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Spectroscopic Studies of Substituted Imidazole Complexes. I. Some Complexes of 2-Methylimidazole

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The preparations are reported of the following complexes of 2-methylimidazole (= L): ML_4X_2 (M = Co; X = I, NO_3. M = Ni, X = Cl, Br, I, NO_3. M = Cu; X = Cl, Br. M = Zn; X = NO_3), ML_2X_2 (M = Co, Ni, Zn; X = Cl, Br, I, NO_3. M = Cu; X = Cl, Br), $NiLCl_2$ and $NiL_{3.5}I_2$. Magnetic susceptibility and electronic and low frequency (90-450 cm^{-1}) vibrational spectral measurements have been made, and the results are discussed and used to assign coordination geometries where possible.

Introduction

As part of a program to elucidate the molecular and electronic structures of complexes of biologically important ligands, we have prepared and studied some complexes of 2-methylimidazole (= L). A few of these compounds have recently been described,[1] but since our infrared measurements extend to lower frequency, and since we prefer different assignments for some of the electronic spectra, we report results for these compounds as well as for those which are new.

Experimental Section

All complexes were dried in vacuum over P_2O_5. Analytical results (C, H, and N by the Microanalytical Laboratory, Imperial College) for all the compounds were good.

CoL_4I_2. 2-methylimidazole and $CoI_2 . 6H_2O$ were mixed in 4: 1 mole ratio in ethanol. After evaporation to small bulk benzene was added until a cloudiness was observed. Deep purple crystals separated from the blue solution and were filtered off and washed with benzene.

$CoL_4(NO_3)_2$ (2 forms). Both forms of this compound were obtained from ethanolic solutions of the calculated quantities of 2-methylimidazole and hydrated cobalt nitrate. *Form A* was obtained as pink crystals on allowing a hot ethanolic solution to cool. After filtration they were washed with acetone and then ether. *Form B*: addition of dichloromethane to the ethanolic solution gave a dark red oil, which yielded purple crystals on storing at 0° for 2 days. (This preparation was found difficult to reproduce, form A or mixtures of A and B being frequently obtained).

CoL_2X_2 (X = Cl, Br, or I). Hot acetone solutions of the cobalt halide and 2-methylimidazole were mixed in 1:2 mole ratio and then filtered. Dichloromethane (X = Cl or Br) or benzene (X = I) were added until a cloudiness developed. Storage at 0°C for 24 hrs gave dark blue crystals which were collected and washed with acetone/dichloromethane (X = Cl or Br) or acetone/benzene (X = I).

$ML_2(NO_3)_2$ (M = Co or Ni). 2-methylimidazole in acetone and the hydrated metal nitrate in 2,2'-dimethoxypropane were mixed in 1.9: 1 mole ratio. The mixture was filtered and solvent was distilled off until an oil formed. This was separated and stored under benzene until it had crystallized. The solid was washed with benzene and then ether.

NiL_4X_2 (X = Cl, Br, I, or NO_3). Hot ethanolic solutions of the appropriate nickel salt and 2-methylimidazole were mixed in 1:4.4 mole ratio. In the case of the *iodide* addition of ether gave the yellow complex, which was recrystallized from acetone. The pale blue *nitrate* slowly precipitated on cooling the solution. It was washed with acetone and ether. The *chloride* and *bromide* separated as green crystals, along with a small amount of the inner complex $Ni(C_4H_5N_2)_2$ [1] which was removed by recrystallizing the products from ethanol.

NiL_2Cl_2. Solid $NiCl_2 . 6H_2O$ was added to an acetone solution of 2-methylimidazole to give a 1:2 mole ratio. The blue solution was boiled and filtered hot. Benzene was added until a cloudiness developed. The purple oil which separated on cooling crystallized during 24 hr to give a yellow solid. This was filtered off and washed with acetone and then ether.

NiL_2X_2 (X = Br or I). The appropriate 4: 1 complex was heated to constant weight in vacuum at 120°C. The blue bromide and dark green iodide were very hygroscopic.

$NiL_{3.5}I_2$. This purple compound was obtained by heating NiL_4I_2 to constant weight in vacuum at 75°C. Calcd. wt. loss for $NiL_4I_2 \rightarrow NiL_{3.5}I_2$: 6.41%; wt. loss found 6.85%.

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[1] W. J. Eilbeck, F. Holmes, C. E. Taylor, and A. E. Underhill, *J. Chem. Soc.* (A), 128, (1968).

Anal. Calcd. for $C_{14}H_{21}I_2N_7Ni$: C, 28.04; H, 3.50; N, 16.35. Found: C, 27.89; H, 3.42; N, 16.19%.

This preparation was not always reproducible in that sometimes the green 2: 1 complex began to form. If this occurred, the heating was stopped and the sample allowed to stand at atmospheric pressure until the green portion had changed to purple (*ca.* 24 hr). Continuation of the heating process then gave only the purple compound.

$NiLCl_2$. Hydrated nickel chloride was refluxed with ethanol/2,2-dimethoxypropane for 15 min., and then a slight excess (1.1: 1 mole ratio) of 2-methylimidazole was added. The solution was evaporated to dryness and the residue was treated with successive portions of acetone, to remove NiL_2Cl_2, until the washings were colorless.

