TABLE II

X-Ray Diffraction Data for [Rh(dien-H)$_2$]I
and [Rh(dien-H)(dien-2H)][a]

[Rh(dien-H)$_2$]I		[Rh(dien-H)(dien-2H)]	
d, Å.	I/I_0	d, Å.	I/I_0
8.52	0.50	8.40	0.25
6.47	0.50	7.64	0.50
6.03	0.10[b]	6.22	1.00
5.63	0.50	5.79	0.20
4.37	1.00	5.01	0.20
3.46	0.20	4.54	0.10[b]
2.94	0.40	4.08	0.20
2.81	0.10	2.91	0.15
2.52	0.15	2.71	0.10
2.37	0.10	2.62	0.10
2.03	0.10	2.52	0.10

[a] See footnote *a*, Table I. [b] Less intense lines not included here.

from 0.2795 g. of K (3.50 molar equivalents). After a digestion period of 1.5 hr. the tan product was separated by filtration and washed with six 30-ml. portions of ammonia. The product then was handled as described above. Analysis of the combined filtrate and washings accounted for 98.8% of the iodine added initially as [Rh(dien)$_2$]I$_3$.

Anal. Calcd. for [Rh(dien-H)(dien-2H)]: Rh, 33.6; N, 27.4. Found: Rh, 34.0; N, 27.4. X-Ray diffraction data are given in Table II and the infrared spectrum is shown in Figure 3.

Properties and Reactions of [Rh(dien-H)(dien-2H)].—This product dissolved readily in water to give a basic solution. The bulk material was somewhat pyrophoric in air; however, when powdered the complex did not burn in air but was very hygroscopic. In an atmosphere of dry He, [Rh(dien-H)(dien-

2H)] appeared to be somewhat unstable, as evidenced by a darkening in color over a period of 1–2 months. The complex was diamagnetic at 25°.

To a suspension of 0.208 g. of [Rh(dien-H)(dien-2H)] in *ca.* 40 ml. of ammonia was added 0.295 g. of NH$_4$I (3.0 molar equivalents in 10.2 ml. of NH$_3$). The product was separated by filtration and washed once with 30 ml. of ammonia. After removal of the solvent, the X-ray diffraction data included in Table I were obtained. The infrared spectrum was identical with that shown in Figure 4.

A 37-mg. sample of [Rh(dien-H)(dien-2H)] was pyrolyzed *in vacuo* to determine whether dien might be liberated. At 200° the complex darkened and a colorless liquid began to condense in the cooler (ambient temperature) portion of the pyrolysis tube. The liquid continued to distil as the temperature was raised slowly to 500°. The liquid that condensed in the trap was identified as dien both by mass spectrographic analysis and by the fact that the melting point of its picrate was identical with that of the picrate prepared from an authentic sample of dien. A black residue consisting mostly of Rh, as shown by an X-ray diffraction pattern, remained in that portion of the tube which was heated.

Reaction of [Rh(dien)$_2$]I$_3$ with 6KNH$_2$.—To 0.5872 g. (8.5 × 10^{-4} mole) in 40 ml. of ammonia was added, slowly, 13.8 ml. of ammonia containing 6.0 molar equivalents of KNH$_2$. The orange solution was aged for 1 hr. with no change in appearance. To this solution was added 6.0 equivalents of NH$_4$I in 10 ml. of NH$_3$. The pink product obtained was washed three times with 20-ml. portions of NH$_3$. The pink product was stable indefinitely in an atmosphere of dry He and dissolved readily in H$_2$O to form a pink neutral solution which became colorless over a period of several hours.

Anal. Calcd. for [Rh(dien)$_2$]I$_3$: Rh, 14.9. Found: Rh, 14.9. X-Ray diffraction data are given in Table I and the infrared spectrum is shown in Figure 4.

