with the findings of Adamson[18] that Co(II) in concentrated aqueous cyanide solutions is present as pentacoordinated $Co(CN)_5^{3-}$ rather than $Co(CN)_5H_2O^{3-}$. In fact, the tendency of d^8 ions such as Ni(II) to bind additional ligands should be even smaller than for a d^7 ion such as Co(II). Adamson reported the preparation of the diamagnetic salt $K_3Co(CN)_5$, earlier misidentified as $K_4Co(CN)_6$. In contrast, no Ni(II) cyanides have been isolated containing more than four CN^- per Ni(II); $K_2Ni(CN)_4$ is obtained from Ni(II) solutions saturated with KCN, even though the principal species in solution is $Ni(CN)_5^{3-}$. In the case of the other d^8 ions, Pd(II), Pt(II), and Au(III), no complex cyanide ion higher than $M(CN)_4^{n-}$ is observed.[19]

Two chemically reasonable structures can be suggested for $Ni(CN)_5^{3-}$—a square pyramid of C_{4v} symmetry and a trigonal bipyramid of D_{3h} symmetry. The presence of three infrared-active CN-stretching vibrations is expected for a structure of C_{4v} symmetry and excludes the bipyramidal structure.

Addition of fluoride to solutions containing $Ni(CN)_4^{2-}$ without free cyanide has negligible effect on the infrared absorption of $Ni(CN)_4^{2-}$. However, iodide ion does show significant interaction with $Ni(CN)_4^{2-}$ based on the increase in integrated absorption coefficient even though no separate new peak is found. This parallels the findings of Bjerrum and Beck,[8] who showed that of the halides, iodide causes the greatest increase in the visible absorption of $Ni(CN)_4^{2-}$. In this latter case, therefore, there is evidence for iodide occupying the fifth coordination position.

---

[18] A. W. Adamson, *J. Am. Chem. Soc.*, **73**, 5710 (1951).

[19] L. H. Jones, J. M. Smith, and R. A. Penneman, unpublished work at Los Alamos Scientific Laboratory, 1963.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, LONDON, ENGLAND

Near-Infrared Spectra of Some Pseudotetrahedral Complexes of Cobalt(II) and Nickel(II)

BY D. M. L. GOODGAME AND M. GOODGAME

Received September 28, 1964

Electronic spectra in the near-infrared region are reported for some pseudotetrahedral complexes of cobalt(II) and nickel(II) of the types MLX_3^- and ML_2X_2, where L = quinoline, benzimidazole, triphenylphosphine, triphenylphosphine oxide, or triphenylarsine oxide, and X = Cl, Br, I, or NCS. The results are discussed in terms of the distortions of the ligand fields from T_d symmetry.

Introduction

Following the calculations of Liehr and Ballhausen[1] and the preparation during recent years of a variety of tetrahedral complexes of nickel(II), the criteria for the recognition of this type of complex have become well established. Even where the symmetry is no higher than C_{2v}, the observed visible spectra are in quite good agreement with the theoretical predictions for T_d symmetry. During recent work on tetrahedral complexes of nickel halides with benzimidazole,[2] a study of the near-infrared spectra suggested that the $^3T_1(F) \rightarrow {}^3T_2$ transition was much more sensitive to deviations from T_d symmetry. We have therefore examined the spectra in this region of a number of nickel(II) complexes with distorted tetrahedral structure. The near-infrared spectra of analogous cobalt(II) complexes have also been studied for comparison with the nickel compounds.

Experimental

Preparation of Compounds.—The quinoline complexes of cobalt(II) halides were prepared by the following general method: quinoline was added to the hydrated cobalt salt in ethanol. The crystalline precipitate was filtered off, washed with ethanol, and dried *in vacuo*.

Anal. Calcd. for $C_{18}H_{14}Cl_2CoN_2$: C, 55.71; H, 3.64. Found: C, 55.63; H, 3.65. Calcd. for $C_{18}H_{14}Br_2CoN_2$: C, 45.31; H, 2.96. Found: C, 44.90; H, 3.46. Calcd. for $C_{18}H_{14}CoI_2N_2$: C, 37.86; H, 2.47. Found: C, 38.14; H, 2.33.

