TABLE I

SOLUBILITIES OVER $Co(NH_3)_6BiI_6(s)$ AND $Co(NH_3)_6I_3(s)$

$[I^-]$, M^{-1}	10^3S, M^{-1} Obsd	Calcd[a]	Calcd[b]	$\bar{n}$
1.6	0.1565	0.1555	0.1565	
				6.03
1.8	0.223	0.225	0.226	
				6.10
2.0	0.309	0.309	0.309	
				6.09
2.3	0.477	0.478	0.477	
				6.08
2.6	0.697	0.694	0.694	
				6.11
3.0	1.088	1.088	1.090	
				6.12
3.5	1.762	1.768	1.780	

[a] $K_7 = \beta_7/\beta_6 = 0.05$; $S = 3.51 \times 10^{-5}[I^-]^3(1 + K_7[I^-])$.
[b] $K_8 = \beta_8/\beta_6 = 0.009$; $S = 3.73 \times 10^{-5}[I^-]^3(1 + K_8[I^-]^2)$.

a complex with $\bar{n} > 6$ strongly supports the view that such a complex really exists.

However, since the effects due to the highest complex are so small, it seems unlikely that it will be possible to determine conclusively the number of iodides in the complex, or its formation constant. Eve and Hume[2] chose BiI_7^{4-}, stating that they got consistent constant values at different wavelengths only with this complex. We cannot agree with this conclusion, however, for the following reason. Although no primary data are given in the paper of Eve and Hume, it is possible to calculate, for different wavelengths, absorbancy values for their five upper ligand concentrations, from the values of K_7, A', and A'' in Table II and from Figure 6 of their paper. These should be close to their measured values. Now, using *one* value of K_8, we can find values of A' and A'' at all wavelengths, so that a set of absorbancies is obtained that never differs from the previous set by more than 0.3%. This shows clearly that it is not possible to conclude from their data whether BiI_7^{4-} or BiI_8^{5-} is formed.

TABLE II

VARIOUS INTERPRETATIONS OF THE DATA OF EVE AND HUME,[2] AT 402.5 mμ[a]

	Absorbancies			
	Obsd	Calcd		
$[I^-]$, M	Ref 2, Figure 3	$K_7 = 0.13$	$K_7 = 0.01$	$K_8 = 0.024$
0.4	0.657	0.656	0.658	0.658
0.8	0.673	0.673	0.673	0.672
1.0	0.681	0.681	0.680	0.680
1.2	0.688	0.688	0.688	0.689
1.4	0.696	0.694	0.695	0.695

[a] Similar agreement is obtained at wavelengths 337 and 465 mμ.

We also feel the choice of value for K_7, based on Figure 4 in the paper of Eve and Hume, is tenuous. The value $K_7 = 0.077$ is rejected because the point of highest A deviates from the straight line for this value. A closer inspection of this point reveals, however, that a change of A (or A'') as small as 0.001 is sufficient to move the point to the line. Certainly, the absorbancy is not determined to better than 0.001. Thus, the only fact shown is that this point is not relevant, for the purpose of Figure 4, for the determination of K_6. Points of higher $[I^-]$ are even less relevant, naturally.

As to K_7, the fact is that sets of absorbancies can be calculated at any wavelength with K_7 as different as 0.13 and 0.01 with a consistency within 0.3%, for the five relevant (highest) $[I^-]$ (Table II). Admittedly, though, the differences in spectra for BiI_6^{3-} and BiI_7^{4-} come out rather high for $K_7 = 0.01$, and for this reason a value $K_7 \approx 0.1$ seems more likely. It should also be noted that for the two ionic strengths, 2 and 4 M, a difference in the constant is to be expected.

To sum up, both investigations show that a complex BiI_n^{3-n} with $n > 6$ is formed. It is not possible, however, to conclude whether this complex is BiI_7^{4-} or BiI_8^{5-} nor to assign any very accurate value to the formation constant of the complex.

It is puzzling that data of this kind are indecisive concerning BiI_n^{3-n} complexes with $n > 6$, whereas similar data involving solubility equilibria lead clearly to postulation of $BiBr_8^{5-}$ [5e] and SnI_8^{6-}.[5g]

CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY,
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Abnormal Mass Spectra of Nickel Schiff Base Chelates

BY EMILY P. DUDEK, ELEANOR CHAFFEE, AND GERALD DUDEK

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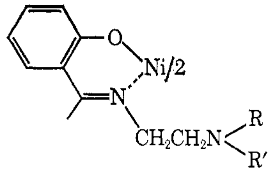
Mass spectrometry has become an important analytical method in the investigation of inorganic compounds,[1,2] particularly in the determination of molecular weight. A knowledge of its limitations is essential for an intelligent application of the method. We, therefore, wish to report systems where the analysis of mass spectral data could easily lead to an erroneous identification of the molecular species originally present.

