Semi-empirical Molecular Orbital Energy Levels of the Hexammine and Chloroammine Complexes of Co(IV)

WALTER A. YERANOS and DAVID A. HASMAN

Department of Chemistry, Michael Faraday Laboratories
Northern Illinois University, DeKalb, Illinois 60115

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Using the recently proposed reciprocal mean for the semi-empirical evaluation of resonance integrals, as well as approximate SCF wave functions for Co^{3+}, the one-electron molecular energy levels of $Co(NH_3)_6{}^{3+}$, $Co(NH_3)_5Cl^{2+}$, and $Co(NH_3)_4Cl_2{}^{1+}$ have been redetermined within the WOLFSBERG–HELMHOLZ approximation. The outcome of the study fits remarkably well with the observed electronic transitions in the u.v. spectra of these complexes and prompts different band assignments than previously suggested.

The electronic structure and bonding of $Co(NH_3)_6{}^{3+}$ has been studied in the WOLFSBERG–HELMHOLZ [1] approximation by several investigators [2–6]. The chloroammine complexes, on the other hand, have been studied in the same aproximation by NAKAMOTO et al. [2]. The aim of the present investigation is to reexamine the electronic structure of $Co(NH_3)_6{}^{3+}$, $Co(NH_3)_5Cl^{2+}$, and $Co(NH_3)_4Cl^{1+}$ in the molecular orbital theory.

Unlike the previous investigation on this series, however, we have included a certain degree of sophistication which we hope will give a more meaningful theoretical basis for the description of the bonding in these complexes.

First, we have used the recently published approximate SCF wave functions [7] for Co^{3+} instead of the "usual" or "modified" SLATER orbitals [8]. Our recent work [9] on XeF_4 has shown beyond any doubt that the nodeless SLATER orbitals are inadequate to give correct overlaps. A careful examination of some previous works [3, 4] shows that the use of even "modified" single SLATER orbitals gives unduly large group overlaps and arbitrarily affects the final results.

Second, we have used the recently proposed reciprocal mean [10] rather than the arithmetic mean [1] to evaluate our resonance integrals. It should be pointed out that the arithmetic mean given by

$$H_{ij} = F_x \, G_{ij} \left(\frac{H_{ii} + H_{jj}}{2} \right)$$

is *insensitive* to the energy separation of the orbitals believed participating in bond formation. That is, whether the orbitals are close or far apart in energy, they are *always* given the same weight. This is indeed not true in the case of the reciprocal mean which is given by

$$H_{ij} = F_x \, G_{ij} \left(\frac{H_{ii} \times H_{jj}}{(H_{ii} + H_{jj})/2} \right)$$

and which is rather *selective*. In essence, the reciprocal mean gives a greater weight to orbitals which are closer to each other than those which are far apart, and in this sense is in perfect agreement with the principles of molecular orbital theory [11].

Third, we have found it rather artificial to keep the COULOMB integrals, in particular H_{dd}, the same throughout the series. We have consequently varied the valence state ionization energy (V.S.I.E.) of the "d" electron in the series so as to have a lower negative charge on the cobalt as well as a better fit with the observed spectra. This is indeed in agreement with JORGENSEN's finding of dependence of the charge on the central ion of a complexe and the V.S.I.E. of its electrons [12].

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Finally, we have attempted including ligand – ligand overlaps in our calculations. Unfortunately, however, the results were not encouraging and no reasonable fit with experiment was possible to obtain. It may well be that in this series the inclusion of ligand – ligand overlap may have tipped the delicate balance of the cancellation of errors so prevalent in semi-empirical methods. A recent paper by WIRTH [6] claims to have obtained a better value of Δ ($\equiv$10 Dq) for $Co(NH_3)_6^{3+}$ by the inclusion of ligand – ligand overlap. A closer examination of Fig. 2 of the said paper, however, reveals that H_{dd} in the complex is taken to be – 7.2 eV. Approximately 17 000 cm^{-1} above the free atom value!

1. Theory

$Co(NH_3)_6^{3+}$, $Co(NH_3)_5Cl^{2+}$, and $Co(NH_3)_4Cl_2^{1+}$ belong to the O_h, C_{4v}, and D_{4h} point groups respectively [13]. Fig. 1 depicts the "general" geometry of the molecules under consideration, where the Co – N and Co – Cl distances were taken as 2.00 Å and 2.33 Å respectively.