The preparation of $(C_2H_5)_4N[Ni(C_7H_6N_2)Br_3]$ and $Ni(C_7H_6N_2)_2X_2$ (X = Br, I) will be reported elsewhere.[2] The other compounds have been described previously.[3-7]

Physical Measurements.—Reflectance spectra were obtained with a Beckman DK2 spectrometer and X-ray powder photographs with an Enraf–Nonius Guinier–De Wolff camera No. II or with a Philips Debije–Scherrer powder camera type PW 1024.

Results

The compounds we have studied are listed in Table I, together with the positions of their electronic absorption bands, obtained by the reflectance technique, in the near-infrared region down to 4000 cm.$^{-1}$. Most of the complexes show absorption in this region due to vibrational overtones, which were identified by comparison with the spectra of the free ligands, of the

---

[1] A. D. Liehr and C. J. Ballhausen, *Ann. Phys.* (N. Y.), **6**, 134 (1959).

[2] M. Goodgame and M. J. Weeks, to be published.

[3] F. A. Cotton, O. D. Faut, and D. M. L. Goodgame, *J. Am. Chem. Soc.*, **83**, 344 (1961).

[4] F. A. Cotton and D. M. L. Goodgame, *ibid.*, **82**, 5771 (1960); D. M. L. Goodgame and F. A. Cotton, *ibid.*, **82**, 5774 (1960).

[5] F. A. Cotton, O. D. Faut, D. M. L. Goodgame, and R. H. Holm, *ibid.*, **83**, 1780 (1961); M. Goodgame and F. A. Cotton, *ibid.*, **84**, 1543 (1962); F. A. Cotton, D. M. L. Goodgame, M. Goodgame, and T. E. Haas, *Inorg. Chem.*, **1**, 565 (1962).

[6] D. M. L. Goodgame, M. Goodgame, and F. A. Cotton, *ibid.*, **1**, 239 (1962).

[7] D. M. L. Goodgame and M. Goodgame, *J. Chem. Soc.*, 207 (1963).

TABLE I

REFLECTANCE SPECTRA OF THE COMPOUNDS IN THE REGION 4000–11,000 CM.$^{-1}$

Compound	Absorption maxima, cm.$^{-1}$
$(C_2H_5)_4N[Co(C_6H_5)_3PBr_3]$	4350, 8000
$(n\text{-}C_4H_9)_4N[Co(C_6H_5)_3PI_3]$	$\sim$4000, 7400
$(C_2H_5)_4N[Co(C_7H_6N_2)Br_3]^a$	4900, 6900
$CH_3(C_6H_5)_3As[Co(C_7H_6N_2)I_3]^a$	4200, 6800
$(C_2H_5)_4N[Ni(C_6H_5)_3PBr_3]$	5990, 8930, 9760
$(n\text{-}C_4H_9)_4N[Ni(C_6H_5)_3PI_3]$	4900–5900 (br, sh), 6900, 7700, 9430
$(C_2H_5)_4N[Ni(C_7H_6N_2)Br_3]^a$	4000–6500 (br), 8700, $\sim$11,000 (sh)
$Co[(C_6H_5)_3P]_2Cl_2$	3900, 6330, 7840, 10,500
$Co[(C_6H_5)_3P]_2Br_2$	6130, 7550, 10,000
$Co[(C_6H_5)_3P]_2I_2$	5700, 7000, 8900
$Ni[(C_6H_5)_3P]_2Cl_2$	$\sim$4500 (br), $\sim$7800 (sh), 9050, 11,100
$Ni[(C_6H_5)_3P]_2Br_2$	$\sim$4600 (br), $\sim$8700 (sh), 11,000
$Ni[(C_6H_5)_3P]_2I_2$	<4200 (br), $\sim$7900 (sh), 10,040
$Co(C_9H_7N)_2Cl_2^b$	4600, 6150, 7300, 8770
$Co(C_9H_7N)_2Br_2^b$	<4300 (br), 6150, 7050, 8550
$Co(C_9H_7N)_2I_2^b$	<4100 (br), 5700, 6900, 8550
$Co(C_9H_7N)_2(NCS)_2^b$	4650,^{c} 8500
$Ni(C_9H_7N)_2Cl_2^b$	$\sim$6700 (br), 10,100, $\sim$11,700 (sh)
$Ni(C_9H_7N)_2Br_2^b$	$\sim$6900 (br), 10,000, $\sim$11,100 (sh)
$Co(C_7H_6N_2)_2Br_2^a$	4400, 6170, 7200, 8900
$Co(C_7H_6N_2)_2I_2^a$	4300, 5780, 6950, 8700
$Ni(C_7H_6N_2)_2Br_2^a$	$\sim$6800 (br), 10,300, $\sim$11,600 (sh)
$Ni(C_7H_6N_2)_2I_2^a$	$\sim$6800 (br), 9900, $\sim$10,800 (sh)
$Co[(C_6H_5)_3AsO]_2Cl_2$	5050, 5820, 6540
$Ni[(C_6H_5)_3AsO]_2Cl_2$	<5000 (br, w), 8000
$Ni[(C_6H_5)_3PO]_2Br_2$	<4300, 7250