CuL_4X_2 (X = Cl or Br). These were prepared as for their nickel analogs.

CuL_2X_2 (X = Cl or Br). These compounds precipitated as yellow-green (chloride) or red-brown (bromide) crystals on mixing solutions of the copper(II) halide and 2-methylimidazole in acetone (chloride) or ethanol (bromide).

$ZnL_4(NO_3)_2$. Benzene was added to a hot acetone solution of zinc nitrate and 2-methylimidazole (in 1:4.4 mole ratio) until the solution became cloudy. The colorless crystals which separated on standing were washed with ether and recrystallized from ethanol/benzene.

ZnL_2X_2. (X = Cl, Br, I, or NO_3). These were prepared as for the cobalt analogs.

Physical Measurements. X-Ray powder photographs were taken on an Enraf-Nonius Guinier-De Wolff camera. The other measurements were carried out as described previously.[2]

Results and Discussion

We have obtained complexes of stoichiometry ML_4X_2 for all the metal ions Co^{2+} through Zn^{2+}, from solutions containing an excess of 2-methylimidazole. In contrast to imidazole,[2,3] no evidence was obtained for the formation of 6: 1 complexes. This may be attributed to the increased steric hindrance by the methyl group. Complexes of 2: 1 stoichiometry were also obtained, more readily than the 4: 1 compounds in the case of cobalt and zinc.

Electronic Spectra and Magnetic Measurements. The room-temperature magnetic moments and diffuse reflectance spectral band energies of the complexes are listed in Table I.

The electronic spectrum and the low magnetic moment observed for $[CoL_4]I_2$ both point to the presence of tetrahedral CoL_4^{2+} ions in that compound. The ligand field strength of 2-methylimidazole (Δ = 5250 cm^{-1}) is slightly greater than that of benzimidazole[4] (Δ = 5100 cm^{-1}) but weaker than that of imidazole itself[5] (Δ = 5380 cm^{-1}) in tetrahedral compounds.

Two forms of $CoL_4(NO_3)_2$ were obtained, one pink (form A), the other purple (form B). The spectrum of A is typical of a distorted octahedral configuration, (the $^4T_{2g}$ level shows a pronounced splitting).

Analytical Results

Compound	Found C	Found H	Found N	Calcd. C	Calcd. H	Calcd. N
CoL_4I_2	30.26	3.79	17.61	29.94	3.79	17.47
$CoL_4(NO_3)_2$ [A]	37.44	4.75	27.31	37.57	4.69	27.39
$CoL_4(NO_3)_2$ [B]	37.96	5.12	27.31	37.57	4.69	27.39
CoL_2Cl_2	32.97	4.26	19.21	32.66	4.08	19.04
CoL_2Br_2	25.35	3.24	14.78	25.08	3.13	14.62
CoL_2I_2	20.45	2.50	11.51	20.13	2.52	11.74
$CoL_2(NO_3)_2$	28.07	3.52	23.77	27.67	3.46	24.17
NiL_4Cl_2	42.10	5.01	24.66	41.91	5.24	24.44
NiL_4Br_2	35.43	4.39	20.42	35.10	4.39	20.48
NiL_4I_2	30.09	3.55	17.76	29.94	3.74	17.47
$NiL_4(NO_3)_2$	37.91	4.96	27.68	37.57	4.69	27.39
$NiL_{3.5}I_2$	27.89	3.42	16.19	28.04	3.50	16.35
NiL_2Cl_2	32.38	4.31	18.80	32.66	4.08	19.05
NiL_2Br_2	25.18	3.46	14.20	25.10	3.13	14.63
NiL_2I_2	20.55	2.72	11.61	20.14	2.52	11.74
$NiL_2(NO_3)_2$	27.96	3.14	23.95	27.67	3.46	24.21
$NiLCl_2$	22.41	3.01	12.99	22.61	2.84	13.23
CuL_4Cl_2	42.09	5.27	23.47	41.48	5.19	24.20
CuL_4Br_2	34.87	4.31	20.14	34.81	4.35	20.30
CuL_2Cl_2	32.64	4.10	18.58	32.17	4.05	18.75
CuL_2Br_2	24.89	3.28	14.48	24.81	3.12	14.44
$ZnL_4(NO_3)_2$	36.98	4.57	27.30	37.08	4.63	27.04
ZnL_2Cl_2	31.87	3.87	18.64	31.95	3.99	18.64
ZnL_2Br_2	24.85	3.00	14.65	24.73	3.08	14.39
ZnL_2I_2	20.77	2.55	10.53	20.68	2.48	11.58
$ZnL_2(NO_3)_2$	27.40	3.36	23.76	27.23	3.41	23.88

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(2) D. M. L. Goodgame, M. Goodgame, P. J. Hayward, and G. W. Rayner-Canham, *Inorg. Chem.*, 7, 2447 (1968).

(3) W. J. Eilbeck, F. Holmes, and A. E. Underhill, *J. Chem. Soc.*, (*A*) 757 (1967).

(4) M. Goodgame and F. A. Cotton, *J. Am. Chem. Soc.*, *84*, 1543 (1962).