a_{1g}	s	$\Sigma(\mathrm{a}_{1g}) = \frac{(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6)}{\sqrt{6}[1 + 4\langle\sigma_1 \mid \sigma_2\rangle + \sigma_1 \mid \rangle\sigma_3\rangle]^{\frac{1}{2}}}$
e_g	d_{z2}	$\Sigma^a(\mathrm{e}_g) = \frac{(2\sigma_5 + 2\sigma_6 - \sigma_1 - \sigma_2 - \sigma_3 - \sigma_4)}{2\sqrt{3}[1 - 2\langle\sigma_1 \mid \sigma_2\rangle + \langle\sigma_1 \mid \sigma_3\rangle]^{\frac{1}{2}}}$
	d_{x2-y2}	$\Sigma^b(\mathrm{e}_g) = \frac{(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4)}{2[1 - 2\langle\sigma_1 \mid \sigma_2\rangle + \langle\sigma_1 \mid \sigma_3\rangle]^{\frac{1}{2}}}$
t_{1u}	p_x	$\Sigma^a(\mathrm{t}_{1u}) = \frac{(\sigma_1 - \sigma_3)}{\sqrt{2}[1 - \langle\sigma_1 \mid \sigma_3\rangle]^{\frac{1}{2}}}$
		$\Pi^a(\mathrm{t}_{1u}) = \frac{(\pi_{y2} + \pi_{x5} - \pi_{x4} - \pi_{y6})}{2[1 + \langle\pi_{y2} \mid \pi_{x5}\rangle - \langle\pi_{y2} \mid \pi_{x4}\rangle - \langle\pi_{y2} \mid \pi_{y6}\rangle]^{\frac{1}{2}}}$
	p_y	$\Sigma^b(\mathrm{t}_{1u}) = \frac{(\sigma_2 - \sigma_4)}{\sqrt{2}[1 - \langle\sigma_2 \mid \sigma_4\rangle]^{\frac{1}{2}}}$
		$\Pi^b(\mathrm{t}_{1u}) = \frac{(\pi_{x1} + \pi_{y5} - \pi_{y3} - \pi_{x6})}{2[1 + \langle\pi_{x1} \mid \pi_{y5}\rangle - \langle\pi_{x1} \mid \pi_{y3}\rangle - \langle\pi_{x1} \mid \pi_{x6}\rangle]^{\frac{1}{2}}}$
	p_z	$\Sigma^c(\mathrm{t}_{1u}) = \frac{(\sigma_5 - \sigma_6)}{\sqrt{2}[1 - \langle\sigma_5 \mid \sigma_6\rangle]^{\frac{1}{2}}}$
		$\Pi^c(\mathrm{t}_{1u}) = \frac{(\pi_{y1} + \pi_{x2} - \pi_{x3} - \pi_{y4})}{2[1 + \langle\pi_{y1} \mid \pi_{x2}\rangle - \langle\pi_{y1} \mid \pi_{x3}\rangle - \langle\pi_{y1} \mid \pi_{y4}\rangle]^{\frac{1}{2}}}$
t_{2g}	d_{xz}	$\Pi^a(\mathrm{t}_{2g}) = \frac{(\pi_{y1} + \pi_{x5} + \pi_{x3} + \pi_{y6})}{2[1 + \langle\pi_{y2} \mid \pi_{x5}\rangle + \langle\pi_{y1} \mid \pi_{x3}\rangle + \langle\pi_{y1} \mid \pi_{y6}\rangle]^{\frac{1}{2}}}$
	d_{yz}	$\Pi^b(\mathrm{t}_{2g}) = \frac{(\pi_{x2} + \pi_{y5} + \pi_{y4} + \pi_{x6})}{2[1 + \langle\pi_{x2} \mid \pi_{y5}\rangle + \langle\pi_{x2} \mid \pi_{y4}\rangle + \langle\pi_{x2} \mid \pi_{x6}\rangle]^{\frac{1}{2}}}$
	d_{xy}	$\Pi^c(\mathrm{t}_{2g}) = \frac{(\pi_{x1} + \pi_{y2} + \pi_{x3} + \pi_{y4})}{2[1 + \langle\pi_{x1} \mid \pi_{y2}\rangle + \langle\pi_{x1} \mid \pi_{y3}\rangle + \langle\pi_{x1} \mid \pi_{x4}\rangle]^{\frac{1}{2}}}$
t_{2u}		$\Pi^a(t_{2u}) = \frac{(\pi_{y2} - \pi_{x5} - \pi_{x4} + \pi_{y6})}{2[1 - \langle\pi_{y2} \mid \pi_{x5}\rangle - \langle\pi_{y2} \mid \pi_{x4}\rangle + \langle\pi_{y2} \mid \pi_{y6}\rangle]^{\frac{1}{2}}}$
		$\Pi^b(\mathrm{t}_{2u}) = \frac{(\pi_{x1} - \pi_{y5} - \pi_{y3} + \pi_{x6})}{2[1 - \langle\pi_{x1} \mid \pi_{y5}\rangle - \langle\pi_{x1} \mid \pi_{y3}\rangle + \langle\pi_{x1} \mid \pi_{x6}\rangle]^{\frac{1}{2}}}$
		$\Pi^c(\mathrm{t}_{2u}) = \frac{(\pi_{y1} - \pi_{x2} - \pi_{x3} + \pi_{y4})}{2[1 - \langle\pi_{y1} \mid \pi_{x2}\rangle - \langle\pi_{y1} \mid \pi_{x3}\rangle + \langle\pi_{y1} \mid \pi_{y4}\rangle]^{\frac{1}{2}}}$
t_{1g}		$\Pi^a(\mathrm{t}_{1g}) = \frac{(\pi_{y1} - \pi_{x5} + \pi_{x3} - \pi_{y6})}{2[1 - \langle\pi_{y1} \mid \pi_{x5}\rangle + \langle\pi_{y1} \mid \pi_{x3}\rangle - \langle\pi_{y1} \mid \pi_{y6}\rangle]^{\frac{1}{2}}}$
		$\Pi^b(\mathrm{t}_{1g}) = \frac{(\pi_{x2} - \pi_{y5} + \pi_{y4} - \pi_{x6})}{2[1 - \langle\pi_{x2} \mid \pi_{y5}\rangle + \langle\pi_{x2} \mid \pi_{y4}\rangle - \langle\pi_{x2} \mid \pi_{x6}\rangle]^{\frac{1}{2}}}$
		$\Pi^c(\mathrm{t}_{1g}) = \frac{(\pi_{x1} - \pi_{y2} + \pi_{y3} - \pi_{x4})}{2[1 - \langle\pi_{x1} \mid \pi_{y2}\rangle + \langle\pi_{x1} \mid \pi_{y3}\rangle - \langle\pi_{x1} \mid \pi_{x4}\rangle]^{\frac{1}{2}}}$