[a] $C_7H_6N_2$ = benzimidazole. [b] C_9H_7N = quinoline. [c] A vibrational overtone occurs near this position, but is superimposed on the electronic band.

cations as their halide salts, or of related complexes showing no electronic absorption in this region. These bands, which are generally weak and sharp compared with those due to the electronic transitions, have been omitted from the table and the diagrams and will not be discussed further.

The compounds $[(C_2H_5)_4N][(C_6H_5)_3PNiBr_3]$ and $[(C_6H_5)_3P]_2NiCl_2$ were found by X-ray powder photography to be isomorphous with their cobalt(II) analogs; (benzimidazole)$_2$NiBr$_2$ has a powder pattern very similar to that of its cobalt analog, but they are probably not strictly isomorphous. The following complexes were not isomorphous with the cobalt compounds: $[(n\text{-}C_4H_9)_4N][(C_6H_5)_3PNiI_3]$, $[(C_2H_5)_4N]$-[(benzimidazole)NiBr$_3$], and $[(C_6H_5)_3P]_2NiBr_2$.

Discussion

In discussing the electronic spectra of the compounds the following notation will be used: for cobalt(II), $^4A_2 \rightarrow {}^4T_2 = \nu_1$, $^4A_2 \rightarrow {}^4T_1(F) = \nu_2$, $^4A_2 \rightarrow {}^4T_1(P) = \nu_3$; for nickel(II), $^3T_1(F) \rightarrow {}^3T_2 = \nu_1$, $^3T_1(F) \rightarrow {}^3A_2 = \nu_2$, $^3T_1(F) \rightarrow {}^3T_1(P) = \nu_3$. In crystal fields of symmetry lower than T_d, the orbital triplet levels are split as shown in Table II.

TABLE II

SYMMETRY CORRELATIONS FOR T_d, C_{3v}, AND C_{2v} SYMMETRIES

T_d	C_{3v}	C_{2v}
A_2	A_2	A_2
T_1	$A_2 + E$	$A_2 + B_1 + B_2$
T_2	$A_1 + E$	$A_1 + B_1 + B_2$

In T_d symmetry, the ν_1 transition for cobalt(II) is electric dipole forbidden, but in C_{3v} and C_{2v} symmetries it becomes partially allowed.

Complexes of C_{3v} Symmetry.—In the cobalt complexes of the type $CoLX_3^-$ the ν_2 band is split into two widely separated components, which may be assigned as transitions to the $^4A_2$ and ^4E upper states. In $[Co(C_7H_6N_2)I_3]^-$ the band at 6800 cm.$^{-1}$ is considerably more intense than that at 4200 cm.$^{-1}$ and may be assigned as the E component. In the other three compounds the two peaks have about the same optical density (Figure 1), but in each case the higher energy band is considerably broader than the lower energy one and is therefore considered to be the E component. The extent of the splitting is greater for triphenylphosphine as ligand than for benzimidazole and greater for the iodides than for the bromides. In $[Co(C_6H_5)_3PI_3]^-$ the position of the lower energy component cannot be accurately placed, as part of the peak lay beyond the range of our measurements.