Complexes of nickel(II) with Schiff bases formed from salicylaldehyde and N-substituted ethylenediamines, $[Salen\text{-}N(R)R']_2Ni^{II}$, have been studied by Sacconi, Holm, and their coworkers.[3,4] Chemical, spectral, and magnetic measurements indicate that $[Salen\text{-}N(H)C_6H_5]_2Ni^{II}$ is a square-planar, four-coordi-



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(1) C. Reichert, J. B. Westmore, and H. D. Gesser, *Chem. Commun.*, 782 (1967), and references contained therein.

(2) J. M. Smith, K. Mehner, and H. D. Kaesz, *J. Am. Chem. Soc.*, **89**, 1759 (1967).

(3) L. Sacconi, P. Nannelli, and U. Campigli, *Inorg. Chem.*, **4**, 818 (1965); L. Sacconi, P. Nannelli, N. Nardi, and U. Campigli, *ibid.*, **4**, 943 (1965).

(4) A. Chakravorty, J. P. Fennessey, and R. H. Holm, *ibid.*, **4**, 26 (1965).

nate nickel compound with a ligand:nickel (L:Ni) ratio of 2:1.[3] On the other hand, in the mass spectrum[5,6] of the compound (Figure 1), not only is the normal molecular ion, L_2Ni^+, found at *m/e* 536, with the isotopic intensity ratio characteristic of one nickel atom, but also a strong multiplet appears at *m/e* 592 with the isotopic abundance expected for two nickel atoms in the ion fragment. Moreover, the intensity of the normal molecular ion is *less than* 5% of that of the higher mass ion. The *m/e* 592 value corresponds to the mass of two ^{58}Ni nuclides plus two Schiff base ligands, each minus a proton. Thus, in contradiction to the chemical evidence,[3] the mass spectrum of the nickel(II) complex of Salen-N(H)C_6H_5 indicates a composition for the compound of two nickel ions bonded to two Schiff base ligands, each less a proton, $[(L - H)_2Ni_2]^+$

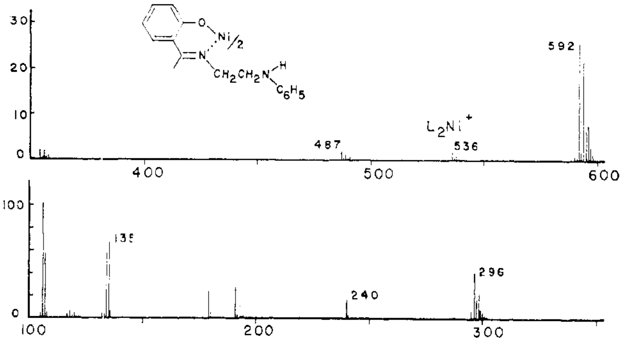
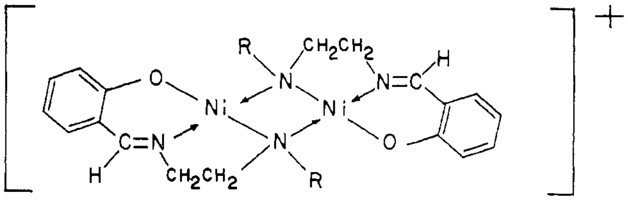


Figure 1.—Mass spectrum of bis[*o*-[N-(2-anilinoethyl)formimidoyl]phenolato]nickel(II) at 70 eV.



This structure implies that the amine hydrogens are lost on formation of the dinickel species. To substantiate this proposal, the amine hydrogens were replaced with deuterium by crystallizing the chelate from CH_3OD. The success of this exchange was indicated by the shift of the L_2Ni^+ peak in the mass spectrum from *m/e* 536 to 538. On the other hand, the peak corresponding to the $[(L - H)_2Ni_2]^+$ species remained at *m/e* 592, verifying that the two hydrogens removed on formation of the dinickel ions are those which exchanged with deuterium—the amine hydrogens. The hydrogens (deuterium) lost by the dinickel species appeared in the LH^+ fragment, the LH^+ peak being shifted up 2 mass units from *m/e* 240 to *m/e* 242 upon deuteration of the complex.

The $[(L - H)Ni]^+$ moiety at *m/e* 296 is invariant with deuteration. This ion most likely results from scission of the $[(L - H)_2Ni_2]^+$ species. A broad metastable peak for the process 592 → 296 is observed at *m/e* 148.

