*Contribution from the Department of Chemistry,
Villanova University, Villanova, Pennsylvania, U.S.A.*

Molecular Orbital Theory for Metal-Ammine Complexes. I. $[Cu(NH_3)_6]^{2+}$, $[Cu(NH_3)_4]^{2+}$ and $[Ni(NH_3)_6]^{2+}$

S. I. Shupack

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The electronic spectra and g-factors of tetragonal $[Cu(NH_3)_6]^{2+}$*, square planar* $[Cu(NH_3)_4]^{2+}$*, and octahedral* $[Ni(NH_3)_6]^{2+}$ *are fitted by using the semi-empirical (SCCC) method. Both hybridized and unhybridized ligand orbitals were tried. In the case of the copper complexes unhybridized ligand functions were necessary, while for the nickel complex both hybridized and unhybridized worked equally well. Only the sigma bonding framework was considered in the calculational model. A good fit of the g-factors, and d–d bands was obtained. The charge transfer bands proved to be the predicted ligand to metal type of transition . The self-consistent charge and configuration parameters for each cation are:* $[Cu(NH_3)_6]^{2+}$, $F_\sigma^u = 2.4$, $Cu(+.527)\ 3d^{9.076}\ 4s^{0.677}\ 4p^{.0720}$; $[Cu(NH_3)_4]^{2+}$, $F_\sigma^u = 1.8$, $Cu(+.912)\ 3d^{9.327}\ 4s^{0.538}\ 4p^{0.224}$; $[Ni(NH_3)_6]^{2+}$, $F_\sigma^u = 1.3$, $Ni(+1.254)\ 3d^{8.610}\ 4s^{0.215}\ 4p^{-.079}$, $F_\sigma^h = 1.8$, $Ni.(+1.088)\ 3d^{8.489}\ 4s^{0.380}\ 4p^{0.044}$. *In general the choice of the metal complexes and model for the calculation tends to avoid the criticisms such as over-estimation of π-bonding and covalency as well as the inability of the method to calculate inter-electron repulsion effects. It is felt that by variation of* F_σ *and utilization of unhybridized ligand orbitals, the Madelung correction to metal VSIE's may be minimized. Furthermore, the calculation predicts that a relatively planar ammine group is necessary in order to fit the experimental data for the* Cu^{II} *complexes. This is in keeping with proton N.M.R. results.*

Introduction

Recently the electronic, magnetic and structural properties of two closely related Cu^{II}-ammine complexes have been published.[1,2,3a,b,c] These complexes contain the tetragonal $[Cu(NH_3)_6]^{2+}$ and square planar $[Cu(NH_3)_4]^{2+}$ cations both having symmetry properties transforming as the point group D_{4h}. The hexammine represents an example of the Jahn-Teller distortion found in similar d^9 complexes such as $Cu(H_2O)_6SiF_6$.[4] The tetraammine can be viewed as the extreme of this tetragonal distortion in that the Z-axis ligands are infinitely removed from the metal ion. Because the molecular properties of these complexes have been well characterized experimentally, they present a good opportunity to apply and test the Wolfsberg-Helmholtz (WH) semi-empirical molecular orbital method.

For this purpose the modification known as the Self-consistent Charge and Configuration method (SCCC) was chosen. This method has been developed in the main by Gray and his students and is clearly presented in refs. 5 and 6. The main assumption is in evaluating the off-diagonal elements, H_{ij}, of the secular determinant $|H_{ij}-G_{ij}E| = 0$ by the expression

$$H_{ij} = -FG_{ij}\frac{H_{ii}+H_{jj}}{2}$$

where F is a parameter which is varied generally from about 2.5 to 1.5. Separate functions F_π and F_σ are used when π- and σ-bonding are involved. Previous work had set $F_\pi = 2.1$ and varied F_σ,[5] but recent publications have varied both.[7] The argument for the direct relationship between H_{ij} and G_{ij} has been put forward by others.[8] A basic criticism of this type of calculation has been its over-estimation of π-bonding and with this, covalency.[9] Moreover, the semi-empirical calculation does not by itself evaluate the inter-electron repulsion energy. R. F. Fenske and his students[9] and others are developing techniques to cope with the problem, but the use of relatively high-speed, large-capacity computers is necessary for the large number of integrals involved. Another point in question is the relative energy of the ligand and metal orbitals as a function of the Madelung energy of the crystal field potential. This has been discussed at length elsewhere.[10]

In order to obviate some of these problems and criticisms, only Cu–N sigma-bonding was considered in this work. This is a reasonable model to take for the metal-ammine complexes. Such a model was used previously in a similar manner.[11,12] Thus, the over-estimation of covalency due to π-bonding may be

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avoided. Furthermore, by using the d^9 complexes, inter-electron repulsion corrections are not necessary. In any case, the SCCC has been well developed and is relatively easy to use. Moreover, with a slower, lower capacity computer the SCCC method is ideally suited to this medium. As to the Madelung energy problem, it has been shown that the ligand VOIP's, listed in ref. 6, for the neutral atoms are adequate. Thus, by varying the metal orbital energies as a function of charge, and varying the H_{ij}'s as a function of *only* F_σ, it may be possible to arrive at a reasonable fit of the electronic transition energies and electron spin resonance g-factors. These are reasonable goals in light of the assumptions made and the state of the art. Also, as an extension, the model is applied to $[Ni(NH_3)_6]^{2+}$.