If this assignment of ^4E above $^4A_2$ is correct, it is likely that $[Ni(C_6H_5)_3PBr_3]^-$, whose tetraethylammonium salt is isomorphous with its cobalt(II) analog, will have a ^3E ground state. The high magnetic moment observed[3] for this compound is in agreement with this. The spectrum observed for this compound (Figure 2) may be interpreted by assuming that the $^3T_2$ state is split with $^3A_1$ above ^3E, the broad band at about 6000 cm.$^{-1}$ being assigned as the transition to ^3E and the sharp peak at 8930 cm.$^{-1}$ that to $^3A_1$.

The high energies of these transitions merit some comment. From the energy of the ν_2 band (9760 cm.$^{-1}$), ν_1 for a regular tetrahedron is predicted[1] at about 5000 cm.$^{-1}$. If a low-symmetry ligand field splits the $^3T_1$(F) level by more than the usual spread of spin–orbit components, the energy of the ground state will be lower than that in T$_d$ symmetry, and, on a simple model, the average energies of the transitions will increase. Moreover, with a ^{3}E ground state, any interaction between the ^{3}E levels will have a larger effect on the energy of ν_1 than on that of ν_2, the splitting of $^3T_1$ being increased and that of $^3T_2$ decreased. The magnitude of the splitting observed for the isomorphous cobalt compound suggests that the $^3T_1$(F) state of the nickel complex may be split by 3000–4000 cm.$^{-1}$, and it is to be expected that the band positions will differ from those predicted for T$_d$ symmetry, as observed.

The spectrum of $(n\text{-}C_4H_9)_4N[Ni(C_6H_5)_3PI_3]$ is rather more complicated than that of its bromo analog. In addition to a broad shoulder at about 5400 cm.$^{-1}$, two maxima are observed below the peak at 9430 cm.$^{-1}$ assigned as ν_2. The magnetic moment of this complex[3] suggests that it has a ^{3}E ground state, so that similarity with the bromo complex might be expected. We consider it unlikely that the peak at 7000 cm.$^{-1}$ (Table I) corresponds to a very weak vibrational band found at 7200 cm.$^{-1}$ for the corresponding cadmium complex and suggest that one of the observed peaks, probably that at 7700 cm.$^{-1}$, may correspond to a spin-forbidden transition, with an upper state arising from the ^{1}D free ion term. A similar origin for the band at 8930 cm.$^{-1}$ in the bromo complex cannot be ruled out, although its intensity supports the suggestion made above.

For the ion $Ni(C_7H_6N_2)Br_3^-$, the peak at 8700 cm.$^{-1}$ is readily assigned as ν_2, and only a single, broad absorption band is observed in the ν_1 region, though there is an indication of splitting into two components. It seems likely that the distortion in this compound is considerably less than in the phosphine complexes, as observed for the cobalt analogs.

Complexes of C_{2v} Symmetry, ML_2X_2.—Except for $Co(quinoline)_2(NCS)_2$, the ν_2 band of the cobalt complexes is split into three components of roughly equal intensity (see Figure 1). For complexes where L contributes a fairly strong ligand field, part at least of the ν_1 band was observed, with quite high intensity, but for some complexes this band lay below the range of our measurements. For the nickel compounds, the nature of the ν_1 band was strongly dependent on the type of ligands present. It is convenient to divide these compounds into three groups, according to the identity of the donor atom in the ligand L, and to compare the results for cobalt(II) and nickel(II) within each group.

Complexes of $(C_6H_5)_3PO$ and $(C_6H_5)_3AsO$.—The total splitting (1500 cm.$^{-1}$) between the three components of ν_2 for $Co[(C_6H_5)_3AsO]_2Cl_2$ is comparable with the width of ν_2 for complexes with four equal ligands.[8] Deviations from T$_d$ symmetry are also expected to be small for the nickel(II) complexes, since these have high magnetic moments.[4] Part of the ν_1 band was observed for both $Ni[(C_6H_5)_3AsO]_2Cl_2$ and $Ni[(C_6H_5)_3PO]_2Br_2$, but its contour was obscured by rather strong vibrational bands. It seems likely that in both cases the band center lay below the range of measurement, as predicted for complexes of nearly T$_d$ symmetry.