Contribution from the Department of Chemistry
Tulane University, New Orleans, Louisiana   70118

Reflectance Spectra and the Coordination of Divalent Metal Ions in 5-Trifluoromethyltetrazole Complexes[1]

By ARLO D. HARRIS, HANS B. JONASSEN, AND RONALD D. ARCHER

The nature of the coordination of Fe(II), Co(II), Ni(II), and Cu(II) with the 5-trifluoromethyltetrazolyl anion has been ascertained on the basis of a correlation of the reflectance spectra with previously reported observations.[2,3] All of the complexes appear to be octahedral or distorted octahedral σ-bonded complexes involving coordination by tetrazolyl anion and water.

Introduction

Jonassen and co-workers[2,3] have prepared complexes of several divalent transition metal ions with the 5-trifluoromethyltetrazolyl anion (Figure 1) and assigned a preliminary structure to the dihydrate of the iron(II) complex on the basis of a Mössbauer-effect study.[3] A re-evaluation of the structure of this com-

pound and some understanding of the others is now possible by correlation of the reflectance spectra with previous measurements of other properties of the complexes. All of the experimental evidence correlates well for σ-bonded tetrazole complexes, in contrast to the π-bonded structure previously entertained for the iron complex.[3]

Experimental

Chemicals.—The chemicals used in this investigation were reagent grade. The tetrazole sample was prepared by Norris,[4,5] whose generosity in supplying a large sample is gratefully acknowledged. The complexes Fe(C$_2$F$_3$N$_4$)$_2$·2H$_2$O, Co(C$_2$F$_3$N$_4$)$_2$·6-

(1) Experimental results presented in part at the Southwest Regional Meeting of the American Chemical Society, Houston, Texas, Dec. 1963, and abstracted in part from a dissertation submitted by A. D. Harris in partial fulfillment of the requirements for the Ph.D., Tulane University, 1964.

(2) H. B. Jonassen, J. D. Terry, and A. D. Harris, *J. Inorg. Nucl. Chem.*, **25**, 1239 (1963).

(3) A. D. Harris, R. H. Herber, H. B. Jonassen, and G. K. Wertheim, *J. Am. Chem. Soc.*, **85**, 2927 (1963).

(4) U. S. Naval Ordnance Test Station, China Lake, Calif.

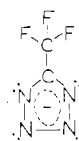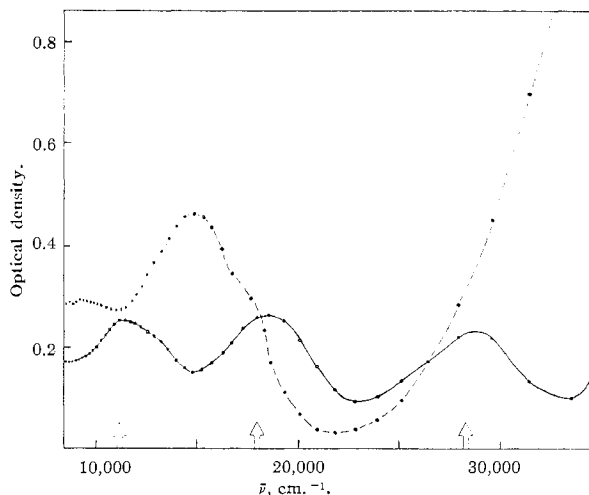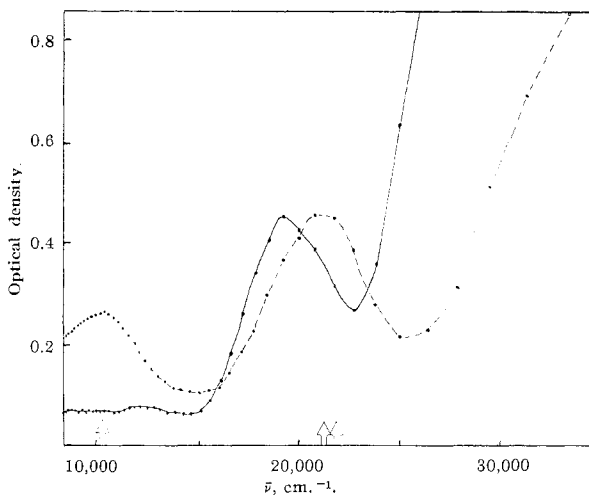(5) W. P. Norris, *J. Org. Chem.*, **27**, 3248 (1962).