Table 1 a. Symmetry Classification of Orbitals Used in O_h Symmetry (including ligand – ligand overlap).

a_{1g}	d_{z2}, s	$\Sigma_1(a_{g1}) = \dfrac{(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)}{2[1 + 2\langle\sigma_1\|\sigma_2\rangle + \langle\sigma_1\|\sigma_3\rangle]^{\frac{1}{2}}}$
		$\Sigma_2(a_{1g}) = \dfrac{(\sigma_5 + \sigma_6)}{\sqrt{2}[1 + \langle\sigma_5\|\sigma_6\rangle]^{\frac{1}{2}}}$
b_{1g}	d_{x2-y2}	$\Sigma(b_{1g}) = \dfrac{(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4)}{2[1 - 2\langle\sigma_1\|\sigma_2\rangle + \langle\sigma_1\|\sigma_3\rangle]^{\frac{1}{2}}}$
a_{2g}	. . .	$\Pi(a_{2g}) = \dfrac{(\pi_{x1} - \pi_{y2} + \pi_{y3} - \pi_{x4})}{2[1 - \langle\pi_{x1}\|\pi_{y2}\rangle + \langle\pi_{x1}\|\pi_{y3}\rangle - \langle\pi_{x1}\|\pi_{x4}\rangle]^{\frac{1}{2}}}$
a_{2u}	p_z	$\Pi(a_{2u}) = \dfrac{(\pi_{y1} + \pi_{x2} - \pi_{x3} - \pi_{y4})}{2[1 + \langle\pi_{y1}\|\pi_{x2}\rangle - \langle\pi_{y1}\|\pi_{x3}\rangle - \langle\pi_{y1}\|\pi_{y4}\rangle]^{\frac{1}{2}}}$
		$\Sigma(a_{2u}) = \dfrac{(\sigma_5 - \sigma_6)\rangle}{\sqrt{2}[1 - \langle\sigma_5\|\sigma_6]^{\frac{1}{2}}}$
b_{2g}	d_{xy}	$\Pi(b_{2g}) = \dfrac{(\pi_{x1} + \pi_{y2} + \pi_{y3} + \pi_{x4})}{2[1 + \langle\pi_{x1}\|\pi_{y2}\rangle + \langle\pi_{x1}\|\pi_{y3}\rangle + \langle\pi_{x1}\|\pi_{x4}\rangle]^{\frac{1}{2}}}$
b_{2u}	. . .	$\Pi(b_{2u}) = \dfrac{(\pi_{y1} - \pi_{x2} - \pi_{x3} + \pi_{y4})}{2[1 - \langle\pi_{y1}\|\pi_{x2}\rangle - \langle\pi_{y1}\|\pi_{x3}\rangle + \langle\pi_{y1}\|\pi_{y4}\rangle]^{\frac{1}{2}}}$
e_g	d_{xz}	$\Pi_1^a(e_g) = \dfrac{(\pi_{y1} + \pi_{x3})}{\sqrt{2}[1 + \langle\pi_{y1}\|\pi_{x3}\rangle]^{\frac{1}{2}}}$
		$\Pi_2^a(e_g) = \dfrac{(\pi_{x5} + \pi_{y6})}{\sqrt{2}[1 + \langle\pi_{x5}\|\pi_{y6}\rangle]^{\frac{1}{2}}}$
	d_{yz}	$\Pi_1^b(e_g) = \dfrac{(\pi_{x2} + \pi_{y4})}{\sqrt{2}[1 + \langle\pi_{x2}\|\pi_{y4}\rangle]^{\frac{1}{2}}}$
		$\Pi_2^b(e_g) = \dfrac{(\pi_{y5} + \pi_{x6})}{\sqrt{2}[1 + \langle\pi_{y5}\|\pi_{x6}\rangle]^{\frac{1}{2}}}$
e_u	p_x	$\Sigma^a(e_u) = \dfrac{(\sigma_1 - \sigma_3)}{\sqrt{2}[1 - \langle\sigma_1\|\sigma_3\rangle]^{\frac{1}{2}}}$
		$\Pi_1^a(e_u) = \dfrac{(\pi_{y2} - \pi_{x4})}{\sqrt{2}[1 - \langle\pi_{y2}\|\pi_{x4}\rangle]^{\frac{1}{2}}}$
		$\Pi_2^a(e_u) = \dfrac{(\pi_{x5} - \pi_{y6})}{\sqrt{2}[1 - \langle\pi_{x5}\|\pi_{y6}\rangle]^{\frac{1}{2}}}$
	p_y	$\Sigma^b(e_u) = \dfrac{(\sigma_2 - \sigma_4)}{\sqrt{2}[1 - \langle\sigma_2\|\sigma_4\rangle]^{\frac{1}{2}}}$
		$\Pi_1^b(e_u) = \dfrac{(\pi_{x1} - \pi_{y3})}{\sqrt{2}[1 - \langle\pi_{x1}\|\pi_{y3}\rangle]^{\frac{1}{2}}}$
		$\Pi_2^b(e_u) = \dfrac{(\pi_{y5} - \pi_{x6})}{\sqrt{2}[1 - \langle\pi_{y5}\|\pi_{x6}\rangle]^{\frac{1}{2}}}$