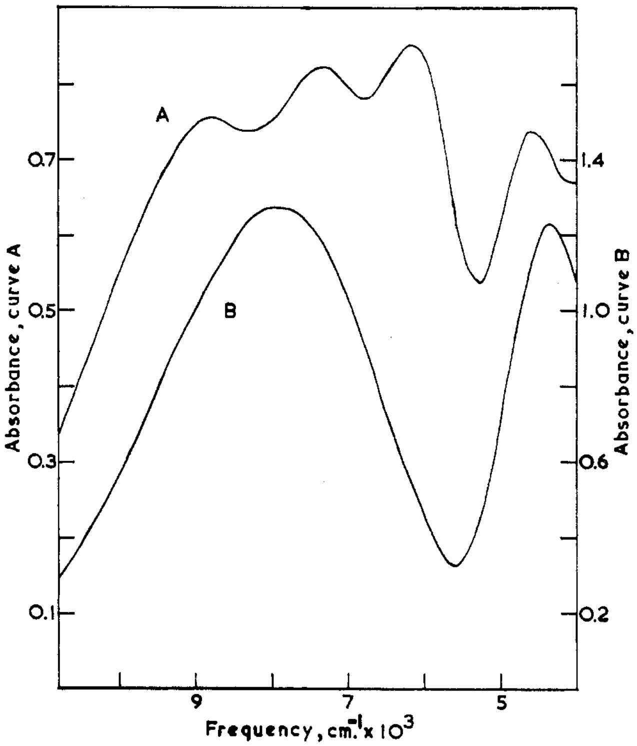

Figure 1.—Absorption spectra of: (A) $Co(quinoline)_2Cl_2$, (B) $[(C_2H_5)_4N][Co(C_6H_5)_3PBr_3]$.

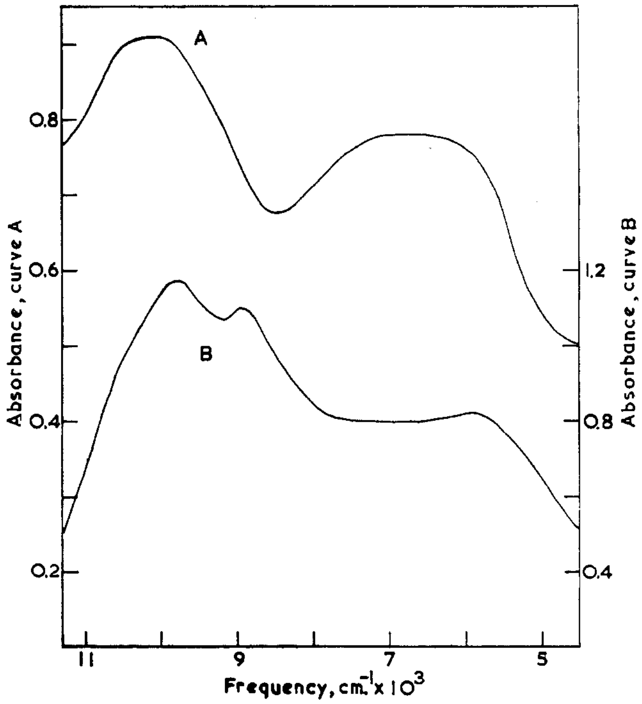

Figure 2.—Absorption spectra of: (A) $Ni(quinoline)_2Cl_2$, (B) $[(C_2H_5)_4N][Ni(C_6H_5)_3PBr_3]$.

---

[8] F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Am. Chem. Soc.*, **83**, 4690 (1961).