Figure 1.—The 5-trifluoromethyltetrazolyl anion.

Figure 2.—Reflectance spectra of $Ni(C_2F_3N_4)_2 \cdot 4H_2O$ (solid line) and $Cu(C_2F_3N_4)_2 \cdot H_2O$ (dashed line). Calculated absorption peaks for nickel(II) complex are indicated by arrows.

Figure 3.—Reflectance spectra of $Fe(C_2F_3N_4)_2 \cdot 2H_2O$ (solid line) and $Co(C_2F_3N_4)_2 \cdot 6H_2O$ (dashed line). Calculated absorption peaks for cobalt(II) complex are indicated by arrows.

H_2O, $Ni(C_2F_3N_4)_2 \cdot 4H_2O$, and $Cu(C_2F_3N_4)_2 \cdot H_2O$ were prepared by the methods previously described by Jonassen and co-workers.[2,3]

Reflectance Spectra.—Reflectance spectra in the near-ultraviolet, visible, and near-infrared regions were obtained with a Beckman Model DU spectrophotometer equipped with a reflectance attachment. The samples were held in circular stainless-steel sample holders 2 mm. deep and 30 mm. i.d. All samples were finely ground with an agate mortar and pestle and dried prior to filling the holder. The surface of the sample was leveled by applying hand pressure to a hard rubber stopper that just fit inside the holder.

Relative reflectance measurements were obtained using $MgCO_3$ as a standard. The relative optical density was read directly from the dial of the instrument with readings taken every 20 mμ (Figures 2 and 3).

Discussion

$Ni(C_2F_3N_4)_2 \cdot 4H_2O$.—The reflectance spectrum of this complex (Figure 2 and Table I) is that expected for an octahedral or distorted octahedral spin-free nickel(II) complex[6-8] with $Dq = 1140$ cm.$^{-1}$ and the Racah parameter $B = 800$ cm.$^{-1}$, neglecting the lower symmetry which actually exists. The calculated peaks are indicated by lines at the bottom of Figure 2. A comparison with other nickel(II) complexes[6] places the 5-trifluoromethyltetrazolyl anion above ammonia and ethylenediamine and probably very close to bipyridyl

Table I

Spectral Assignments for Several 5-Trifluoromethyltetrazolyl Complexes

Complex	$\bar{\nu}$, cm.$^{-1}$	Assignment	
$Ni(C_2F_3N_4)_2 \cdot 4H_2O(s)$	11,400	$^3A_{2g}$	$\leftrightarrow$ $^3T_{2g}$
	$(13,200)^a$		b
	18,500	$^3A_{2g}$	$\leftrightarrow$ $^3T_{1g}(F)$
	28,500	$^3A_{2g}$	$\leftrightarrow$ $^3T_{1g}(P)$
$Ni(C_2F_3N_4)_2(aq)$	$17,500^c$	$^3A_{2g}$	$\leftrightarrow$ $^3T_{1g}(F)$
	$27,800^c$	$^3A_{2g}$	$\leftrightarrow$ $^3T_{1g}(P)$
$Cu(C_2F_3N_4)_2 \cdot H_2O(s)$	9,000	$^2B_{1g}$	$\leftrightarrow$ $^2A_{1g}$
	14,700	$^2B_{1g}$	$\leftrightarrow$ $^2B_{2g}$
	17,900	$^2B_{1g}$	$\leftrightarrow$ ^2E_g
$Fe(C_2F_3N_4)_2 \cdot 2H_2O(s)$	19,300	$^1A_{1g}$	$\leftrightarrow$ $^1T_{1g}$
$Co(C_2F_3N_4)_2 \cdot 6H_2O(s)$	10,400	$^4T_{1g}(F)$	$\leftrightarrow$ $^4T_{2g}$
	21,300	$^4T_{1g}(F)$	$\leftrightarrow$ $^4T_{1g}(P)$