(5) W. J. Davis and J. Smith, Abstract 3.14, Annual Meeting of the Chemical Society, Dublin, April 1968.

Table I. Diffuse Reflectance Spectra[a] and Room-temperature Magnetic Moments of some 2-methylimidazole Complexes

	μ_{eff}(B.M.)	Frequency (kK)
CoL_4I_2	4.28	~5.0 vbr, 8.93 s, 17.6 vs, 18.6 sh, f.
$CoL_4(NO_3)_2$ [A]	4.96	6.8 m, 10.0 m, 18.9 s, 19.9 s, 21.2 sh.
$CoL_4(NO_3)_2$ [B]	4.99	6.35 br, sh, 8.90 m, 17.1 s, 18.5 sh, f.
CoL_2Cl_2	4.49	4.65 m, 6.20 s, 7.45 s, 8.90 s, 16.0 vs, 16.5 vs, 17.3 vs, f.
$CoL_2(NO_3)_2$	4.51	[g] 7.87 m, 9.50 m, 14.5 m, 18.6 s.
NiL_4Cl_2	3.28 [d]	4.7 m, 10.0 w, 14.5 m, ~17.4 sh, ~20.2 sh, 24.4 m.
NiL_4Br_2	3.19 [e]	4.7 m, 9.7 w, 14.5 m, ~17.1 sh, ~20.0 sh, 24.4 s.
(at 95°K)	—	5.0 m, 10.3 w, ~12.1 sh, 15.0 m, 17.3 w, 21.5 sh, 24.6 s.
NiL_4I_2	Dia.	14.9 vw, 22.0 m.
$NiL_4(NO_3)_2$	3.19	9.43 w, 16.1 w, 25.9 w.
$NiL_{3.5}I_2$	2.60	~4.7 br, w, 8.77 w, 11.4 m, 12.3 m, 18.9 s, 26.9 vs.
(at 95°K)	—	~4.5 brw, 8.77 w, 11.3 m, 12.3 m, 18.9 s, ~22.4 sh, 25.9 s.
NiL_2Cl_2	3.20	6.95 m, 12.7 m, 18.9 sh, 22.6 s.
(at 95°K)	—	6.90 m, 13.1 ms, ~18.6 wsh, ~20.0 wsh, 22.8 ms.
[b]	—	10.3 (ε=46), 12.1 sh, 17.8 (ε=128).
(Zn, Ni)L_2Cl_2 [c]	—	g, 10.3, 12.2 sh, 16.8 sh, 18.3.
NiL_2Br_2	3.53	5.8 brs, 6.7 sh, 10.1 s, 16.1 s, 17.7 s.
NiL_2I_2	3.41	g, 6.9 s, 10.0 s, 15.4 vs, 22.0 vs, 23.8 shvs, 27.6 vs.
$NiL_2(NO_3)_2$	3.24	8.65 w, ~13.3 sh, 15.1 m, 24.8 m.
$NiLCl_2$	3.48	~6.0 sh, 7.30 w, 11.8 w, 12.8 w, ~18.5 sh, 20.6 w.
CuL_4Cl_2	1.79	15.0 vs.
CuL_4Br_2	1.78	15.9 vs.
CuL_2Cl_2	1.88	9.5 vs, 12.0 vs, ~21.0 sh, 26.8 vs.
CuL_2Br_2	1.85	8.77 vs, 11.4 vs, 20.6 sh, 25.0 vs.

[a] At room-temperature unless stated otherwise. [b] 0.002 *M* in acetone. [c] Nominal 5 mole% in Ni. [d] Obeys Curie-Weiss Law 130-300°K with $\Theta = -27°$. [e] Obeys Curie-Weiss Law 80-300°K with $\Theta = -22°$. [f] Spin-forbidden bands above 17 kK omitted. [g] Low energy bands obscured by vibrational bands.

The magnetic moment of A is in accord with the presence of six coordinate cobalt(II).

The coordination geometry in form B is less easily deduced from the evidence available. Its electronic spectrum is very similar to that of CoL_4I_2, but the relatively high magnetic moment (4.99 B.M.) is at variance with a tetrahedral ligand field. As discussed by Lions *et al.*,[6] five coordinate cobalt(II) complexes with coordination geometries derived from the square pyramid can have electronic spectra closely resembling those expected for a tetrahedral ligand field (*e.g.* β—Co(paphy)Cl_2 [7]), but may possess magnetic moments in the range commonly found for six coordinate cobalt(II) systems (even as high as 5.5 B.M. for $[Co\{(C_6H_5)_2CH_3AsO\}_4ClO_4]ClO_4, H_2O$). In view of the unusual geometry found[8] for NiL_4X_2 (X = Cl or Br) (discussed below) we suggest that form B of $CoL_4(NO_3)_2$ either contains five coordinate cobalt(II) or that one of the anions may be only weakly coordinated, so that the electronic spectral and magnetic properties resemble those of a truly five coordinate compound. Infrared spectral studies failed to resolve this problem as bands due to 2-methylimidazole prevented unambiguous assignment of the nitrate bands.