Calculational Method

The calculations were performed for the model species $[MN_x]$ where X=4,6. Only the lone pair was used, and the hydrogen contribution to the ligand wave function was considered insignificant. In the case of the planar NH_3^+ species this is justified.[3c] This is because it has been shown that a planar NH_3^+ species best fits the proton NMR data for the copper(II) ammines.[3c]

Previous reports[6,7] have outlined the SCCC prescription. However, some further comment is in order about various points. For example, the VSIE's of copper for the d^n configuration, cannot be used for the $Cu^0 \rightarrow Cu^I$ ionization in that n would be eleven. Thus, in order to use three curves to determine d-VSIE's, the energies of the $3d^{n-1}4s^2$ configurations were taken along with the $3d^n4s$ and $3d^n4p$ configurations for n=10. The $3d^{n-1}4s^2$ VSIE curve may be described as $14.0\,q^2+110.8\,q+132.5$, where q equals the metal charge.

As mentioned previously, the Madelung energy can change the ligand VOIP's as compared to the published average of configuration energies taken from atomic spectroscopy. However, Jørgensen *et al.*[10] have shown that the neutral atom ionization potentials adequately represent the ligand VOIP's. This is further strengthened in the case of the oxides and chlorides by the fact that the ionization potential of many of these is similar to those of the respective neutral atoms. However, this is not the case for the ligand of interest in this work (N, 117.3 kK[6]; NH_3, 81.89 kK[13]; 1 kK = 1×10^3 cm^{-1}); so the effect of various ligand VOIP's was explored. The average of configuration energies N_{2s} = −206.2 kK; N_{2p} = −106.4 kK gave the proper ordering of the energy level for F_σ = 2.00. Other choices of VOIP's gave varying results. Calculation of the overlap integrals S_{ij} was performed using the basis set for nitrogen published by Clementi.[14] The Cu^I functions were taken from Richardson's papers.[15,16] Metal-nitrogen bond lengths were obtained from ref. 3a for the Cu^{II} hexaammine, 2.05 and 2.62 Å; and the Cu^{II} tetraammine, 2.07 Å, taken from ref. 17. As for the Ni–N bond, this was estimated from ref. 18 to be 2.00 Å. Table I lists the S_{ij}'s. The G_{ij}'s tabulated in Table II were evaluated using the metal-ligand combinations listed elsewhere.[6,12]

Table I. Diatomic Overlaps. S_{ij}

Bond distance Å	Cu–N			Ni–N
Type	2.05	2.07	2.62	2.00
$s_Ms_L\sigma$	0.2812	0.2758	0.1496	0.3013
$s_Mp_L\sigma$	0.2252	0.2238	0.1601	0.2198
$p_Ms_L\sigma$	0.4405	0.4347	0.2747	0.1839
$p_Mp_L\sigma$	0.2317	0.2339	0.2261	−0.0696
$d_Ms_L\sigma$	0.0675	0.0652	0.0229	0.1134
$d_Mp_L\sigma$	0.0855	0.0836	0.0384	0.1198

Table II. G_{ij}'s

		3d2s_L		3d2p_L		4s2s_L		4s2p_L		4p2s_L		4p2p_L	
Complex	D_{4h}	H	U[a]	H	U	H	U	H	U	H	U	H	U
$[Cu(NH_3)_4]^{2+}$	a_{1g}	−.0372	−.0675	−.0731	−.0855	.3098	.5623	.3851	.4502				
	a_{2u}	4p	N.B.										
	b_{1g}	.0590	.1169	.1266	.1481								
	b_{2g}	3dxy	N.B.										
	e_g	3dxy,	3dyz	N.B.									
	e_u									.3146	.6229	.2802	.3277
	D_{4h}												
$[Cu(NH_3)_6]^{2+}$	a_{1g}	−.0359	−.0652	−.0715	−.0843	.3040	.5517	.3827	.4476				
	[b]	.0163	.0324	.0465	.0544	.1060	.2116	.1936	.2264				
	a_{2u} [b]									.1962	.3885	.2733	.3197
	b_{1g}	.0570	.1129	.1238	.1448								
	b_{2g}	3dxy	N.B.										
	e_g	3dxz,	3dyz	N.B.									
	e_u									.3105	.6148	.2828	.3308
	O_h												
$[Ni(NH_3)_6]^{2+}$	a_{1g}					.3721	.7381	.4604	.5384				
	e_g	.1082	.1964	.1774	.2075								
	t_{2g}	3dyz,	3dxz,	3dxy	N.B.								
	t_{1u}									.1433	.2601	−.0841	−.0984

[a] H and U stand for hybridized and unhybridized. [b] Metal-Nitrogen along z axis.