Table 1 b. Symmetry Classification of Orbitals Used in D_{4h} Symmetry (including ligand—ligand overlap).

a_1	d_{z2}, s, p_z	$\Sigma_1(a_1) = \dfrac{(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)}{2[1 + 2\langle\sigma_1\|\sigma_2\rangle + \langle\sigma_1\|\sigma_3\rangle]^{\frac{1}{2}}}$
		$\Sigma_2(a_1) = \sigma_5$
		$\Sigma_3(a_1) = \sigma_6$
b_1	d_{x2-y2}	$\Sigma(b_1) = \dfrac{(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4)}{2[1 - 2\langle\sigma_1\|\sigma_2\rangle + \langle\sigma_1\|\sigma_3\rangle]^{\frac{1}{2}}}$
b_2	d_{xy}	. . . .
e	d_{xz}, p_x	$\Sigma^a(e) = \dfrac{(\sigma_1 - \sigma_3)}{\sqrt{2}[1 - \langle\sigma_1\|\sigma_3\rangle]^{\frac{1}{2}}}$; $\Pi^a(e) = \Pi_{x5}$
	d_{yz}, p_y	$\Sigma^b(e) = \dfrac{(\sigma_2 - \sigma_4)}{\sqrt{2}[1 - \langle\sigma_2\|\sigma_4\rangle]^{\frac{1}{2}}}$; $\Pi^b(e) = \Pi_{y5}$

Table 1 c. Symmetry Classification of Orbitals Used in C_{4v} Symmetry (including ligand—ligand overlap).

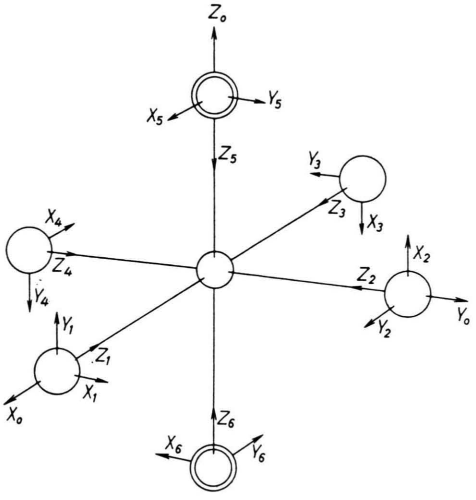

Fig. 1. "General" Geometry of Molecules Studied.