The compounds CoL_2X_2 (X = Cl, Br, or I) are pseudo-tetrahedral, and $CoL_2(NO_3)_2$ appears to be quite analogous to the corresponding imidazole complex.[2]

The electronic spectrum and magnetic moment of $NiL_4(NO_3)_2$ are as expected for an essentially octahedral geometry (in contrast to form A of $CoL_4(NO_3)_2$ there was no detectable splitting of the $^3T_{2g}$ or $^3T_{1g}$ levels of the nickel ion from the room-temperature spectrum).

However, the spectra of the corresponding chloride and bromide were quite different from that of the nitrate (Figure 1) and also from those of apparently similar compounds such as $Nipy_4Cl_2$.[9,10] X-Ray work[8] has shown that although the anions in NiL_4Br_2 are in *trans*-coordination positions the Ni-Br bond distances differ appreciably (2.53 and 3.57 Å), because of the steric influence of the methyl groups of the heterocyclic ligands, which, unexpectedly, do not adopt a staggered array. The chloride is isomorphous with the bromide.

These compounds represent an interesting situation in which the ligand fields are intermediate between the usual centro-symmetric, tetragonally distorted octahedral complexes Ni(amine)$_4X_2$ and five coordinate

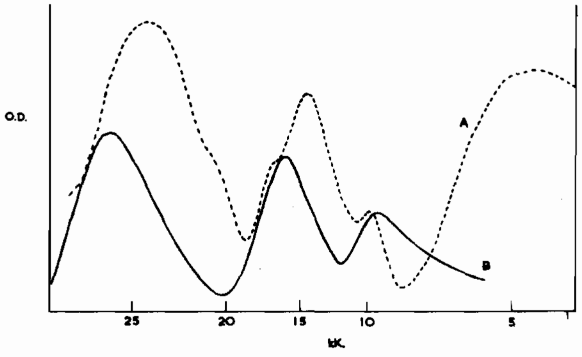

Figure 1. Reflectance spectra of: A, Ni(2—methylimidazole)$_4$Br$_2$; B, Ni(2—methylimidazole)$_4$(NO$_3$)$_2$.

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(6) F. Lions, I. G. Dance, and J. Lewis, *J. Chem. Soc.* (*A*), 565 (1967).

(7) paphy = pyridine—2—aldehyde—2'—pyridylhydrazone

(8) F. Akhtar, D. M. L. Goodgame, M. Goodgame, G. W. Rayner-Canham, and A. C. Skapski, *Chem. Commun.* (*London*), in press.

(9) D. M. L. Goodgame, M. Goodgame, M. A. Hitchman, and M. J. Weeks, *J. Chem. Soc.* (*A*) 1769 (1966).

(10) D. A. Rowley and R. S. Drago, *Inorg. Chem.*, 6, 1092 (1967); 7, 795 (1968).

compounds with square pyramidal configuration. The relatively high intensities of the spectral bands reflect the non-centrosymmetric (C_{4v}) environment of the nickel ion.

Although the ligand field symmetry is known we are unable to make an unambiguous, complete assignment of the spectra. The band at 4.7 kK is clearly $^3B_1 \rightarrow ^3E^a$ (E^a and E^b refer to the lower and the higher orbital doublet terms derived from ^3F), and the bands at 24.0 and ~20 kK are probably due to transition to $^3E(P)$ and $^3A_2(P)$ respectively. The three bands at 9 - 18 kK are less easily assigned. Three spin-allowed bands are expected in this region, namely transitions to the $^3B_2$, $^3A_2$ (F), and $^3E^b$ levels. From Ciampolini's calculations[11] and earlier assignments[12] of the spectra of square pyramidal nickel(II) complexes, one expects $^3E^b$ to be higher in energy than $^3A_2$ (F),[13] although the relative order of $^3A_2$ (F) and $^3B_2$ is less easily predicted.

The intensity of the 14.5 kK band for NiL_4X_2 (X = Cl or Br) suggests that this is $^3E^b$. The weaker bands at ~10 kK and 17 - 17.5 kK may both be transitions to the orbital singlet levels. It seems unlikely that $^3B_2$ would be as high as 17 kK, as this would imply a very strong in-plane field and there is no evidence for this from the Ni–N bond length (2.14 Å) in NiL_4Br_2. Assignment of the band at ~10 kK to $^3B_1 \rightarrow ^3B_2$ would then require either $^3A_2$(F) > $^3E^b$, or that the 17 kK band is a spin-forbidden transition to a $^1B_1$ level derived from ^1D as this is symmetry allowed in C_{4v}. Definite assignment of the 17 kK band must await single crystal polarised spectral studies, but, unfortunately, these compounds display severe crystal twinning.

It is interesting to note that the spectra of the above compounds are very similar to that of Ni(dienMe)Cl_2 [14] which is thought[15] to have a structure similar to that of its cobalt(II) analog.[16] In view of the differences in the geometries of NiL_4Br_2 and Co(dienMe)Cl_2 these results emphasize again the limitations of the use of electronic spectra for assigning structures.

Another compound with a spectrum closely resembling that of NiL_4Cl_2 is one of the magnetically anomalous isomers of Ni(benzimidazole)$_4Cl_2$ [17] (compound V of ref. 17). However neither NiL_4Cl_2 nor its bromo-analog displayed the unusual magnetic properties possessed by the benzimidazole complex, although the Curie Law was not obeyed over the range studied (Table I).