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As part of the prescription for the SCCC method the ligand orbitals are hybridized as shown:

$$\Phi_{hyb} = {}^1/_2\chi_{2s} + \sqrt{3}/_2\chi_{2p}$$

The same result was found by Higachi[19a] using a limited basis set SCF-LCAO calculation for NH_3 where $\widehat{HNH} = 105°$. More recent methods also generally agree with this choice.[19b]

Table II lists both hybridized and unhybridized G_{ij}'s. N.M.R. results show that a planar ammine group best fits the spin distribution in the copper ammine.[3b,c] It will be shown, in keeping with this, that only the unhybridized ligands functions will give a good fit of the experimental results. Ligand-ligand overlaps were not taken into account since the ligand orbitals of interest are pointed towards the metal and the others are involved with the hydrogens. Furthermore the ligand-ligand distances are, in the XY plane = 2.90 Å; from the XY plane to the Z axis = 3.4 Å, and along the Z axis 5.24 Å. These distances indicate that ligand-ligand overlaps are relatively insignificant.

Results

In the case of the Cu^{II} ammines, Δ_1 values just about double in going from the hybridized to unhybridized system. This is of course consistent with the weighting factor doubling the ligand 2s participation in the G_{ij}'s shown in Table II. Varying F_σ, for the hybridized functions, in order to obtain the proper Δ_1, eventually gave the wrong energy level ordering before the proper Δ_1 value was reached. This was true for the copper complexes but not for the nickel complex. Thus, by using the unhybridized ligand functions and varying F_σ the "best fit" of the electronic spectra was obtained as calculated in Table III (a and b), IV (a and b), and V. As for the $[Ni(NH_3)_6]^{2+}$ both unhybridized and hybridized "best fit" values are given in Tables IV (a+b) and V.

Tabulation of the F_σ values, energy levels, eigenvectors, VSIE's, charges and configurations, and one electron population of the occupied orbitals is displayed in Tables III and IV for the "best" calculations. The energy level diagrams are shown in Figures 1, 2, 3a, b. It should be pointed out that the dotted lines connecting the a.o.'s to the m.o.'s represent a one electron participation (or population) of greater than 10%. Brackets are used over a series of m.o.'s to reduce the number of lines from the a.o.'s.

The Landé g-factors may be evaluated after Pryce[20] for the Cu^{II} complexes in a tetragonal field as follows

$$g_{ij} = 2\left[1-\lambda\sum_{n\neq o}\frac{\langle\psi_o|L_i|\psi_n\rangle\langle\psi_n|L_j|\psi_o\rangle}{E_n-E_o}\right]$$

Since the ground state wave function ψ_o includes the $d_{x^2-y^2}$ orbital, $L_i=L_j=L_z$ and $L_i=L_j=L_x$. Using these operators and realizing that the ligand terms disappear since they are sigma s and p terms the following

Table IIIa. Molecular Orbitals of $[Cu(NH_3)_6]^{2+}$

Irreducible Representation D_{4h}	Energy kK[b]	$F_\sigma^u = 2.4$ Cu(+.527) $3d^{9.076}$ $4s^{0.677}$ $4p^{.0720}$ Eigenvectors and Population Parameters[a]							Electron Occupancy
		3d	4s	4p	$\underline{2s}$[c]	$\underline{2p}$	$\overline{2s}$	$\overline{2p}$	
$6a_{1g}$	+527.09	−.1381	1.5185		−1.0433	−.8706	−.3895	−.4223	
$3e_g$	+199.29			1.3724	− .9766	−.5841			
$3a_{2u}$	+ 34.65			1.1202			−.5505	−.5805	
$3b_{1g}$	−89.92	.4502			− .1624	−.9550			
$5a_{1g}$	−101.12	.2623	.0350		.0082	.4555	−.0485	−.8753	
$2e_u$	−111.37			−.1698	.1747	−.9339			
$2a_{2u}$	−113.57			−.2497			−.1639	−.8943	
$4a_{1g}$	−125.29	−.0302	−.2233		.3729	−.7369	.1502	−.4046	
$2b_{1g}$	−163.25	−.7572 (.5581)[a]			.5933 (.3013)	−.3242 (.1407)			1
$3a_{1g}$	−174.00	.8874 (.7802)[a]	.0899 (.0094)		.2057 (.0406)	−.1147 (.0173)	−.3753 (.1229)	.1412 (.0296)	2
b_{2g}	−179.18	1.0000 (1.0000)[a]							2
e_g	−179.18	1.0000 (1.0000)[a]							4
$1a_{2u}$	−209.88			.1472 (.0747)			.9339 (.9256)	−.0072 (−.0003)	2
$2a_{1g}$	−211.62	−.3674 (.1531)[a]	−.0495 (.0037)		.2780 (.0763)	.0227 (.0007)	−.8632 (.7644)	−.0289 (.0017)	2
$1a_{1u}$	−214.00			.1965 (.1426)	.8679 (.8480)	−.0121) (−.0006)			4
$1b_{1g}$	−223.36	.5089 (.3097)[a]			.7968 (.6806)	.0681 (.0096)			2
$1a_{1g}$	−250.01	.1091 (.0160)[a]	−.3956 (.3252)		−.6598 (.5840)	−.0295 (.0064)	−.2229 (.0675)	−.0090 (.0008)	2

VSIE 3d=−179.18 4s=−118.75 4p= −61.39 [a] Values for one electron population. [b] Kilokaysers. [c] Underlined orbitals are in the XY plane. Overlined orbitals are along Z axis.

