		Z OCH$_3$	CH$_3$	H	Br	Cl	NO$_2$	Assignments
Ni^{2+}	ν_1 [b]	8180	8120	8100	8150	8140	8250[d]	$^3A_{2g} \to {}^3T_{2g}$
	ε_1 [c]	6.5	5.6	4.8	3.8	3.5	—	
	ν_2	13400	13400	13400	13600	13700	13000	$\to {}^3T_{1g}(F)$
	ε_2	6.5	5.1	3.8	3.4	3.5		
	ν_3	15100	15000	14900	15100	15100	14800	$\to {}^1E_g(D)$
	ε_3	5.0	4.7	3.0	2.9	3.2	—	
	ν_4	25500	24900	24900	25200	25300	23000	$\to {}^3T_{1g}(P)$
	ε_4	26.0	20.8	10.2	12.0	12.5	—	
Co^{2+}	ν_1	7830	7650	7860	7840	8040	7920	$^4T_{1g}(F) \to {}^4T_{2g}$
	ε_1	5.7	6.0	16.6	24.0	4.3	4.0	
	ν_2	19400	19200	19700	19800	19600	19900	$\to {}^4A_{2g}$
	ε_2	33.0	18.7	65.0	85.3	18.1	19.8	
	ν_3	20700	20600	20800	20700	20700	20800	$\to {}^4T_{1g}(P)$
	ε_3	28.0	15.5	65.4	86.5	17.5	20.1	

[a] 0.02 *M* solution of complex with 6 : 1 molar excess of ligand. [b] Absorption maxima reported in cm^{-1}. [c] Extinction coefficient (l mole^{-1}cm^{-1}). [d] Mull spectrum.

Table V. Ligand field calculations for $[M(4\text{-}ZC_8H_8NO)_6](ClO_4)_2$

Z	ν_2 calc'd	ν_2 [a] obs	Dq (cm^{-1})	β
NICKEL PERCHLORATE COMPLEXES				
OCH$_3$	13600	13400	818	0.93
CH$_3$	13600	13400	812	0.89
H	13600	13400	810	0.89
Br	13700	13600	815	0.91
Cl	13600	13700	814	0.91
NO$_2$	13700	13900 [b]	825	0.75
COBALT PERCHLORATE COMPLEXES				
OCH$_3$	19400	19400	1030	0.97
CH$_3$	19200	19200	1020	0.98
H	19700	19700	1050	0.98
Br	19800	19800	1050	0.98
Cl	19600	19600	1040	0.96
NO$_2$	19900	19900	1060	0.98

[a] The values of ν_{obs} correspond for nickel(II) to the transition $^3A_{2g} \to {}^3T_{1g}(F)$ and for cobalt(II) to the transition $^4T_{1g} \to {}^4T_{2g}$. [b] In this case ν_{obs} corresponds to the average of the two transitions, $^3A_{2g} \to {}^3T_{2g}$ and $^3A_{2g} \to {}^3T_{1g}(F)$.

the excess ligand in solution was to shift the dissociation equilibrium to favor the undissociated complex. Measurements were made using Beckman 1 cm matched quartz cells with an acetone blank. The electronic spectrum of the nickel(II) complex of 4-nitroacetanilide was taken by means of a Nujol mull.[17] These data appear in Table IV.

Magnetic Moments. The magnetic susceptibilities were determined by the Gouy technique. The calibrant used was $Hg[Co(SCN)_4]$.[18] Diamagnetic corrections were calculated using Pascal's constants.[19] The calculated magnetic moments are presented in Table III.

Infrared Spectra and Conductance Data. Infrared absorption spectra of the ligands and their complexes were obtained on a Beckman IR5A infrared spectrophotometer as Nujol mulls. Conductance measurements were made at a temperature of 24° to 26°C using 0.002 molar solutions of the complexes in spectroquality nitromethane. The data are listed in Tables II and III.