Our experimental results for the magnetic moments and electronic spectra of the compounds NiL_2X_2 (X = Cl, Br, or I) are in reasonably good agreement with those reported previously,[1] except for the moment of NiL_2Cl_2 for which we find $\mu_{eff} = 3.20$ B.M. compared with the earlier[1] value of 3.41 B.M. We agree with the conclusions of Eilbeck *et al.*[1] that the bromo and iodo complexes are pseudotetrahedral and the chloride is polymeric octahedral, but some features of the electronic spectra of these compounds require further consideration.

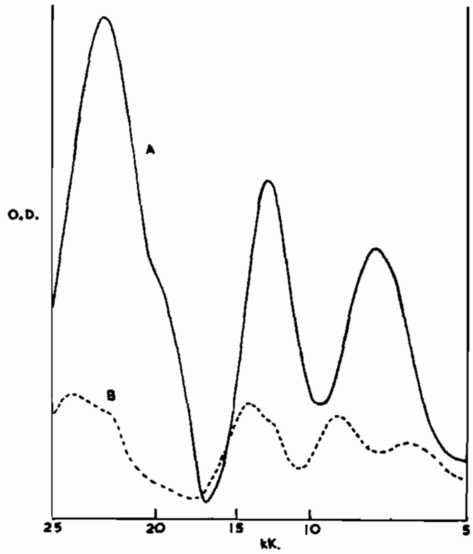

Figure 2. Reflectance spectra of: A, Ni(2—methylimidazole)$_2Cl_2$; B, Nipy$_2Cl_2$.

It was suggested[1] that the spectrum of NiL_2Cl_2 is very similar to those of related polymeric complexes such as Ni(pyridine)$_2Cl_2$.[9,10] However, this is not the case (Figure 2), and the differences are significant. In contrast to the pyridine complex, the spectrum of the 2-methylimidazole compound shows no detectable band splitting, even at 95°K. [The absence of splitting for the $^3A_{2g} \rightarrow ^3T_{2g}$ transition at 6.95 kK, which is very marked for Nipy$_2Cl_2$, supports the suggestion[1] that the weak shoulder (we observe two at 95°K) on the low frequency side of the $^3A_{2g} \rightarrow ^3T_{1g}$ (P) band is a spinforbidden band]. The implication of little departure from O_h ligand field symmetry is supported by the fact that the band energies agree closely with those expected[18] for that symmetry with $\Delta \approx 7$ kK. This Δ value is surprisingly low, being only slightly larger than that (6.6 kK) found[19] for nickel(II) surrounded by six bridging chloride ions. Both the relatively low Δ value and the high ligand field symmetry can probably be attributed to steric repulsion between the methyl groups of the heterocyclic base and the chloride ions in the $(NiCl_2)_n$ chain, causing the Ni–N bond to be longer than usual. The steric effects may, by destroying the centre of symmetry, also explain why the spectral bands are relatively intense compared with those of *e.g.* Ni(pyridine)$_2Cl_2$.

This compound appears to lie very close to the point where, in a range of closely related compounds Ni(amine)$_2X_2$, there is a change from polymeric octahedral to tetrahedral geometry. In acetone and in solid solution in tetrahedral ZnL_2Cl_2 spectra characteristic of the pseudotetrahedral configurations were obtained (Table I).

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(11) M. Ciampolini, *ibid.*, *5*, 35 (1966).
(12) *e.g.* C. Furlani, *Coord. Chem. Rev.*, *3*, 141 (1968).
(13) This order is also found for tetragonally distorted six coordinate complexes.
(14) dienMe = bis(2-dimethylaminoethyl)methylamine.
(15) M. Ciampolini and G. P. Speroni, *Inorg. Chem.*, *5*, 45 (1966).
(16) M. Di Vaira and P. L. Orioli, *Chem. Commun.* (*London*) 590 (1965).
(17) D. M. L. Goodgame, M. Goodgame, and M. J. Weeks, *J. Chem. Soc.* (*A*) 1125, (1967).
(18) A. D. Liehr and C. J. Ballhausen, *Ann. Phys.*, *6*, 134 (1959).
(19) D. M. L. Goodgame, M. Goodgame, and M. J. Weeks, *J. Chem. Soc.*, 5194 (1964).

Previous assignments[1] of the spectra of the pseudotetrahedral compounds NiL_2X_2 ($X = Br$ or I) are also, in our view, incorrect. Citation[1] of earlier work[20] on the tetrahalonickelate(II) anions in apparent support of assignment of the band 5–7 kK as ν_2 ($^3T_1$ (F) $\rightarrow$ $^3A_2$) and that at ~ 10 kK as a spin-forbidden transition to a component from the ^1D free ion term, did not take into account the changes in ligand field strength and symmetry on passing from NiX_4^{2-} to *approximately* tetrahedral NiN_2X_2 chromophores. Nor does the intensity of the ~ 10 kK band (Figure 3) suggest its assignment as a spin forbidden band. Instead, following assignments made previously[21] for related compounds with quinoline and benzimidazole, we assign the 10 kK band as ν_2 and the broad absorption at 5–7 kK as the transition(s) to one or more components of the split $^3T_2$ level.