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(19) (a) J. Higuchi, *J. Chem. Phys.*, *24*, 535 (1956); (b) U. Kaldor, *J. Chem. Phys.*, *46*, 1981 (1967).

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Table IIIb. Molecular Orbitals of $[Cu(NH_3)_4]^{2+}$

Irreducible Representation D_{4h}	Energy kK[b]	3dσ	4sσ	4pσ	2sσ	2pσ	Electron Occupancy of filled levels
		$F_\sigma^u = 1.8$ Cu(+.912) $3d^{9.327}\ 4s^{0.538}\ 4p^{0.224}$					
		Eigenvectors and One Electron Population Parameters[a]					
$4a_{1g}$	+161.66	−.1860	1.3693		−.9777	−.8877	
$3e_u$	+ 88.05			1.3934	−.9248	−.5872	
a_{2u}	− 76.10			1.000			
$3b_{1g}$	− 99.97	.2722			−.0784	−1.0028	
$2e_u$	−109.75			−.1822	.1362	−.9316	
$3a_{1g}$	−122.16	.0480	.3251		−.3709	.8105	
$2b_{1g}$	−180.49	−.8006			.6605	−.1272	1
		(.5943)			(.3745)	(.0313)	
$2a_{1g}$	−194.35	−.9672	−.1540		−.1736	.0468	2
		(.9279)	(.0355)		(.0338)	(.0028)	
b_{2g}	−196.10	1.0000					2
		(.1.0000)					
e_g	−196.10	1.0000					4
		(.1.0000)					
$1e_u$	−207.20			.0835	.9461	−.0123	4
				(.0559)	(.9443)	(−.0002)	
$1b_{1g}$	−218.75	.5673			.7561	.0308	2
		(.3746)			(.6219)	(.0035)	
$1a_{1g}$	−225.96	.2289	−.3179		−.7478	.0096	2
		(.0638)	(.2333)		(.7044)	(−.0015)	

VSIE 3d = −196.10 4s = −131.95 4p = −76.10[b] [a,b] See Table IIIa.

Table IVa. Molecular Orbitals of $[Ni(NH_3)_6]^{2+}$

On Irreducible Representation	Energy kK[b]	3dσ	4sσ	4pσ	2sσ	2pσ	Electron Occupancy of filled levels
		$F_\sigma^u = 1.3$ Ni(+1.254) (+1.254) $3d^{8.610}\ 4s^{.215}\ 4p^{-.079}$					
		Eigenvectors and One Electron Population Parameters[a]					
$3a_{1g}$	+311.04		2.4231		−1.8377	−1.4670	
$3t_{1u}$	− 84.59			1.0331	−.2051	.1998	
$3e_g$	−102.69	.2151			−.0647	−1.0229	
$2t_{1u}$	−106.61			−.1018	−.0188	.9852	
$2a_{1g}$	−117.56		−.3936		.3372	−.7741	
$2e_g$	−185.26	−.9012			.6429	−.0058	
		(.6993)[a]			(.2995)	(.0011)	2
t_{2g}	−195.92	1.0000					
		(1.0000)[a]					6
$1t_{1u}$	−206.70			.0666	−1.0153	.0052	
				(−.0132)	(1.0132)	(−.0000)	6
$1a_{1g}$	−207.65		.1379		.8959	−.0362	
			(.1075)		(.8939)	(−.0014)	2
$1e_g$		.4801			.7903	−.0230	
	−212.07	(.3027)[a]			(.6990)	(−.0018)	4

VSIE 3d = −195.92 4s = −139.43 4p = −90.33[b] [a,b] See Table IIIa.

Table IVb. Molecular Orbitals of $[Ni(NH_3)_6]^{2+}$

On Irreducible Representation	Energy kK[b]	3dσ	4sσ	4pσ	2sσ	2pσ	Electron Occupancy of filled levels
		$F_\sigma^u = 1.8$ Ni(+1.088) $3d^{8.489}\ 4s^{.330}\ 4p^{.044}$					
		Eigenvectors and One Electron Population Parameters[a]					
$3a_{1g}$	+21.05		1.1008		−.5763	−.9368	
$3t_{1u}$	−79.69			.9908	−.1800	.2896	
$3e_g$	−97.14	.3301			−.0849	−1.0037	
$2t_{1u}$	−107.58			−.2089	.0402	.9609	
$2a_{1g}$	−133.36		−.4833		.4082	−.6698	
$2e_g$	−179.00	−.8313			.5865	−.1562	
		(.6614)[a]			(.2912)	(.0474)	2
t_{2g}	−189.98	1.0000					
		(1.0000)[a]					6
$1t_{1u}$	−206.39			.0399	.9935	.0011	
				(.0073)	(.9927)	(.0000)	6
$1e_g$	−215.48	.4950			.8130	.0326	
		(.2915)[a]			(.7046)	(.0039)	4
$1a_{1g}$	−217.19		.3063		.8452	−.0034	
			(.1987)		(.8107)	(−.0005)	2

VSIE 3d = −189.98 4s = −133.53 4p = −86.28[b] [a,b] See Table IIIa.