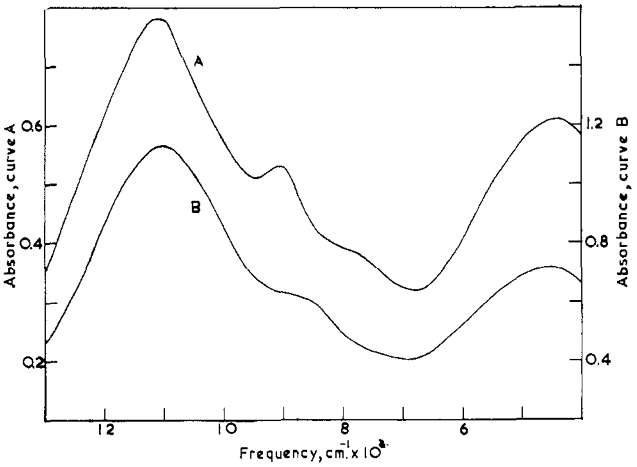

Figure 3.—Absorption spectra of: (A) $Ni[(C_6H_5)_3P]_2Cl_2$, (B) $Ni[(C_6H_5)_3P]_2Br_2$.

Complexes of Quinoline and Benzimidazole.—In each of the cobalt halide complexes, the ν_2 band has a total spread of about 2400–3000 cm.$^{-1}$ (Figure 1). Absorption assigned to ν_1 was observed in all cases, but it is not certain whether the single band represents the whole of ν_1, or only one component of a split band. From the positions of ν_1 and ν_2, it seems that benzimidazole provides a slightly stronger ligand field than does quinoline, as found for six-coordinate nickel complexes.[9] The splitting of the ν_2 band suggests that the distortion in Co(quinoline)$_2$I$_2$ is little greater than that in the chloro and bromo complexes, and is even less than that in Co(benzimidazole)$_2$I$_2$, although the planarity of Ni(quinoline)$_2$I$_2$ has been attributed to steric factors.[10] In Co(quinoline)$_2$(NCS)$_2$, the ν_2 band is unsplit, but its position suggests that quinoline provides a somewhat stronger ligand field than does the isothiocyanate ion.

The nickel complexes of these ligands all have a rather broad "flat-topped" band at about 6800 cm.$^{-1}$ (Figure 2). It seems probable that this comprises either two, or all three, components of ν_1. The unexpectedly high energy may again be attributed to the distortion, which makes meaningless any attempt to assign an average Δ value based on the T$_d$ energy level diagram.

Complexes of Triphenylphosphine.—The splittings of 3000–4000 cm.$^{-1}$ shown by the ν_2 band for the cobalt complexes are the greatest shown by any compound we have studied. However, only for the chloro complex was any component of ν_1 observed, and this was at about 3900 cm.$^{-1}$. It seems that the ν_1 bands occur at appreciably lower energies for these than for the complexes with nitrogen donors, although ν_2 centers at about the same energy (for the iodides) or even higher (for the chlorides and bromides). In the phosphine compounds the splitting of ν_2 decreases from chloride to iodide. The chloro complex is isomorphous with its nickel analog, in which the appreciable distortion may be attributed[11] to the steric requirements of the phosphine ligands, and it may be that the larger halide ions compete more successfully with the phosphines for the space around the metal ion, thus decreasing the distortion.

In addition to the peak at 10,000–11,000 cm.$^{-1}$ assigned as ν_2, the nickel complexes (Figure 3) have a rather broad band at 4000–4600 cm.$^{-1}$, a shoulder at about 7800–8700 cm.$^{-1}$, and, in the chloro complex only, a sharp band at 9050 cm.$^{-1}$. While the low-energy bands are almost certainly components of the ν_1 transitions, assignment of the absorption in the 8000–9000 cm.$^{-1}$ region is complicated by the possibility of transitions to upper states arising from the ^{1}D free ion term. The relative intensities suggest that the absorption at 9050 cm.$^{-1}$ (chloride), 8700 cm.$^{-1}$ (bromide), and 7900 cm.$^{-1}$ (iodide) may well be the highest components of ν_1. However, with such large splittings, mixing of the ^{3}B$_1$ and ^{3}B$_2$ components of the ^{3}T$_1$ and ^{3}T$_2$ states will be appreciable, and it seems scarcely justified to regard the observed bands as arising solely from the ^{3}T$_2$ upper state.