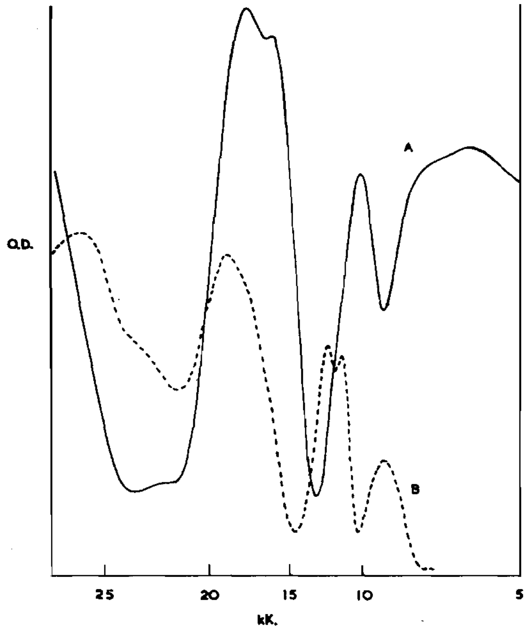

Figure 3. Reflectance spectra of: A, Ni(2—methylimidazole)$_2$Br$_2$; B, Ni(2-methylimidazole)$_{3.5}$I$_2$ (at 95°K).

On heating diamagnetic NiL_4I_2 at 75° in vacuo a purple compound with the unexpected stoichiometry $NiL_{3.5}I_2$ was obtained. The magnetic moment (Table I) is below the spin-only value for nickel(II). The main features of the electronic spectrum (Table I, Figure 3) resemble those observed for some distorted, tetrahedral nickel complexes such as Ni(2,2′-dipyridylamine)X_2 ($X = Br$ or I),[22] but with a hypsochromic band shift, and with the addition of a shoulder at $\sim 22{,}400$ cm^{-1}. This last corresponds quite well with the 22 kK band observed for NiL_4I_2, and one can rationalize the spectrum, low magnetic moment, and stoichiometry of $NiL_{3.5}I_2$ on the basis of a structure containing planar NiL_4^{2+} and pseudotetrahedral $[NiL_3I]^+$ cations in 1:1 ratio. X-ray powder photographs showed that the purple product was not merely a mechanical mixture containing unreacted NiL_4I_2. Attempts to obtain complexes containing the NiL_3I^+ cation from solution were unsuccessful. However, ethanol solutions of NiL_4I_2 gave spectra similar to that of solid $NiL_{3.5}I_2$. Addition of 2-methylimidazole to these solutions caused complete conversion of the solute species to planar NiL_4^{2+} suggesting the presence of an equilibrium:

$$\underset{\text{(planar)}}{NiL_4^{2+}} \rightleftharpoons \underset{\text{(pseudotetrahedral)}}{NiL_3X^{n+}} + L$$

where X may be an iodide ion or a solvent molecule. Additional support for the suggested nature of $NiL_{3.5}I_2$ is provided by the low frequency infrared spectrum (see later). On heating at 120° this compound is converted to NiL_2I_2.

The electronic spectrum and magnetic moment of $NiL_2(NO_3)_2$ both suggest that this has a distorted octahedral configuration. The spectrum of $NiLCl_2$ resembles that of $NipyCl_2$[19] with a small bathochromic band shift, and the magnetic moment is relatively high as found[19,23] for other polymeric, octahedral Ni(amine)X_2 compounds.

In contrast to the results for imidazole[2], cupric iodide complexes could not be obtained; instead the usual redox reaction occurred with formation of cuprous iodide and iodine. The spectrum of CuL_4Br_2 shows that it resembles CuL_4Cl_2[1] in having a tetragonal structure, whereas the CuL_2X_2 ($X = Cl$ or Br) compounds are tetrahedral.

Vibrational Spectra (400-90 cm^{-1}). The vibrational band frequencies of 2-methylimidazole are listed in Table II and those of its complexes in Tables II-IV. The infrared active bands at 374 and 353 cm^{-1} in the free ligand are replaced by a single infrared and Raman active band at 380-390 cm^{-1} upon complexing. The band at ~ 267 cm^{-1} is also raised in frequency in many of the complexes but its proximity to metal-ligand modes in some cases makes it uncertain as to whether this is a general effect.

4 : 1 Compounds (Table II). The F_2 Co–N stretch (ν_3) of the tetrahedral cation in CoL_4I_2 is close to the ligand band at ~ 270 cm^{-1}, and it is not certain which of the two absorptions in the 280 cm^{-1} region may be assigned as ν_3. The infrared spectrum of $ZnL_4(NO_3)_2$ closely resembles that of CoL_4I_2, and differs from those of $CoL_4(NO_3)_2$ (both forms) and $NiL_4(NO_3)_2$ We conclude that the zinc nitrate complex contains tetrahedral ZnL_4^{2+} cations. The Raman spectrum of this compound has a band at 213 cm^{-1} not observed in the infrared spectrum, and this is probably due to the A_1 ν(Zn–N) mode. The infrared bands at 163 cm^{-1} for CoL_4I_2 and at 174 cm^{-1} for $ZnL_4(NO_3)_2$ are tentatively assigned as the F_2 (N–M–N) bend.