Table V. Spectral Data

D_{4h}	$[Cu(NH_3)_4]^{2+}$ Observ. [a]	Calc.	$[Cu(NH_3)_6]^{2+}$ Observ. [b]	Calc.		$[Ni(NH_3)_6]^{2+}$ Observ. [c]	Calc.
$2a_{1g} \rightarrow 2b_{1g}$(d–d)	13.40 (xy) 13.50 (z)	13.87	10.50 - 11.20	10.85	$t_{2g} \rightarrow e_g$(d–d)	10.90	10.97 10.65 [f]
$1b_{2g} \rightarrow 2b_{1g}$(d–d)	15.50 (xy)	15.61	15.60 - 16.40	15.94	$t_{2g} \rightarrow e_g$(d–d)	17.50 [d] 28.20	
$1e_g \rightarrow 2b_{1g}$(d–d)	17.00 (xy)(z)	15.61	15.60 - 16.40	15.94	$t_{1u} \rightarrow e_g$(L–M)		27.39 21.43 [f]
$1e_u \rightarrow 2b_{1g}$(L–M)		26.71	31.20 - 40.00 [e]				
$1a_{2u} \rightarrow 2b_{1g}$(L–M)				46.63			

[a] Energy in Kilokaysers and see Table IIIa for Calc. data and ref. 1 for reflectance spectra. [b] See Table IIIb for Calc. data and ref. 2 for reflectance spectra. [c] See Table IVa, b for Calc. data and ref. 22 for solution spectra. [d] These are the excited states. Other very weak bands due to vibronic effects are discussed in ref. 20 pg. 269. [e] A series of bands are reported for the reflectance spectra in ref. 1. [f] For unhybridized ligand orbitals.

equations are obtained

$$g_{zz} = g_{\parallel} = 2\left[1 - \frac{4\lambda\langle\Phi_{d_{x^2-y^2}}|\Phi_{d_{x^2-y^2}}\rangle\langle\Phi_{d_{xy}}|\Phi_{d_{xy}}\rangle}{E_{d_{xy}} - E_{d_{x^2-y^2}}}\right]$$

$$g_{xx} = g_{yy} = g_{\perp} = 2\left[1 - \frac{\lambda\langle\Phi_{d_{x^2-y^2}}|\Phi_{d_{x^2-y^2}}\rangle\langle\Phi_{d_{yz}}|\Phi_{d_{yz}}\rangle}{E_{d_{yz}} - E_{d_{x^2-y^2}}}\right]$$

The spin orbital coupling constant λ is related to the atomic function ξ_{3d} by

$$\lambda = \frac{-\xi_{3d}}{2S}$$

Thus the value for λ can then be taken directly as -820 cm^{-1}.[21] Furthermore, the d_{xy} and d_{yz} orbitals which are normally involved in the π-system are perforce non-bonding. It follows then that $\langle\Phi_{d_{xy}}|\Phi_{d_{xy}}\rangle$ and $\langle\Phi_{d_{yz}}|\Phi_{d_{yz}}\rangle$ equal one. The equations then reduce to

$$g_{\parallel} = 2 + \frac{8(820)\,a^2}{E_{d_{xy}} - E_{d_{x^2-y^2}}}, \quad g_{\perp} = 2 + \frac{2(820)\,a^2}{E_{d_{yz}} - E_{d_{x^2-y^2}}}$$

The term a^2 may be taken as the square of the eigenvector of the d-orbital portion of ψ_o, or the Mulliken one electron population parameter which includes the metal-ligand overlap integrals. For Ni^{II}, d^8 in an O_h field the g-factor equation has been derived by Owen[22] as

$$g = 2 - \frac{8\lambda a^2}{\Delta}$$

where $\lambda = -\frac{1}{2}$ $\quad\xi = -324$ cm^{-1}.

The calculated and observed g-factors and various a^2 values are given in Table VI.

Discussion

Copper-Ammine Complexes. d–d bands. The model used in this calculation is based on the SCCC method. However, only the σ-structure of the complexes has been considered. The assignment of the copper-ammine spectra was accomplished experimentally by others[1,2] based on the tetragonal distortion of the ^2D state of d^9 copper. It is clear from Table V that the calculational model fits the observed d–d bands quite well. Since the e_g and b_{2g} levels in the Cu^{II} complexes are usually π-m.o.'s, they have perforce become non-bonding and accidentally degenerate. Experimentally the hexaammine complex does not split these levels sufficiently to be resolved in the reflectance spectrum.[1] But in the tetraammine they are shown to be separate shoulders which have been resolved by Gaussian analysis.[2] In any case the possible ad-mixture of excited states due to vibronic effects, configuration interaction or other mechanisms

