ion minus a CH_2O fragment. The peaks at *m/e* 470 and 440 and the LH^+ fragment at *m/e* 179 all are half the intensity of the base peak at *m/e* 148 (loss of 31 from the 179 peak).

A second group of nickel complexes has been investigated in which the side chain of the salicylaldimine does not contain a readily removable hydrogen as in *n*-propyl, *sec*-butyl, *t*-butyl, $-CH_2CH_2N(CH_3)_2$, or $-CH_2CH_2OCH_3$. For these compounds, the mass spectra are normal and the binuclear species are present but at low abundance (less than 1% of the molecular ion). The mass of these ions is 58 units above the molecular ion and not 58 − 2. Apparently the loss of two protons is the difference in the mass spectra of two groups of compounds; by removal of two protons, the high-mass species are stabilized.

The production of polynuclear ions has also been observed with nickel chelates derived from ethylenediamines and acetyldimedone (dimedone = 5,5-dimethyl-1,3-cyclohexanedione).[10] Thus the phenomenon appears to be general with nickel chelates.

The high-mass species may result from thermal alterations of the complexes on the direct insertion probe; however, the compounds melt without *reported* decomposition.[3,4] Furthermore, after obtaining a spectrum of a complex, but before complete consumption of the sample, the probe was inspected. The sample remaining on the probe showed no *observable* change. On complete consumption of the sample, no residue was found on the probe.

Since the yield of the dimeric species can be high (to ~100%) and since a deliberate effort has been made to keep the ion concentration low through high spectrometer sensitivity, an ion–molecule reaction to produce the dimer appears improbable.[7a] A molecule–molecule reaction at the sample surface yielding the dimer and a neutral ligand (LH^+) is more likely. This second process is supported by the deuterium-labeling experiment which indicates that the hydrogen (deuterium) in the LH^+ ion is the hydrogen (deuterium) lost from the $[(L - H)_2Ni_2]^+$ ion.

The presence of high-mass species reported here is another example[11] which indicates that caution must be used in determining molecular weights by mass spectral analysis when other potential chelating sites are available. This is analogous to the finding by Biemann, *et al.*,[12] that organic reactions can occur in suitably disposed alkaloids generating higher molecular weight species.

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Correspondence

The Use of Vibronic Interactions in the Assignment of the Infrared Spectrum of $Co(NH_3)_6{}^{3+}$

Sir:

The assignment of the infrared-active metal–ligand stretching mode of $Co(NH_3)_6{}^{3+}$ has long been a subject of discussion and controversy.[1–10] This controversy, however, had remained dormant until recently when Watt and Klett suggested[9] that the nature of the stretching and deformation modes of $Co(NH_3)_6{}^{3+}$ remained unresolved. In a subsequent note, this was contradicted by Shimanouchi and Nakagawa.[10] On the basis of the results of a normal coordinate analysis, the latter authors assigned the weak ir band at 503 cm^{-1} and the strong band at 325 cm^{-1} to the $\tilde{\nu}_3(t_{1u})$ and $\tilde{\nu}_4(t_{1u})$ vibrations of the $Co(NH_3)_6{}^{3+}$ moiety. The purpose of the present correspondence is to confirm the assignments of Shimanouchi and Nakagawa from a completely different approach—by the use of the results of the low-temperature, polarized, near-uv crystal spectrum of $[Co(NH_3)_6][Co(CN)_6]$ which was recently reported by Wentworth.[11]

From the theoretical point of view, electric dipole transitions between orbitals of the same parity and predominantly localized on the central ion of centric transition metal complexes are Laporte forbidden.[12] Nonetheless, such transitions, although weak in intensity, are ordinary occurrences in the spectra of these complexes and, in essence, account for the diversity of colors of the ions of the transition metal complexes. It is presently believed, by most workers in the field, that these transitions are due to the admixture of states of different parity *via* perturbations caused by an ungerade vibration which in essence destroys the "static" center of symmetry and makes the transition *vibronically* allowed.[13,14] Specifically, in the case of the octahedral $Co(NH_3)_6{}^{3+}$ moiety, such distortion is indeed theoretically expected to be due to the $\tilde{\nu}_3(t_{1u})$, $\tilde{\nu}_4(t_{1u})$, and $\tilde{\nu}_6(t_{2u})$ vibrational modes, as well as

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to combinations of modes whose direct product includes the t_{1u} and/or t_{2u} irreducible representations of the O_h group.[15] It is important to note that (i) in most vibronic interactions the effective combinations are those which are mixed with the totally symmetric mode transforming as A_{1g},[11,16,17] and that (ii) in general, the vibrational levels in the excited states differ from those of the ground state by approximately[18] ±10–20%. In the specific case of $Co(NH_3)_6^{3+}$, on the other hand, since the electronic transition is to an antibonding orbital, a decrease in the vibrational levels in the excited state is expected. (This point was brought to the author's attention by one of the referees.)