The symmetry classifications of the central ion's and the ligand's symmetry orbitals are given in Tables 1 a, 1 b and 1 c. It should be noted that the ligand symmetry orbitals given are normalized including ligand – ligand overlap. For the $|3d\rangle$, $|4s\rangle$, and $|4p\rangle$ orbitals of Co^{3+} RICHARDSON functions[7] were used, while the $|2s\rangle$ and $|2p\rangle$ functions of nitrogen and $|3s\rangle$ and $|3p\rangle$ functions of chlorine were taken from CLEMENTI's tables[14]. Complete sp^3 hybridization for the nitrogen atom in ammonia, and complete sp hybridization for the chlorine ion were assumed. Using the symmetry orbitals given previously (neglecting ligand – ligand overlap), the group overlaps given in Table 2 were obtained. These, in essence, are *reduced* diatomic overlaps which were evaluated by a computer program written in this laboratory. The wave functions used in this investigation are given in Table 3.

Furthermore, within the framework of the WOLFSBERG–HELMHOLZ approximation we equated the COULOMB integrals to the V.S.I.E. of the atoms considered. Our starting values were the same as the final results of COTTON and HAAS[5, 15] for $Co(NH_3)_6{}^{3+}$. The refinement procedure followed by us was as follows: (i) adjust the V.S.I.E.'s and the parameter F_x in the resonance integrals of $Co(NH_3)_6{}^{3+}$ until the charge on the metal became nearly zero and Δ was equal to the experimental value of 21.1 KK, (ii) adjust $H_{\sigma\sigma}$ and $H_{\pi\pi}$ for chlorine in $Co(NH_3)_5Cl^{2+}$ and $Co(NH_3)_4Cl_2{}^{1+}$ respectively till the best fit for certain electronic transitions were obtained (see Table 4). The one-electron transitions of $2e_g \rightarrow 3a_{1g}$ and $b_{2g} \rightarrow 2b_{1g}$ in $Co(NH_3)_5Cl^{2+}$, as well as the $2e_g \rightarrow 3a_{1g}$ and $b_{2g} \rightarrow 3\,a_{1g}$ transitions in $Co(NH_3)_4Cl_2{}^{1+}$ were fitted to the experimental values of band Ia and Ib (see Fig. 2). As mentioned earlier it was necessary to vary H_{dd} in all the members of the series. The final V.S.I.E. used for the atoms considered in this investigation are given in Table 5.

C_{4v}	D_{4h}
$\langle s \vert \Sigma_1(a_1)\rangle = 2\langle s \vert \sigma_{NH_3}\rangle$	$\langle s \vert \Sigma_1(a_{1g})\rangle = 2\langle s \vert \sigma_{NH_3}\rangle$
$\langle s \vert \Sigma_3(a_1)\rangle = \langle s \vert \sigma_{NH_3}\rangle$	$\langle s \vert \Sigma_2(a_{1g})\rangle = \sqrt{2}\langle s \vert \sigma_{Cl}\rangle$
$\langle s \vert \Sigma_2(a_1)\rangle = \langle s \vert \sigma_{Cl}\rangle$	$\langle d_{z2} \vert \Sigma_1(a_{1g})\rangle = -\langle d_\sigma \vert \sigma_{NH_3}\rangle$
$\langle p_z \vert \Sigma_3(a_1)\rangle = -\langle p_\sigma \vert \sigma_{NH_3}\rangle$	$\langle d_{z2} \vert \Sigma_2(a_{1g})\rangle = \sqrt{2}\langle d_\sigma \vert \sigma_{Cl}\rangle$
$\langle p_z \vert \Sigma_1(a_1)\rangle = \langle p_\sigma \vert \sigma_{Cl}\rangle$	$\langle d_{x2-y2} \vert \Sigma(b_{1g})\rangle = \sqrt{3}\langle d_\sigma \vert \sigma_{NH_3}\rangle$
$\langle d_{z2} \vert \Sigma_2(a_1)\rangle = \langle d_\sigma \vert \sigma_{NH_3}\rangle$	$\langle d_{xz} \vert \Pi_2^a(e_g)\rangle = \sqrt{2}\langle d_\pi \vert \Pi_{Cl}\rangle$
$\langle d_{z2} \vert \Sigma_2(a_1)\rangle = \langle d_\sigma \vert \sigma_{Cl}\rangle$	$\langle p_x \vert \Sigma(e_u)\rangle = \sqrt{2}\langle p_\sigma \vert \sigma_{NH_3}\rangle$
$\langle d_{z2} \vert \Sigma_3(a_1)\rangle = \langle d_\sigma \vert \sigma_{NH_3}\rangle$	$\langle p_x \vert \Pi_2^a(e_u)\rangle = \sqrt{2}\langle p_\pi \vert \Pi_{Cl}\rangle$
$\langle d_{x2-y2} \vert \Sigma(b_1)\rangle = \sqrt{3}\langle d_\sigma \vert \sigma_{NH_3}\rangle$	$\langle p_z \vert \Sigma(a_{2u})\rangle = \sqrt{2}\langle p_\sigma \vert \sigma_{Cl}\rangle$
$\langle p_x \vert \Sigma^a(e)\rangle = \sqrt{2}\langle p_\sigma \vert \sigma_{NH_3}\rangle$	O_h
$\langle p_x \vert \Pi_{x5}\rangle = \langle p_\pi \vert \Pi_{Cl}\rangle$	$\langle s \vert \Sigma(a_{1g})\rangle = \sqrt{6}\langle s \vert \sigma_{NH_3}\rangle$
$\langle d_{xz} \vert \Pi_{x5}\rangle = \langle d_\pi \vert \Pi_{Cl}\rangle$	$\langle d_{z2} \vert \Sigma(e_g)\rangle = \sqrt{3}\langle d_\sigma \vert \sigma_{NH_3}\rangle$
	$\langle p_z \vert \Sigma(t_{1u})\rangle = \sqrt{2}\langle p_\sigma \vert \sigma_{NH_3}\rangle$