Table VI. g-factors

Complex	Observed		Calculated		$b_{1g}(3dx^2-y^2)$ Calc		e_g(3dxz,3dyz) b_{2g} (3dxy) Calc.
	$g_{\perp}$	$g_{\parallel}$	$g_{\perp}$	$g_{\parallel}$	a^2	$a^{2'}$ [b]	a^2
$[Cu(NH_3)_4]^{2+}$	2.05	2.22	2.06 2.06	2.25 2.28 [c]	0.59	0.64	1.00
$[Cu(NH_3)_6]^{2+}$	2.05	2.21	2.06	2.24	0.56	0.58	1.00
$[Ni(NH_3)_6]^{2+}$	2.14		2.16 2.16 [c] 2.19 [c,f]		0.66 0.70	0.68 [d] 0.81	1.00 [e] 1.00 [f]

[a] For experimental see refs. 1, 2, 22. [b] $a^{2'}$ is calculated from the eigenvector and a^2 is the one electron population. [c] Calculated using $a^{2'}$. [d] From t_{2g} (3dxy, 3dxz, 3dyz). From e_g ($3dx^2-y^2$, $3dz^2$). [f] For unhybridized ligand orbitals.

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(21) D. S. McClure, «Electronic Spectra of Molecules and Ions in Crystals», (Academic Press, Inc. Solid State Reprints, New York, 1959), Part II, Table VIII, pg. 78.

(22) J. Owen, *Proc. Roy. Soc.* (London), *A226*, 183 (1955).

may cause the larger separation of the b_{2g} and e_g levels. The calculational method is limited in this area.

In order to affect a good fit of the d–d bands, unhybridized ligand a.o.'s had to be used. This is in contrast to the SCCC method[6] where only hybrid orbitals are used. But this is consistent with the NMR result in refs. 3b and c in which a planar NH_3^+ best fits the spin density distribution. From Figures 1 and 2 it can be seen that the d–d bands contain contributions which are mainly from the metal d-orbitals and ligand s-orbitals. Hybridization reduces the 3d2sσ overlap and thus the off-diagonal integrals, H_{ij}, by almost one-half, Table II. This would indicate that the s-ligand interaction is mainly the cause of splitting the d-orbitals.

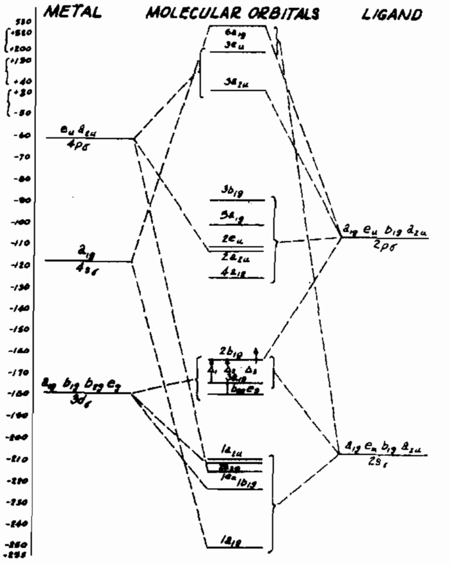

Figure 1. Energy levels for $[Cu(NH_3)_6]^{2+}$ $F^u_\sigma = 2.4$.

Charge transfer bands. The expected type of charge-transfer band is a ligand to metal (L–M).[7] This is readily apparent because the complex contains a relatively neutral ligand and a positively charged central metal atom. Moreover, as the positive charge increases, the energy of the band should decrease. Figures 1, 2 and Table IIIa, b show these expectations to be the case. The experimental data for the hexaammine show two bands in the range given in Table V. The two most likely assignments are $1a_{2u} \rightarrow 2b_{1g}$ ($^2B_{2u}$) and $1e_u \rightarrow 2b_{1g}$ (^2E_u). The first one is not allowed by symmetry, but may become allowed through various mechanisms such as vibronic coupling. It is clear that both these bands meet the requirement of a ligand to metal transition. The calculation shows that the $1a_{2u}$ and $1e_u$ levels are 92% and 85% nitrogen 2sσ respectively while the $2b_{2g}$ level is 56% copper 3dσ. For the square planar ammine the $1e_u \rightarrow 2b_{2g}$ (^2E_u) assignment is the most likely characterization. Here there is 94% nitrogen 2sσ contribution to the $1e_u$ level and 59% copper 3dσ in the $2b_{1g}$ level. However, it should be noted that no charge transfer spectrum has been reported for the tetraammine.[2] Finally in the calculation there is no reasonable candidate for a metal-ligand charge transfer band with lower energy than the ligand→metal type.

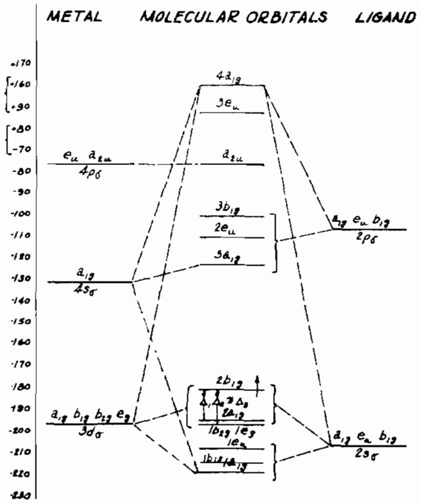

Figure 2. Energy levels for $[Cu(NH_3)_4]^{2+}$ $F^u_\sigma = 1.8$.