The band at 243 cm^{-1} for NiL_4X_2 ($X = Cl$ or Br) is assigned as the ν(M–N) E mode. Although the A_1 M–N stretch is formally infrared active in C_{4v} symmetry it is either very weak or is hidden by the 280 cm^{-1} ligand band. The 218 cm^{-1} band for NiL_4Br_2

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Table II. Infrared (IR) and Raman (R) Spectra (450-90 cm^{-1}) of 2-methylimidazole (L) and Some ML_4X_2 Complexes.

Compound		cm^{-1}
L	IR	374 m, 353 s, 265 s, 163 m, 149 s, 128 w, 114 m, 96 s.
	R	268 m, 168 w, 148 vs.
$ZnL_4(NO_3)_2$	IR	388 mbr, 275 s, 174 s.
	R	382 s, 280 s, 213 w.
CoL_4I_2	IR	388 s, 286 s, 277 sh, 163 s.
$CoL_4(NO_3)_2$ (A)	IR	384 s, br, 280 s, 230 s, vbr, 110 s, br.
$CoL_4(NO_3)_2$ (B)	IR	423 s, 383 s, 312 m, 278, s ~180 vbr, 110 s, br.
NiL_4Cl_2	IR	385 s, 277 s, 243 s, 135 s, br.
NiL_4Br_2	IR	386 s, 281 s, 243 m, 218 m, 133 w, 111 m, 92 s.
NiL_4I_2	IR	424 s, 400 m, 383 m, 365 m, 292 m, 280 m, ~260 sh, 198 w, 95 m.
	R	424 wsh, 402 w, 228 m, 214 s, 196 w.
$NiL_4(NO_3)_2$	IR	391 s, br, 286 s, 257 m, 213 w, ~195 m, vbr, 110 m, br.
CuL_4Cl_2	IR	389 s, 283 s, 256 w, 215 m, 125 s, br.
CuL_4Br_2	IR	388 s, 284 s, 260 w, 214 s, 106 s, 93 s.

Table III. Infrared (IR) and Raman (R) Spectra (90-400 cm^{-1}) of Some Tetrahedral ML_2X_2 Complexes (L = 2-methylimidazole).

Compounds [a]		Ligand bands	ν(M–X)	ν(M–N)	Other bands
CoL_2Cl_2	IR	384 s, 272 ms [c]	316 s, 305 s	233 vw [d]	163 s, br, 114 mw
CoL_2Br_2	IR	382 s, 269 s, br [c]	241 ms [c] 189 s	—	178 w, 145 ms
CoL_2I_2	IR	382 s, 272 s	212 s, 167 s	260 mw	140 m
NiL_2Br_2	IR	382 s, 270 s [c]	233 s [c] 189 s	—	150 sh, 137 s
NiL_2I_2	IR	382 s, 267 ms [c]	208 ms, 180 ms	~250 sh	137 m
CuL_2Cl_2	IR	385 s, 266 m [c]	294 s, br	237 w [d]	217 mw, 173 s, 151 s 130 w, 110 m
CuL_2Br_2	IR	383 s, 271 s	251 s, [c] 200 ms	—	180 s, 158 s
ZnL_2Cl_2	IR	382 s, 267 s [c]	302 sh, 287 s	240 m	162 s br, 125 s
	R	388 w, 280 s	295 ms	237 ms	151 w
ZnL_2Br_2	IR	381 s, 268 s [c]	216 ms, 192 s	246 ms, br	161 s, 147 m
	R	387 mw, 288 m, 276 ms [c]	195 s	246 w	179 m, 145 w
	R [b]	392 m, 278 m	191 s, pol.	—	174 w
ZnL_2I_2	IR	380 s, 265 s	195 s, 175 s [d]	242 s, 226 m	140 ms [e]
	R	385 w, 277 mw	180 m [d]	—	148 s [e]
	R [b]	392 m, 275 mw	~180 vw, sh	—	145 s, [e] pol.

[a] Solid unless stated otherwise. [b] Acetone solution. [c] Possibly also contains ν(M–N) band. [d] Tentative assignment. [e] Possibly ν(Zn–I).

is assigned as ν(Ni–Br), involving the bromine atom more closely bound to the metal ion. The much more distant bromine atom is unlikely to give a vibrational band above 200 cm^{-1}, but instead would be expected to give absorption at very low frequency similar to a lattice mode. If the commonly observed[24] ν(M–Br)/ν(M–Cl) relationship is obeyed by these NiL_4X_2 compounds, the observation of ν(Ni–Br) at 218 cm^{-1} would imply that the strong absorption at 277 cm^{-1} in NiL_4Cl_2 contains both the 2-methylimidazole band and that due to ν(Ni–Cl) involving the short Ni–Cl bond.

The spectra of the tetragonal copper complexes CuL_4X_2 show two anion-independent bands above 150 cm^{-1}, apart from ligand bands. We assign these as the components of the E_u ν(M–N) mode split by departure of the CuN_4 unit from D_{4h} symmetry.