* Not including ligand—ligand overlaps.

Table 2. Group Overlaps and Their *Reduced* Diatomic Overlaps *.

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[13] Tables of Interatomic Distances and Configurations in Molecules and Ions, Special Publication No. 11, The Chemical Society, London 1958.

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[15] T. E. HAAS, private communication.

Cobalt (IV)	$\lvert 3d\rangle = 0.598\lvert\varphi_3(5.55)\rangle + 0.526\lvert\varphi_3(2.50)\rangle$
	$\lvert 4p\rangle = 0.08945\lvert\varphi_2(11.05)\rangle - 0.32051\lvert\varphi_3(4.385)\rangle + 1.04545\lvert\varphi_4(1.86)\rangle$
	$\lvert 4s\rangle = -0.02047\lvert\varphi_1(26.375)\rangle + 0.0692\lvert\varphi_2(10.175)\rangle - 0.1697\lvert\varphi_3(4.69)\rangle + 1.0118\lvert\varphi_4(1.45)\rangle$
Nitrogen	$\lvert 2s\rangle = -0.21658\lvert\varphi_1(6.500)\rangle - 0.00841\lvert\varphi_1(11.13)\rangle + 0.08958\lvert\varphi_2(1.27)\rangle + 0.68905\lvert\varphi_2(1.8)\rangle + 0.36685\lvert\varphi_2(3.01)\rangle - 0.12646\lvert\varphi_2(5.23)\rangle$
	$\lvert 2p\rangle = 0.27164\lvert\varphi_2(1.0580)\rangle + 0.51301\lvert\varphi_2(1.628)\rangle + 0.29307\lvert\varphi_2(3.024)\rangle + 0.01208\lvert\varphi_2(7.203)\rangle$
Chlorine	$\lvert 3s\rangle = 0.076821\lvert\varphi_1(17.36)\rangle + 0.00155\lvert\varphi_1(28.02)\rangle - 0.29086\lvert\varphi_2(6.78)\rangle + 0.04414\lvert\varphi_2(15.60)\rangle + 0.62296\lvert\varphi_3(2.97)\rangle + 0.51991\lvert\varphi_3(1.86)\rangle - 0.16296\lvert\varphi_3(6.00)\rangle$
	$\lvert 3p\rangle = -0.17972\lvert\varphi_2(7.68)\rangle - 0.00854\lvert\varphi_2(14.20)\rangle + 0.57105\lvert\varphi_3(2.62)\rangle + 0.54233\lvert\varphi_3(1.46)\rangle - 0.11524\lvert\varphi_3(5.92)\rangle$

Table 3. Analytical S.C.F. Functions Used in This Investigation.