It should be realized that the SCCC and similar methods generally do most poorly, in fitting the charge transfer spectra.[9] In any case this calculation has elaborated the expected general features of these bands.

Landé g-factors. One of the most interesting features of the tetragonally distorted d^9 copper complexes in their g-factors. Some complexes exhibit isotropic values but by cooling the anisotropic values may be observed.[4] A temperature-dependent averaging mechanism is believed to be occurring.[4] In any case, the square planar ammine complex should exhibit *only* anisotropic g-factors and this is the limiting case for the hexaammine complex as is shown in Table VI. Calculating the g-factors is accomplished with the equations given previously. a^2_{3d} can either be taken as the square of the eigenvector of the 3d a.o. portion of $\psi 2b_{2g}$, or as the electron population residing on the 3d a.o. portion. Either procedure works quite well because the 3d2sσ overlaps are small. The former procedure has been advocated by others,[9] but for a limited basis set. The fact that the calculational model may be extended to calculate other related parameters is a good indication of the effectiveness of the method considering the previously mentioned limitations.

The covalency of a complex has often been related to a^2. If $a^2 = 1$, the bonding has been considered as ionic, and when $a^2 = 0.5$ this is considered as the extreme of covalency.[9,23] It seems in the square planar and tetragonal complexes that the a^2 criteria of bonding is misleading. After all, what is the degree of covalency along the Z axis of a planar complex where there is no ligand? Is the a^2, to be used, the ψb_{2g} or ψa_{1g} value? Furthermore, more than one a^2 is involved in calculating the g-factors. Comparing the g-factors to the free electron value also presents difficulties even if the average value $g_{AV} = {}^2/_3 g_{\parallel} + {}^1/_3 g_{\perp}$ is used.

This is because, in the planar compounds, one is averaging over ligand voids about the metal. If one takes the directional g-values of the square planar ammine, and compares them to the biuret and dimethylglyoxime Cu^{II} complexes,[23] it is clear that the respective $g_{\parallel}$ and $g_{\perp}$ values are essentially equal. Is the covalency the same whether or not the ligand can delocalize the electron? Not very likely! It should also be pointed out that using the equations and parameters presented previously to calculate the Landé factor that as a^2 increases, the positive deviation of the g-factor increases from 2.00. Furthermore, calculation of the g values involve participation of excited states. How do these participate in covalency? Conclusions about these matters must wait for better criteria for covalency in these complexes.

General. Finally a comparison with previous work is in order. Roos[12] has calculated the electronic properties of $[Cu(NH_3)_6]^{2+}$ using a semiempirical SCF-MO method. Two-electron integrals were evaluated, but the number of these were reduced by the zero differential overlap (ZDO) approximation. As for the H_{ij}'s these were determined by a method similar to the (WH) method. Hybridized sp^3 ligand functions were used and the VOIP value was taken as the first ionization potential of ammonia. The axial bond length, R_{ax}, was not known at the time of this calculation so it was considered as a variable using the tetragonal parameter $\lambda = \sqrt{1-(R_p/R_{ax})^2}$. In fitting the spectra the (WH) parameter, for the H_{ij}'s, k, was found to be 2.88 and R_{ax} was 2.60 Å. The k value is larger than F_σ (2.4) as Roos predicted it should be. However, in evaluating the "cohesive energy" in the axial bonds and taking into consideration configurational mixing of the $^2A_{1g}$ state, R_{ax} became 2.25 Å. The covalency parameter, a^2, of the b_{2g} orbital found by the SCF method was 0.85. This would of course give larger g-factors than those calculated by the method used in this paper. It is not clear yet whether this semiempirical SCF method offers advantages over others being proposed.[9] But, in terms of computer time and memory space and number of assumptions made, this author feels that the (SCCC) method offers comparable results and simpler operation. Moreover, the SCCC method predicts that a planar ammine gives the best fit to the experimental data.

$[Ni(NH_3)_6]^{2+}$. As a further application of the model presented in the previous paragraphs the molecular parameters of $[Ni(NH_3)_6]^{2+}$ were calculated. This complex has a triplet ground state so that excited states due to electron repulsions exist. The model can only calculate the ground state energies and Δ parameters. Table IVa,b and Figure 3a, b give the pertinent data.