The N-methylamine complex of nickel, [Salen-N(H)$CH_3]_2Ni^{II}$, with a *cis*-octahedral structure in the solid state,[3] displays (Figure 2) a peak at *m/e* 468 corresponding to $[(L - H)_2Ni_2]^+$. The abundance of this high mass ion is slightly less than that of the molecular ion, L_2Ni^+, at *m/e* 412. There also appear, albeit at low intensities, ions at higher masses, such as *m/e* 530, containing two metal ions and several ligands. These ions are reminiscent of the polymeric species observed with the acetylacetonates.[7,8]

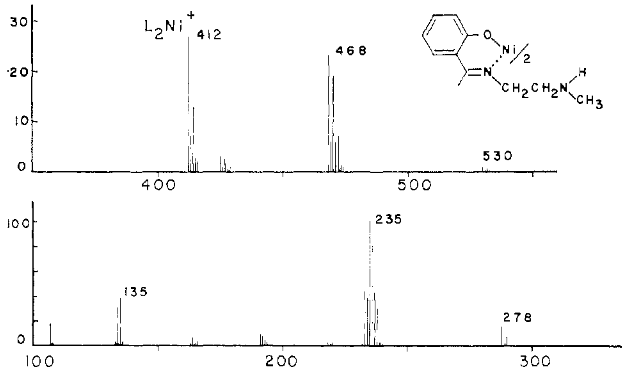
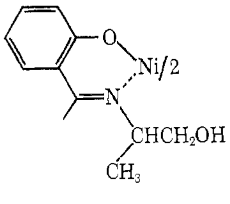


Figure 2.—Mass spectrum of bis[*o*-[N-(2-methylaminoethyl) formimidoyl]phenolato]nickel(II) at 70 eV.

In the case of bis(N-methyltrimethylenediamine-salicylaldimine)nickel(II), a monomeric, octahedral compound,[3] where the alkyl side chain is extended by one methylene unit, the intensity of the dinickel species (at *m/e* 496) drops markedly. It is only 10% of the intensity of the molecular ion at *m/e* 440 and 3% of the base peak at *m/e* 248 (corresponding to $[(L - H)Ni]^+$). This may be due in part to the ability of the ethylenediamines to form a five-membered ring, while the trimethylenediamines must form the less favored six-membered ring.[9]

The hydrogens lost from the side chain to form the dinickel species need not be from nitrogen. With bis-[2-(1-hydroxy)propylsalicylaldimine]nickel(II), the molecular ion at *m/e* 414 is of negligible intensity as compared to the dinickel species $[(L - H)_2Ni_2]^+$ and the equally strong *m/e* 440 species attributed to the dinickel



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(5) Mass spectra were obtained on an AEI MS-9 mass spectrometer using direct insertion of the sample and the minimum sample temperature necessary to obtain a usable spectrum. To this end, both the source sensitivity (trap current) and electron multiplier sensitivity were set at higher values than normal. The temperature was usually 160–200°.

(6) The large mass difference between nickel ions at *m/e* 58 and 60 and hydrocarbon fragments at the same nominal mass allows ready identification of Ni^+ in the spectrum. In several cases the intensity of Ni^+ has been several per cent of the base peak.

(7) (a) C. G. MacDonald and J. S. Shannon, *Australian J. Chem.*, **19**, 1545 (1966); (b) J. Macklin and G. Dudek, *Inorg. Nucl. Chem. Letters*, **2**, 403 (1966).

(8) If appreciably higher ion source temperatures are employed, these high-mass fragments increase greatly in intensity. In addition, there is a very large increase in the intensity of the lower mass organic fragments suggesting appreciable thermal decomposition under these forcing conditions.

(9) I. Poulsen and J. Bjerrum, *Acta Chem. Scand.*, **9**, 1407 (1955); F. A. Cotton and F. E. Harris, *J. Phys. Chem.*, **59**, 1203 (1955).

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.

[10] E. P. Dudek and coworkers, unpublished observations.

[11] E. P. Dudek and M. Barber, *Inorg. Chem.*, **5**, 375 (1966).

[12] D. W. Thomas and K. Biemann, *J. Am. Chem. Soc.*, **87**, 5447 (1965).

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

[1] D. G. Hill and A. F. Rosenberg, *J. Chem. Phys.*, **22**, 148 (1954); **24**, 1219 (1956).

[2] M. Kobayashi and J. Fujita, *ibid.*, **23**, 1354 (1955).

[3] I. Nakagawa and S. Mizushima, *Bull. Chem. Soc. Japan*, **28**, 589 (1955).

[4] S. Mizushima, I. Nakagawa, and J. V. Quagliano, *J. Chem. Phys.*, **23**, 1367 (1955).

[5] D. B. Powell and H. Sheppard, *J. Chem. Soc.*, 3108 (1956).

[6] G. M. Barrow, R. H. Krueger, and F. Basolo, *J. Inorg. Nucl. Chem.*, **2**, 340 (1956).

[7] T. Shimanouchi and I. Nakagawa, *Spectrochim. Acta*, **18**, 89 (1962).

[8] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963.

[9] G. W. Watt and D. S. Klett, *Inorg. Chem.*, **3**, 782 (1964).

[10] T. Shimanouchi and I. Nakagawa, *ibid.*, **3**, 1805 (1964).

[11] R. A. D. Wentworth, *Chem. Commun.*, 532 (1965).

[12] O. Laporte, *Phys. Rev.*, **61**, 302 (1942).

[13] J. H. Van Vleck, *ibid.*, **41**, 67 (1937).

[14] W. A. Yeranos, *Z. Naturforsch.*, **21**, 1864 (1966).