Complex Ion	Band	Exp.	Nakamoto		This Work	
$Co(NH_3)_6^{3+}$ (Ref.[18])	Ia Ia′	2.61	2.59	$t_{2g} \rightarrow e_g$	2.60	$t_{2g} \rightarrow e_g$
$Co(NH_3)_5Cl^{2+}$ (Ref.[18])	Ia	2.32	1.90	$3e \rightarrow 4a_1$	2.34	$3e \rightarrow 4a_1$
	Ib	2.65	2.20	$b_2 \rightarrow 4a_1$	2.59	$b_2 \rightarrow 4a_1$
	II	3.41	2.99	$2e \rightarrow 4a_1$	3.84	$2e \rightarrow 4a_1$
11	III	4.61	4.00	$3a_1 \rightarrow 4a_1$	4.14	$2e \rightarrow 2b_1$
	IV	5.46	5.19	$2e \rightarrow 2b_1$	5.29	$3a_1 \rightarrow 4a_1$
$Co(NH_3)_4Cl_2^{1+}$ (Ref.[17])	Ia	1.97	1.79	$2e_g \rightarrow 3a_{1g}$	1.74	$2e_g \rightarrow 3a_{1g}$
	Ib	2.60	2.20	$b_{2g} \rightarrow 3a_{1g}$	2.35	$b_{2g} \rightarrow 3a_{1g}$
	II	3.09	3.26 3.67	$2e_g \rightarrow 2b_{1g}$ $b_{2g} \rightarrow 2b_{1g}$	3.14	$b_{2g} \rightarrow 2b_{1g}$
	III	4.09	3.75 4.25	$2e_u \rightarrow 3a_{1g}$ $1a_{2u} \rightarrow 3a_{1g}$	3.71 4.32	$2e_u \rightarrow 2b_{1g}$ $1a_{2u} \rightarrow 3a_{1g}$
	IV	4.89	5.22	$2e_u \rightarrow 2b_{1g}$	5.16	$1e_u \rightarrow 3a_{1g}$

* **All experimental values obtained from solution spectra.**

Table 4. Comparison of the Experimental * and Calculated Values of the One-Electron Transitions in eV.

		VSIE (−eV)		
atom	orbital	O_h	C_{4v}	D_{4h}
Co	H_{ss}	5.00	5.00	5.00
	H_{pp}	8.25	8.25	8.25
	H_{dd}	11.50	12.00	12.50
N	$H_{\sigma\sigma}$	14.50	14.50	14.50
Cl	$H_{\sigma\sigma}$	—	13.50	13.50
	$H_{\pi\pi}$	—	13.00	13.00
Fx		2.68	2.68	2.68
Charge on cobalt		+0.002	−0.197	−0.416

Table 5. Final Atomic V.S.I.E.'s and Charge Distributions on Cobalt.

2. Determination of the M.O. Energies and Discussion of Results

Using the scaled diatomic overlaps given in Table 2, the one-electron molecular orbital energies were determined by solving the symmetrized secular determinant. In brief, a matrix C was sought which diagonalized the unsymmetric matrix product $G_\psi^{-1} H_\psi$, such that:

$$C^{-1} G_\psi^{-1} H_\psi C = H_\varphi(\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_n)$$

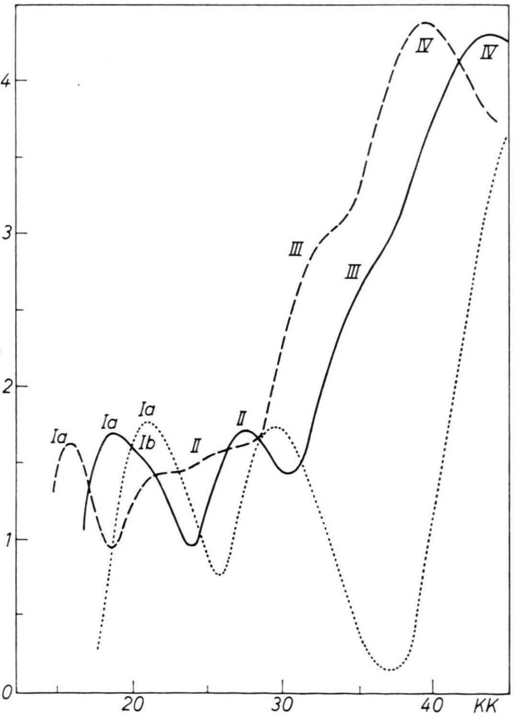

Fig. 2. Absorption Spectra: (i) $Co(NH_3)_6^{3+}$ ········, (ii) $Co(NH_3)_5Cl^{2+}$ ———, (iii) $Co(NH_3)_4Cl_2^{1+}$ – – – –.

where the components of the row vector $|\Phi\rangle$ in:

$$|\Phi\rangle = |\Psi\rangle C$$

were the one-electron molecular orbitals. Furthermore, the MULLIKEN population analysis on the central atom in each case was calculated according to the recipe given by BALLHAUSEN and GRAY [16]. The final charge distributions on the cobalt, in the series studied, are given in Table 4, while the final M.O. energy levels as well as their electron occupancies are given in Figs. 3 a, 3 b, and 3 c.