Results and Discussion

The stoichiometries indicated by the analytical results found in Table I are reasonably consistent with 6: 1 ligand to metal coordination for the acetanilides studied. Some discrepancy between theoretical and analytical percentage composition may be explained by the difficulty of removing unreacted ligand from the products. Both the Ni^{II} and Co^{II} complexes with 4-nitroacetanilide and the Ni^{II} complex with 4-bromoacetanilide gave considerable difficulty in this respect. Vigorous washing tended to remove some of the ligand from these complexes, while limited washing did not remove all of the excess ligand. In an effort to keep the complexes intact, these samples were not washed extensively. As a result, the analytical percentages of carbon, hydrogen, and nitrogen were found to be higher than the theoretical values, due to unreacted ligand.

Conductance data presented in Table III suggest 2: 1 electrolytes in nitromethane for all of the complexes with the exception of 4-nitroacetanilide complex of nickel(II). The presence of 2: 1 electrolytes are consistent for complexes of a dipositive complex cation, $M(4\text{-}ZC_8H_8NO)_6^{2+}$, with two perchlorate anions. In the case of the 4-nitro complex of nickel(II) the conductance value indicates a 1: 1 electrolyte. This seems to suggest that the complex is dissociating and perchlorate anions are, at least in part, replacing the dissociated ligand. Similar conductance values were found for the 4-nitrobenzamide complex of nickel(II).[7]

The calculated magnetic moments for most of the nickel(II) complex are all within the allowed range for high spin octahedral complexes (2.80-3.50 BM).[19]

---

(17) R. H. Lee, E. Griswold, and J. Kleinberg, *Inorg. Chem.*, 3, 1278 (1964).

(18) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).

(19) B. N. Figgis and J. Lewis, in *Modern Coordination Chemistry*, J. Lewis and R. G. Wilkins ed., Interscience, New York, 1960 pp. 400-454.

Those of cobalt(II) are, on the other hand, larger than those usually reported for cobalt(II) high spin octahedral complexes (4.30-5.20 BM).[19] However, the effect of spin-orbit coupling in cobalt(II) is such that the next higher spin only value man be exceeded. Values up to 5.5 BM[19] have previously been observed.

The most commonly reported infrared absorption frequencies are the characteristic N-H stretching frequency, amide I, amide II, amide III, and C-N stretching bands. There has been much controversy as to the exact assignments for the amide vibrational modes. Bellamy[20] has made the following assignments: the amide I band (very close to 1640 cm^{-1}) has been assigned as being almost exclusively the carbonyl stretching frequency; the amide II band (appearing around 1550 cm^{-1}) has been assigned to a mixed N-H deformation and C-N stretching mode; and the amide III band (1305-1200 cm^{-1}) has been assigned to a mixed vibration of C-N and N-H vibrational modes. The assignment of a pure C-N stretching frequency presents some difficulty. Aggarwal and Singh[12] have assigned the C-N stretching frequency to the absorption in the 1010 cm^{-1} region while Szymanski[21] reported the C-N stretching frequency in the 1260 cm^{-1} region.

Generally amides have been observed to bond through the carbonyl oxygen.[22] Consequently one would expect the amide I band to shift to lower energy while any stretching frequencies having predominate C-N character should shift to higher energy. The amide I bands of the cmplexes studied showed shifts of 30 to 39 cm^{-1} to lower frequencies when compared to the amide I absorption bands of the free ligands. The amide III band, on the other hand, consistently shifted to higher energy. This shift can be attributed to the C-N character of the amide III band. However, it is also possible that the bands found around 1010 cm^{-1} and 1260 cm^{-1} have some C-N stretching character since both bands are generally shifted to higher energy upon complexation. On the basis of the above shifts, it appears that coordination is occuring through the carbonyl oxygen for the nickel(II) and cobalt(II) complexes.