^{a} A breakdown of the spectrum into individual bands shifts this shoulder to approximately 14,000 cm.$^{-1}$. ^{b} Although this shoulder has been assigned as ^1E_g, C. K. Jørgensen, *Acta Chem. Scand.*, 9, 1362 (1955), this designation has been challenged because of the intensity of the peak; see ref. 7. ^{c} Calculated from the data in ref. 2.

and *o*-phenanthroline in the spectrochemical series. It appears that two of the six coordination positions are filled by water in the solid. This conclusion is based on the following: In water the complex shows absorption maxima at 17,500 and 27,800 cm.$^{-1}$ for the continuous variations maximum ratio of 2 ligands:1 metal. These $^3T_{1g}$ peaks in solution are undoubtedly for the coordination of two nitrogens and four oxygens to the nickel. The energy shift for the solid corresponds to the loss of two water molecules; *i.e.*, the shift is about that observed for the replacement of two water molecules by one ethylenediamine molecule.[6]

An alternate explanation is possible since shifts of this magnitude could result from the phase change and the change in the method of measurement. The difficulty in removing any of the four remaining water molecules from the solid supports this interpretation.

A magnetic moment of 2.8 B.M. and shifts in the infrared frequency assigned to the $N=N$ and H_2O deformation have been observed,[2] in agreement with the above spectral information. The $N=N$ shift is small and suggestive of σ-bonding to the lone pairs rather than π-bonding. On the other hand, none of the meas-

(6) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, 1962, Chapters 5, 7, 15.
(7) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., New York, N. Y., 1962.
(8) W. Manch and W. C. Fernelius, *J. Chem. Educ.*, 38, 192 (1961).

urements proves the relative number of nitrogen and oxygen atoms coordinated to the nickel.

$Cu(C_2F_3N_4)_2 \cdot H_2O$.—The reflectance spectrum for the monohydrate of $Cu(C_2F_3N_4)_2$ (Figure 2 and Table I) is very similar to that observed[6,8] for distorted octahedral complexes of copper(II) with strong nitrogen donors; in fact, the spectrum is almost identical with those of the $Cu(bipy)_3{}^{2+}$ and $Cu(o\text{-phen})_3{}^{2+}$ ions.[6] This observation supports the above-noted strong ligand field strength for this nitrogen donor with nickel(II). The low-energy band ($^2A_{1g}$), which results because of the Jahn–Teller distortion observed for copper(II) complexes, is lower than that observed for diaquo complexes having four nitrogen donors[6]; therefore, it seems probable that at least five of the coordination positions are filled by nitrogen atoms. The stoichiometry and previous measurements are in agreement with this conclusion as is the ratio of the energy of the principal ligand field band of the copper complex to the energy of the first spin-allowed band of the nickel complex. The observed ratio of about 1.3 is between that usually noted for complexes with six identical ligands (≈ 1.4) and complexes of low tetragonality (≈ 1.1), but the ratio is considerably removed from the ratio observed for strongly tetragonal complexes.[6]