d–d Bands. The $t_{2g} \rightarrow e_g$ transition gives rise to Δ. Δ may be fitted by using both hybridized and unhybridized ligand sigma orbitals. The two methods give comparable results. It would be consistent with the copper work to use only the unhybridized ligand functions. Preliminary work on the Co^{III} and Cr^{III} shows this to be the case, so far. However, in hopes of extending the method to the Pd^{II}, Pt^{II}, Au^{III} tetraammines and Rh^{III} and Ir^{III} hexaammines the favorability of either assumption must be kept open. However, it is clear that the unhybridized NH_3 functions are best for copper system. The energy levels involved in the d–d transitions are in the expected order as seen in Figure 3a, b. Because of the assumptions made in this calculation the t_{2g} m.o. is non-bonding. Since, as both Figure 3a and Figure 3b show, the d–d transitions are mainly dependent on the interaction of the metal d-orbitals with the ligand s-orbitals, hybridization and unhybridization must be offset by varying the F_σ values. This sensitivity is born out by the fact that F_σ^u (u = unhybridized) is smaller than F_σ^h (h = hybridized). The sole use of d-metal and s-ligand orbitals as a minimum basis set for these calculations seems a distinct possibility. This will be tested in future work. It should be noted that the calculation predicts the proper ground state electron occupancy. This is not the case for the high spin $[Co(NH_3)_6]^{2+}$ where a doublet state was calculated.

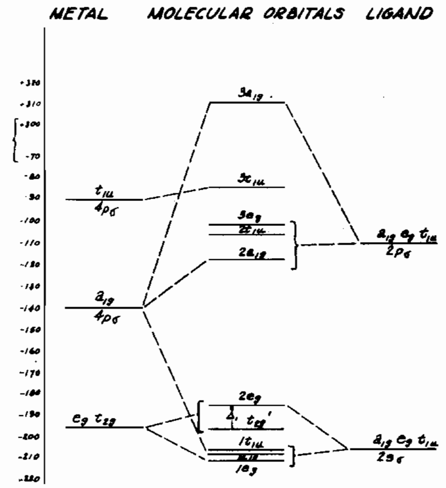

Figure 3a. Energy levels for $[Ni(NH_3)_6]^{2+}$ $F_\sigma^u = 1.8$.

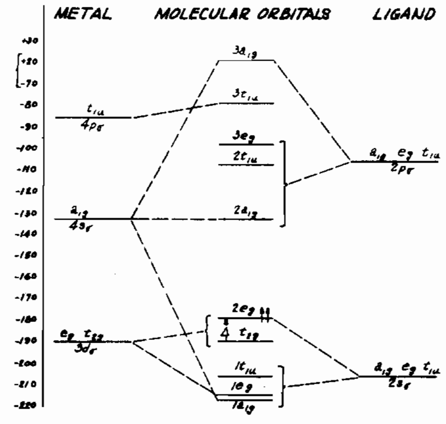

Figure 3b. Energy levels for $[Ni(NH_3)_6]^{2+}$ $F_\sigma^u = 1.3$.

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(23) A. K. Wiersema and J. J. Windle, *J. Phys. Chem.*, **68**, 2316 (1964).

Charge transfer bands. As stated previously the expected type of charge transfer band is ligand-metal. The best candidate is the $1t_{1u} \rightarrow 2e_g$ transition giving rise to the $^3T_{1u}$ state, a symmetry allowed transition. In the hybridized case $\psi 1t_{1u}$ is 99% ligand 2s and $\psi 2e_g$ is 66% 3d in character while for the unhybridized case the percentages are 100% 2s and 70% 3d respectively. Whether the energies of the m.o.'s are real or relative values is not known.[24] The hybridized calculation does give the larger value for the L→M band and the expected value should be larger than any calculated.

Landé g-factor. The calculation of the g-factor for $[Ni(NH_3)_6]^{2+}$ relies on the equations developed by Owen[22] as previously put forth in this paper. The g-value is taken from that reported for $Ni(NH_3)_6Br_2$. As in the copper case a^2 and not $a^{2'}$ gives the better fit. $a^{2'}$ gives the largest deviation from experimental for the unhybridized case. NMR studies[3b] indicate that the ammine geometry lies between the planar and pyramidal forms so that the degree of s-p mixing lies between the extremes of the hybridized and unhybridized test systems. In any case an excellent fit of the experimental values is again obtained.

Comparison with the work of Cotton and Haas[11] shows that F_σ obtained in their calculation is close to the value obtained in this work for the hybridized case. Their work considered only the sp^3 hybrid and took its energy as the first ionization potential of ammonia or the first ionization potential of atomic nitrogen. It is interesting to speculate that the overlap integral for the sp^3 hybrid with the metal d (*i.e.* the weighted sum of $S_{3d^2 s_{L\sigma}} + S_{3d^2 p_{L\sigma}}$) sufficiently increases the H_{ij} values, overcoming the smaller ligand and metal H_{ii} values. The charge on the metal is smaller than reported in this paper by a factor of at least four. A fit of the g-factors was not carried out. It should be noted that the Δ value for $[Co(NH_3)_6]^{2+}$ was evaluated, but the ground state electron-configuration obtained was not mentioned.

In conclusion it would then appear that the SCCC method does an excellent job in evaluating the molecular properties of the complexes discussed here. However, further work on extending the model, with the modifications mentioned herein is necessary to allow one to make a more definitive statement about the generality of the model. Further testing of the similar aquo-complexes is anticipated; however, preliminary calculations show the need for considering metal-ligand π-bonding.

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(24) M. Zerner and M. Gouterman, *Theoret. Chim. Acta* (Berl.), *4*, 44 (1966).