Finally the predicted as well as the experimental electronic transitions [17, 18] are given in Table 4. Upon examination of the latter, one notices that several sets of transitions in the chloroammine complexes differ from previous assignments. There is, unfortunately, no physical method to decide which, if any, is the correct assignment. All things considered, however, our assignments give a better fit to the experimental values hitherto published.

Acknowledgment

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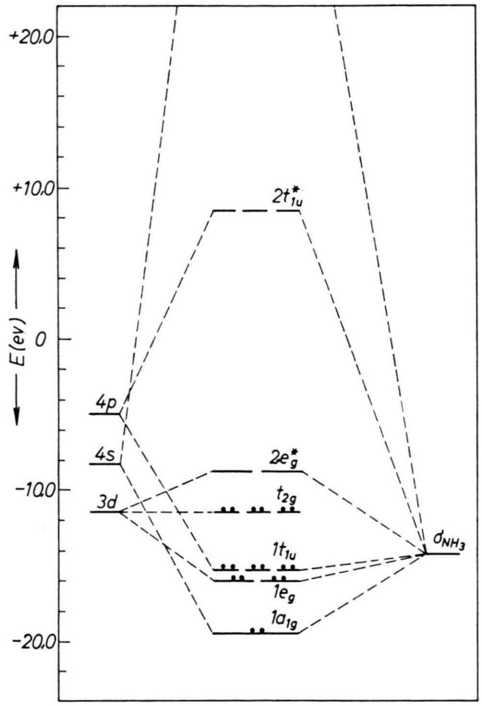

Fig. 3 a. One-electron M.O. Energy Levels of $Co(NH_3)_6{}^{3+}$.

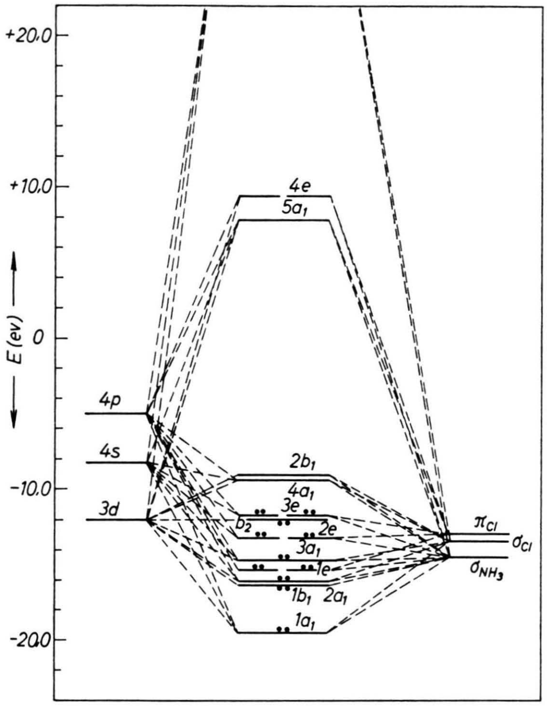

Fig. 3 b. One-electron M.O. Energy Levels of $Co(NH_3)_5Cl^{2+}$.

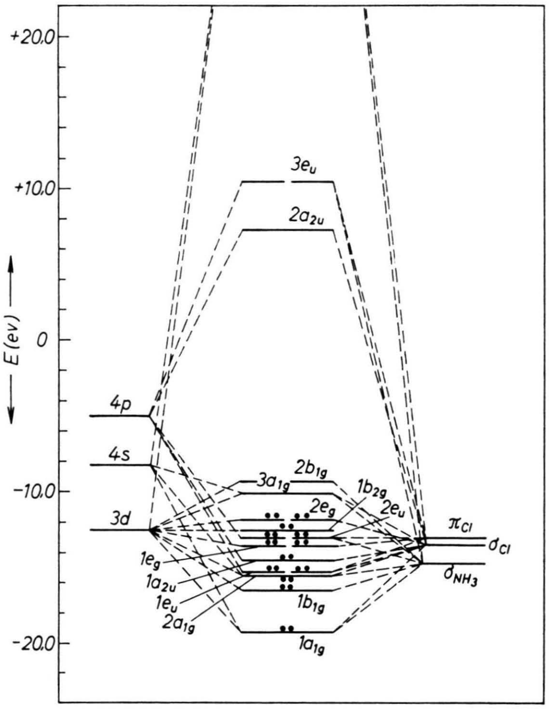

Fig. 3 c. One-electron M.O. Energy Levels of $Co(NH_3)_4Cl_2{}^{1+}$.

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