The low frequency infrared spectra of the two forms of $CoL_4(NO_3)_2$ are quite different. Moreover the spectrum of the purple isomer (B) differs from that of CoL_4I_2 and supports the conclusions drawn from the magnetic measurements that form B does not contain tetrahedral CoL_4^{2+}, despite the similarity of the electronic spectrum of this compound to that of CoL_4I_2. However in the absence of definite structural information assignment of the low frequency infrared bands is not really warranted.

2 : 1 Compounds. Indentification of the two ν(M–halogen) bands for the tetrahedral compounds (Table III) was straightforward for most of them, although the higher frequency ν(M–Br) band is in the ν(M–N) region for M = Co, Ni, or Cu, and the absorptions observed at 241, 233, and 251 cm^{-1} respectively may contain both ν(M–Br) and ν(M–N) in these cases. Our assignment of the A_1 ν(Zn–I) mode to the band at 175 cm^{-1} is tentative, another possibility being the band at 140 cm^{-1}. Previous work[25] on other tetrahedral $Zn(ligand)_2I_2$ compounds favors the higher frequency band as the symmetric Zn–I stretch. However, the Raman results suggest that the lower frequency band may be ν_{symm}(Zn–I). The strongest band in the low frequency Raman spectrum of ZnL_2Br_2 is that at 195 cm^{-1} (solid), and at 191 cm^{-1} for acetone solutions. This band is polarised and is reasonably assigned to the A_1 ν(Zn–Br) mode. Although the Raman spectrum of solid ZnL_2I_2 has a band at 180 cm^{-1}, apparently corresponding to that at 175 cm^{-1} in the infrared spectrum, this band appears as only a very weak shoulder in the solution spectrum. On the other hand, the strongest Raman band in the solid state spectrum is that at 148 cm^{-1} and this also appears strongly in solution and is polarised. [For com-

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Table IV. Infrared Spectra (90-400 cm^{-1}) of Some 2-methylimidazole Complexes.

NiL_2Cl_2	388 m, s, br 267 sbr, ~225 s, vbr, ~180 s, vbr.
$NiLCl_2$	387 mw, br, 267 m, ~200 s, vbr.
$NiL_{3.5}I_2$	414 s, 384 s, 357 m, ~294 sh, 283 s, br, ~260 sh, 191 ms, 175 ms, 164 ms, 152 ms, 90 s, vbr.
$CoL_2(NO_3)_2$	382 m, 286 s, br, 270 sh, 185 s, 140 m, vbr, 96 m.
$NiL_2(NO_3)_2$	384 m, 306 s, 287 s, 194 m, 177 m, 100 w.
$ZnL_2(NO_3)_2$	386 s, 294 sh, 277 sbr, 254 sh, 170 m, ~125 w, vbr.
$ZnL_2(NO_3)_2$ (R) [a]	394 w, 277 m, 237 m, 169 m.

[a] Raman spectrum (solid state)

parison, the F_2 and A_1 modes of the ZnI_4^{2-} ion are at 165 and 118 cm^{-1} respectively[26]].

Clear assignment of the ν(M–N) modes is not possible for many of the compounds listed in Table III. The main complication is the presence of the ligand band in the 270 cm^{-1} region and the uncertainty as to the extent this is shifted on coordination. However we do not agree with a previous suggestion[1] that this 270 cm^{-1} band invariably masks the ν(M–N) absorptions. The bands at 242 and 226 cm^{-1} in the infrared spectrum of ZnL_2I_2 are very probably the ν(M–N) bands and similar assignments may be made for bands in the 230-260 cm^{-1} region for the corresponding chloride and bromide, and for some of the other complexes. Identification of the ν(M–N) band for the bromide complexes of Co, Ni, and Cu is prevented by the presence of the higher frequency ν(M–Br) band.

Our experimental results for the low frequency infrared spectrum of the polymeric, octahedral compound NiL_2Cl_2 (Table IV) appear to disagree in part with those tabulated by Eilbeck *et al.*[1] There is strong, broad absorption with maxima at ~225 and ~180 cm^{-1}. As in the case of other halide-bridged 2:1 complexes,[24] the ν(M–X) and ν(M–N) frequencies are insufficiently resolved for clear assignment, but the infrared results support the postulated polymeric structure. The spectrum of $NiLCl_2$ is also of this type (Table IV).

$NiL_{3.5}I_2$. The low frequency infrared spectrum of this compound tends to support the presence of planar NiL_4^{2+} ions in addition to distorted tetrahedral nickel environments. In particular the spectrum has a strong band at 414 cm^{-1} and a medium band at 357 cm^{-1} corresponding to the bands at 424 and 365 cm^{-1} for NiL_4I_2. Infrared evidence concerning the nature of the tetrahedral component is less certain. The band at 283 cm^{-1} is much broader and stronger than that for NiL_4I_2 (compare ν_3, ν(Co–N), for tetrahedral CoL_4^{2+} at 286 cm^{-1}) and there are three medium-strong bands below 190 cm^{-1}, not shown by NiL_4I_2, in the region where ν(M–I) for a tetrahedral species might be expected.

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