Inner Complexes.—The near-infrared spectrum of bis(N-isopropylsalicylaldimino)nickel(II), which has a distorted tetrahedral structure,[12] has been reported.[13] A band at 6700 cm.$^{-1}$ was assigned as ν_2, and two peaks at 14,100 and 16,900 cm.$^{-1}$ as ν_3. This position of ν_2 is lower than that reported for the NiI$_4^{2-}$ ion,[14] and comparison with our results suggests an alternative assignment. That the ligand field in this compound is fairly strong, as well as distorted, is shown by the spectrum of the isomorphous cobalt complex,[13] which has components of ν_2 at about 8000 and 11,000 cm.$^{-1}$. By analogy with our compounds, it seems that the peak at 6700 cm.$^{-1}$ in the nickel chelate may be derived from a ν_1 band, with ν_2 at 14,100 cm.$^{-1}$ and ν_3 at 16,900 and 19,100 cm.$^{-1}$.

General Conclusions.—The low-energy electronic spectra of the cobalt complexes accord well with expectation. The observed splitting pattern for the ν_2 band is that predicted by group-theoretical arguments, and it appears reasonable to use the magnitude of the splitting as a guide to the amount of distortion. The intensity of the ν_1 band also seems to reflect the departures from true T$_d$ symmetry.

In the nickel complexes, the splitting of the ν_1 band, and the lack of agreement between its position and that predicted,[1] give clear indications of departures from regularity. In this respect this band is more useful than the ν_2 and ν_3 bands, which are less sensitive to these effects, and may therefore be used only as a criterion of an approximately tetrahedral geometry. For many of the complexes, departures from T$_d$ symmetry are so severe that interpretations of the spectra

---

(9) D. M. L. Goodgame, M. Goodgame, and M. J. Weeks, *J. Chem. Soc.*, in press.

(10) W. Ludwig and G. Wittmann, *Helv. Chim. Acta*, **47**, 1265 (1964).

(11) G. Garton, D. E. Henn, H. M. Powell, and L. M. Venanzi, *J. Chem. Soc.*, 3625 (1963).

(12) M. R. Fox, E. C. Lingafelter, P. L. Orioli, and L. Sacconi, *Nature*, **197**, 1105 (1963).

(13) L. Sacconi, P. Paoletti, and M. Ciampolini, *J. Am. Chem. Soc.*, **85**, 411 (1963).

(14) D. M. L. Goodgame, M. Goodgame, and F. A. Cotton, *ibid.*, **83**, 4161 (1961).

on the basis of a simple perturbation of the T_d model are of only limited usefulness.

Another feature of the spectrum for Ni(II) which is sensitive to changes in symmetry is the intensity of the ν_2 band. In the strong-field limit of T_d symmetry this becomes a two-electron transition and is therefore expected to be rather weak. In reflectance spectra it is observed to have an optical density less than, or about equal to, that of the ν_1 band. In C_{3v} and C_{2v} symmetries, however, a component of the ν_3 band becomes the two-electron transition, and the ν_2 band may increase in intensity relative to the other bands. This has been previously observed[3] for the complexes of triphenylphosphine, and it has been noted[14] that when solvolysis of the tetrahalonickelate ions occurs, the solvated species absorb more strongly in the ν_2 region than do the unperturbed anions. However, in view of the contributions to the intensity of these bands which may be made by mixing with charge-transfer transitions,[15] observation of these effects must be interpreted with caution.

For the nickel(II) complexes of C_{2v} symmetry, a reasonable indication of the extent of distortion from T_d symmetry may be obtained by considering the splitting and position of ν_1 and also the magnitude of the magnetic moment. However, with compounds of C_{3v} symmetry the spectrum may well be more informative than the magnetic measurements, unless these are very detailed, since large distortions may occur, as in the phosphine complexes, while the nickel ion retains considerable orbital contribution, if the ^3E level lies lowest.

Acknowledgment.—We thank Dr. D. Rogers for the use of X-ray cameras.