$Fe(C_2F_3N_4)_2 \cdot 2H_2O$.—The major absorption peak for the iron complex of this series (Figure 3 and Table I) has an energy between those of octahedral $Fe(bipy)_3{}^{2+}$ and $Fe(o\text{-phen})_3{}^{2+}$, which have major extinction peaks at 19,100 and 19,600 cm.$^{-1}$, respectively.[6] This band in the latter two chelates has been assigned as an electron-transfer band from the t_{2g} level of the iron d electrons to the π^* level of the ligands.[9] On the other hand, Ballhausen[7] has estimated spin-paired iron(II) complexes to have $Dq \geq 1500$ cm.$^{-1}$. This estimate would place the $^1A_{1g} \leftrightarrow {}^1T_{1g}$ band near or above 15,000 cm.$^{-1}$, or in the region of the electron-transfer peak observed in the spin-paired tris(bipyridyl)- and tris-(o-phenanthroline)iron(II) chelates. The intensity of the band at 19,300 cm.$^{-1}$ in the pink 5-trifluoromethyltetrazolyl complex is weak, suggesting that it is a d $\leftrightarrow$ d band, namely $^1A_{1g} \leftrightarrow {}^1T_{1g}$, or that $Dq \approx 2200$ cm.$^{-1}$ and $B \approx 1000$ cm.$^{-1}$ if the spin-free and spin-paired states are of about equal energy.[6,10] The assumption that a paramagnetic state lies close to the spin-paired ground state is based on the reported magnetic moment of 1.10 B.M.,[2] which is much too low for either spin-paired or spin-free tetrahedral iron(II).[11] Paramagnetic states mixing with ground states also have been observed for cobalt(III) ammine complexes,[12] which are spin-paired d^6 complexes, too. The large Dq value is typical of

spin-paired iron(II). Hexacyanoferrate(II) has a Dq value of over 3000[6] and the bipyridyl and o-phenanthroline complexes must have a Dq value of about the same magnitude as the tetrazole complex as indicated by the absence of a lower lying $^1A_{1g} \leftrightarrow {}^1T_{1g}$ band. Octahedral, spin-paired iron(II) is not expected to show any quadrupole splitting in Mössbauer-effect studies,[13] in agreement with earlier results.[3,13] The small shift observed in the N=N infrared frequency[2] is more in line with σ-bonding than the earlier proposed π-bonding,[3] which was based on the lack of quadrupole splitting. Group theoretical reasons have also been given[14] against the previous assignment. A polymeric structure with four tetrazolyl nitrogens and two water molecules bonded to each iron with each tetrazolyl ion bonded to two iron(II) ions should give an insoluble complex, as observed, and could have the physical properties noted above.

$Co(C_2F_3N_4)_2 \cdot 6H_2O$.—Two strong absorption bands for octahedral, spin-free cobalt(II) are easily assigned from the reflectance spectrum of $Co(C_2F_3N_4)_2 \cdot 6H_2O$ (Figure 3) as noted in Table I. Fitting these peaks[6,7] gives $Dq = 1160$ cm.$^{-1}$ and $B = 820$ cm.$^{-1}$ and places the unobserved, two-electron, $^4T_{1g}(F) \leftrightarrow {}^4A_{2g}$ absorption at 21,900 cm.$^{-1}$. This weaker transition is masked by the more intense $^4T_{2g}$ band. The Dq value noted for this complex is considerably greater than the Dq value for the hexaaquocobalt(II) ion (950 cm.$^{-1}$)[7] and the hexaamminecobalt(II) ion (1010 cm.$^{-1}$),[6] thus showing that the insoluble complex involves coordination to the tetrazolyl anion. The similarity to the Dq value for nickel(II) is gratifying and is similar to the observed results for other nitrogen bases.[6] Apparently some of the water is involved in lattice hydration only. The infrared and magnetic moment studies[2] are in agreement with the above conclusion.

Thus a consistent pattern of octahedral coordination by the 5-trifluorotetrazolyl anion and water has been found for all of the complexes. However, the high microsymmetry (pseudo-octahedral) makes it impossible to determine the exact number of water molecules involved in the coordination.

(9) C. K. Jørgensen, *Acta Chem. Scand.*, **11**, 166 (1957).

(10) D. S. McClure, *Solid State Phys.*, **9**, 399 (1959).

(11) As noted by a referee, a temperature dependence study of the magnetic moment of this complex would be interesting.

(12) B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, New York, N. Y., 1960, Chapter 6.

(13) E. Fluck, W. Kerler, and W. Neuwirth, *Angew. Chem. Intern. Ed. Engl.*, **2**, 277 (1963).

(14) P. S. Braterman, private communication.