Thus, regarding the NH_3 ligand as one unit, the $Co(NH_3)_6^{3+}$ ion was treated as a seven-body problem. Using the assignments of Shimanouchi and Nakagawa[10] a normal coordinate analysis was performed with different "reasonable" sets of Urey–Bradley force constants.[19] Trends upon change of force constants were studied, and finally the most suitable set of force constants was adopted. (The adopted values were: $K = 1.34$ mdyn/Å, $H = 0.22$ mdyn/Å, and $F = 0.18$ mdyn/Å.) Then, *and only then*, were these used to calculate the frequencies of the isotopic species $Co(ND_3)_6^{3+}$. Table I gives the experimental as well as calculated values, and it can be seen that the agreement is rather good.

TABLE I

CALCULATED AND OBSERVED FREQUENCIES (IN CM^{-1})

Freq[a]	Vibrational mode	$Co(NH_3)_6^{3+}$	$Co(ND_3)_6^{3+}$	Absolute isotopic shifts
$\tilde{\nu}_1(a_{1g})$	Co–N str	454	418	36
$\tilde{\nu}_2(e_g)$	Co–N str	383	352	31
$\tilde{\nu}_3(t_{1u})$	Co–N str	504 (503)	482	22
$\tilde{\nu}_4(t_{1u})$	N–Co–N def	329 (325)	308 (310)	(15)
$\tilde{\nu}_5(t_{2g})$	N–Co–N def	357	329	28
$\tilde{\nu}_6(t_{2u})$	N–Co–N def	252	232	20

[a] Observed frequencies are given in parentheses.

Now, if one assumes that the 503- and 325-cm^{-1} bands in the ir spectrum *are* indeed the $\tilde{\nu}_3$ and $\tilde{\nu}_4$ modes, respectively, one would then expect a series of progressions in the low-temperature, polarized vibronic spectrum of $Co(NH_3)_6^{3+}$ due to: (i) the $\tilde{\nu}_3$ mode and separated approximately by 400–450 cm^{-1}, (ii) the $\tilde{\nu}_4$ mode and separated approximately by 260–290 cm^{-1}, (iii) the $\tilde{\nu}_6$ mode and separated approximately by 200–230 cm^{-1}, and/or (iv) a combination band with $\tilde{\nu}_1$, the value of the latter ranging from approximately 360 to 400 cm^{-1}.

The polarized crystal spectrum of $[Co(NH_3)_6][Co(CN)_6]$ at 80°K is reported by Wentworth[11] to exhibit *a uniquantal progression*[20] *of a* 420 ± 10 *vibration and its combination band with a* 390 ± 10 *vibration* (the italics are ours). It is obvious that at 80°K, vibronic transitions due to the $\tilde{\nu}_3$ and the $(\tilde{\nu}_1 + \tilde{\nu}_3)$ modes are becoming discernible. It is indeed gratifying to note that not only is the vibronic spectrum of $Co(NH_3)_6^{3+}$ explained by the Shimanouchi and Nakagawa[10] assignments but that the vibronic structure of $Co(ND_3)_6^{3+}$ *can* be calculated[21] and observed[11] as expected!

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[19] H. C. Urey and C. A. Bradley, Jr., *Phys. Rev.*, **38**, 1969 (1931).

[20] The vibrational quanta are superimposed on the band whose maximum is reported to be at 4720 Å.

[21] The observed separations of the progressions are of a 380 ± 10 cm^{-1} mode, and its combination band with a 340 ± 15 cm^{-1}, while the calculated values are 386–420 and 334–386 cm^{-1}, respectively.

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The Nature of the Intermediate in Unimolecular Octahedral Aquation

Sir:

Studies of the dependence of the rate of aquation of cobalt(III) complexes of the type $Co(en)_2ACl^{n+}$ (en = ethylenediamine) led Ašperger and Ingold[1] to postulate a duality of mechanism that depended upon the electron displacement properties of A. This proposal was later refined in the light of further evidence relating especially to the steric course[2] by postulating that (i) if A possessed an extra pair of electrons that could be donated to the metal to compensate for the loss of the departing ligand, a unimolecular mechanism was favored and (ii) in the absence of such assistance the mechanism was bimolecular. The stereochemical rules required that the intermediate must have a trigonal-bipyramidal form when A was originally *trans* to the leaving group which would therefore lead to steric change, whereas the bimolecular attack would be adjacent to the leaving group and therefore result in substitution with retention of configuration. These proposals extended a similar discussion by Basolo and Pearson some years earlier[3] where the π-bonding aspects of the process were stressed.

Later work involving the nonsolvolytic reactions of these complexes could provide no evidence in support of the bimolecular mechanism and any dependence of rate on the concentration of the entering nucleophile could be accounted for in terms of an equilibrium preassociation of the reagents. The rate of the subsequent interchange was rarely very sensitive to the nature of the entering group.[4]

It was suggested that all of these observations could be accounted for by an essentially dissociative mechanism in which the duality of response to the electron

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