(15) H. A. Weakliem, *J. Chem. Phys.*, **36**, 2117 (1962).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE UNIVERSITY OF TEXAS, AUSTIN, TEXAS 78712

Deprotonation Reactions of Bis(diethylenetriamine)rhodium(III) and -iridium(III) Halides[1,2]

BY GEORGE W. WATT AND B. JACK McCORMICK

Received September 14, 1964

Treatment of bis(diethylenetriamine)rhodium(III) and -iridium(III) halides with potassium amide in liquid ammonia at −33.5° has led to the isolation and characterization of [Rh(dien-H)$_2$]I, [Rh(dien-H)(dien-2H)], and [Ir(dien-H)(dien-2H)] and to evidence for related species not isolated. The effect of deprotonation upon the infrared spectra and possible implications relative to the origin of the protons abstracted are discussed.

Deprotonation of ethylenediamine complexes of transitional metals, M, of charge $n+$ to provide species of the general type $[M^{n+}(\text{en-}x\text{H})_y]^{(n-yx)+}$ has been observed in aqueous solution with gold,[3] in anhydrous ethylenediamine with osmium,[4] and in anhydrous liquid ammonia with platinum,[5,6] palladium,[7] iridium,[8] and rhodium.[9] While the extension of these studies to polyfunctional ligands such as diethylenetriamine and triethylenetetramine was in progress, Baddley, *et al.*,[10] reported the synthesis of [Au(dien-H)X]X and some of its properties, but the question of whether the primary or secondary nitrogen is deprotonated was not unequivocally resolved.

The experiments described below show that protons on the nitrogen atoms in $[\text{Rh(dien)}_2]^{3+}$ and $[\text{Ir(dien)}_2]^{3+}$ are sufficiently acidic in liquid ammonia at −33.5° to permit their removal by reaction with amide ion, at least to a limited extent, *i.e.*

$$[\text{Rh(dien)}_2]^{3+} + \text{NH}_2^- = [\text{Rh(dien-H)(dien)}]^{2+} + \text{NH}_3 \quad (1)$$

$$[\text{Rh(dien-H)(dien)}]^{2+} + \text{NH}_2^- = [\text{Rh(dien-H)}_2]^{+} + \text{NH}_3 \quad (2)$$

$$[\text{Rh(dien-H)}_2]^{+} + \text{NH}_2^- = [\text{Rh(dien-H)(dien-2H)}] + \text{NH}_3 \quad (3)$$

Although effects to demonstrate this reaction sequence by following the reactions potentiometrically were not successful, isolation and characterization of the products of (2) and (3) incontrovertibly establish that such acid–base reactions do occur. Even though the product of (1) was not isolated, it seems reasonable to postulate this reaction as the first of the series.

Apparently, a similar series of reactions occurs in the case of $[\text{Ir(dien)}_2]^{3+}$; however, the evidence here is considerably less substantial than in the rhodium case since only [Ir(dien-H)(dien-2H)] was isolated and partially characterized. In contrast to the reactions of $[\text{Ir(en)}_3]^{3+}$ and $[\text{Rh(en)}_3]^{3+}$ with amide ion,[8,9] the

---

[1] This work was supported by the Robert A. Welch Foundation and the U. S. Atomic Energy Commission.

[2] dien denotes the tridentate diethylenetriamine ligand; (dien-nH) indicates the same ligand from which n protons have been removed.

(3) B. P. Block and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **73**, 4722 (1951).

(4) F. P. Dwyer and J. W. Hogarth, *ibid.*, **75**, 1008 (1953).

(5) G. W. Watt, R. E. McCarley, and J. W. Dawes, *ibid.*, **79**, 5163 (1957).

(6) G. W. Watt and J. W. Dawes, *ibid.*, **81**, 8 (1959).

(7) G. W. Watt and R. Layton, *ibid.*, **82**, 4465 (1960).

(8) G. W. Watt, L. E. Sharif, and E. P. Helvenston, *Inorg. Chem.*, **1**, 6 (1962).

(9) G. W. Watt and J. K. Crum, forthcoming publication.

(10) W. H. Baddley, F. Basolo, H. B. Gray, C. Nölting, and A. J. Poe, *Inorg. Chem.*, **2**, 921 (1963).