Some additional support for cordination through oxygen comes from a consideration of molecular models of the complexes. It was found that six ligand molecules could be placed around a central metal ion if coordination occurs through the oxygen. Attempts to make models with coordination through nitrogen failed to produce more than four ligands bonded to the metal ion·

The visible spectra absorption maxima of the complexes along with their extinction coefficients are listed in Table IV. The energy transition assignments were made on the basis of relative intensities and the close agreement between the calculated and observed transitions. The electronic spectral data in Table IV are typical of octahedral nickel(II) and cobalt(II) complexes.

The visible spectra of the cobalt(II) and nickel(II) complexes were solved in the weak field formalism.[23,24] The Dq values given in Table IV range from 810 to 825 cm^{-1} for the nickel(II) complexes and from 1020 to 1060 cm^{-1} for the cobalt(II) complexes. These values do not vary with sufficient magnitude or regularity to justify any ordering of the Dq values in a spectrochemical series. It is, however, interesting to note that the Dq values found for both the 4-nitroacetanilide complexes are higher than those of the other complexes. The nitro group has a large deactivating effect which would cause the ligand to be less basic by withdrawal of electron density from the carbonyl oxygen. This in turn would produce a weaker field and a lower value of Dq if the only factor of concern were the donor ability of the ligand. Since experimentally for each series of complexes the Dq values are virtually constant, another factor must also affect the Dq values. It is suggested that π-back-bonding (metal to ligand) is enhanced by electron deactivating groups and that the opposing effects of basicity and π-back-donation somewhat balance each other. Studies[3,4] of hexakis(4-nitropyridine N-oxide)nickel(II) perchlorate relative to similar complexes with other 4-substituents (COCH$_3$, C, H, CH$_3$, and OCH$_3$) have also suggested that π-back-bonding is facilitated by the lowered electron density on the oxygen which in turn increases the Dq value.

From a consideration of pka values acetanilide (–1.56)[25] is much less basic than pyridine N-oxide (0.79),[26] quinoline N-oxide (0.86),[27] and acetamide (–0·70).[25] Yet the nickel(II) and cobalt(II) complexes of acetanilide have Dq values that are as large or larger than those of pyridine N-oxide[2,4] (Ni^{2+} 794 cm^{-1}; Co^{2+} 950 cm^{-1}), quinoline N-oxide[5] (Ni^{2+} 790 cm^{-1}; Co^{2+} 976 cm^{-1}), and acetamide[28] (Ni^{2+} 824 cm^{-1}). The weaker base, acetanilide, should have smaller Dq values on the basis of electrostatic perturbation and metal-ligand σ bonding effects. Ligand to metal π-bonding would not contribute much in any of these cases since the π-bonding orbitals of nickel(II) and cobalt(II) are already filled. Acetanilide should on the basis of constructed models have at least as much steric hinderance as the above mentioned ligands except possibly that of acetamide. The only remaining interaction by which to intepret this increase in the Dq values is increased metal to ligand π-back-bonding.

(20) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley and Sons, Inc. New York, 1958 pp. 203-212.

(21) H. A. Szymanski, *IR Theory and Practice of Infrared Spectroscopy*, Plenum Press, New York, 1958 p. 291.

(22) E. W. Randall, C. M. Silcox Yoder, and J. J. Zuckerman, *Inorg. Chem.*, *5*, 2240 (1966).

(23) C. J. Ballhausen, *Introduction to Ligand Field Theory*, McGraw Hill Co., New York, 1962 p. 256.

(24) R. S. Drago, *Physical Methods in Inorganic Chemistry*, Rheinhold Publishing Corporation, New York, 1965 p. 410.

(25) C. A. Streuli, *Anal. Chem.*, *31*, 1652 (1959).

(26) H. H. Jaffé and G. O. Doak, *J. Am. Chem. Soc.*, *77*, 4441 (1955).

(27) R. Whyman, D. B. Copley, and W. E. Hatfield, *ibid.*, *89*, 3135 (1967).

(28) R. S. Drago, D. W. Meek, M. D. Joesten, and L. LaRoche, *Inorg. Chem.*, *2*, 124 (1963).