low frequencies necessarily indicate a nonbridging cyanide group. Indeed, the compound $KCu(CN)_2$, which is bridged *via* the nitrogen group,[27] has been reported to have C–N frequencies at 2085 and 2105 cm^{-1}.[19] The infrared data for potassium dicyanocuprate(I) have been confirmed by us, and therefore the low C–N frequencies observed for the cyanoamine complexes are not inconsistent with bridging of the type proposed. An X-ray study[27] has shown that the ion $Cu(CN)_2^-$ is angular in $KCu(CN)_2$, and if such is also the case for the complexes under discussion, bridging in the solid state would be expected to reduce the symmetry of the complex cation. This would explain the splittings and the shifts observed in the infrared spectra. Although the dicyanocuprate(I) ion is intuitively preferable as the anion, the vibrational spectra do not permit the distinction between this and the ion $Cu_2(CN)_4^{2-}$.

The visible data indicate that this bridging is retained for the ethylenediamine complex, in solutions at concentrations above 10^{-2} *M*, and that for the ammonia complex the bridging is not retained in solution. A possible explanation for this difference is the effect of the methylene groups attached to the coordinating nitrogen in the case of the ethylenediamine complex which is absent in the ammonia complex. The methylene groups would be expected to reduce the dielectric in the neighborhood of the cation and hence favor the association of the ion $Cu(CN)_2^-$ with $Cu(en)_2^{2+}$ as compared to $Cu(NH_3)_4^{2+}$. That the difference is not great is shown by the observation that, as the concentrations are decreased, dissociation occurs and an unmodified $Cu(en)_2^{2+}$ ion is observed in the absorption spectrum. It is concluded therefore that the complexes under discussion contain the ions $Cu(NH_3)_4^{2+}$ and $Cu(en)_2^{2+}$ and that under certain circumstances bridging can occur with the anion, probably $Cu(CN)_2^-$.

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(27) D. T. Cromer, *J. Phys. Chem.*, **61**, 1388 (1957).

CONTRIBUTION FROM CYANAMID EUROPEAN
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Preparation and Electronic Spectra of Some Acidopentaammineiridium(III) Complexes

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Received March 4, 1966

A series of complex compounds of the type $[Ir^{III}(NH_3)_5X]Y_n$ has been prepared where X = I^-, Br^-, SCN^-, N_3^-, ONO^-, ^-OOCH, $^-OOCCH_3$, OH^-, ONO_2^-, H_2O, NCS^-, NO_2^- and Y = Cl^- or ClO_4^-, and their visible, ultraviolet, and infrared spectra were recorded. Assignment of the linkage isomers is possible on the basis of the spectrochemical series. The observed bands are interpreted as ligand field and electron-transfer transitions using common theoretical procedures. The infrared spectra, conductivity measurements, and molecular weight determinations furnish further evidence for the proposed complex formulation.

Introduction

The ultraviolet absorption bands of rhodium(III) pentaammine complexes were found[1] to follow closely the spectrochemical series established by Tsuchida.[2] The spectra of six-coordinated pentaammine d^6 complexes such as Co(III), Rh(III), and Ir(III) show only small deviations from octahedral symmetry at normal temperatures. For Co(III) complexes the low-symmetry component of the ligand field manifests itself[3] by a splitting of the first spin-allowed band $^1A_{1g} \rightarrow {}^1T_{1g}$. The second band does not seem to be affected, although according to the predictions of Yamatera[4] it should be split by the same amount. For the corresponding Rh(III) and Ir(III) compounds no term splittings can be detected,[1,5] but some show minor deviations from a Gaussian curve. It is therefore possible, in particular for the higher transition group ions, to classify the observed ligand field transitions according to term symbols of the octahedral group and define an approximate cubic ligand field parameter $\Delta = 10Dq$.[6] Instead of using the position of the first absorption band when establishing the spectrochemical series, as was originally done by Tsuchida,[2] we prefer to order the ligands according to their ligand field parameters Δ, since this classification eliminates various effects of electron interaction in the d shell and leaves the ligand field strength as a physical parameter describing the ligand–central atom interaction. The position of a molecular ligand in the spectrochemical series is, in general, determined by the atom attached to the central ion. We therefore expect ambidentate ligands to occupy different places in this series depending on the way they are linked to the central ion. It is therefore

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(1) H.-H. Schmidtke, *Z. Physik. Chem.* (Frankfurt), **45**, 305 (1965).
(2) R. Tsuchida, *Bull. Chem. Soc. Japan*, **13**, 388, 436 (1938).
(3) M. Linhard and M. Weigel, *Z. Physik. Chem.* (Frankfurt), **11**, 308 (1957).
(4) H. Yamatera, *Bull. Chem. Soc. Japan*, **31**, 95 (1958).
(5) F. Monacelli, F. Basolo, and R. G. Pearson, *J. Inorg. Nucl. Chem.*, **24**, 1241 (1962).
(6) R. G. Schlapp and W. G. Penney, *Phys. Rev.*, **41**, 194 (1932); **42**, 666 (1932).

possible to assign the linkage isomers on the grounds of the visible and ultraviolet spectra.

In this paper we have extended the spectrochemical series of iridium pentaammines by recording the spectra of some newly prepared compounds. These are discussed together with the spectra of other known complexes of this type on the basis of the usual theoretical procedures. In particular the linkage isomerism of the thiocyanato and nitro complexes are investigated more closely.

Experimental Section

Preparation of the Complexes. (a) **Preparation of Thiocyanato- and Isothiocyanatopentaammineiridium(III) Perchlorate.**—The perchlorate $[Ir(NH_3)_5H_2O](ClO_4)_3$ (0.8 g) and sodium thiocyanate (0.87 g, an eightfold excess) were refluxed in water (50 ml) for 8 hr. The almost colorless solution was filtered while hot to remove impurities and yielded crystals after standing for 15 hr. The product was collected on a filter, washed with alcohol, and recrystallized from water giving large, white crystals of the isothiocyanato complex (yield 65%). *Anal.* Calcd for $[Ir(NH_3)_5(NCS)](ClO_4)_2$: C, 2.25; H, 2.83; N, 15.72; S, 6.00; Cl, 13.26; Ir, 35.96. Found: C, 2.46; H, 3.06; N, 15.93; S, 5.93; Cl, 13.09; Ir, 35.73.

The filtrate from the above preparation was reduced to a volume of 8 ml by evaporation *in vacuo*. A small amount of precipitate (7 mg) was removed by filtration and the yellow filtrate slowly further evaporated in a vacuum desiccator, where long, pale yellow crystals grew from the surface, until it was reduced to a volume of about 1 ml, when the product was filtered off and washed with alcohol to remove adhering sodium thiocyanate. The crystals were dissolved in a small amount of warm 10% perchloric acid and the solution slowly evaporated *in vacuo* until crystals formed. After filtering and washing with alcohol the crystals were dried in a desiccator (yield 16.2%). *Anal.* Calcd for $[Ir(NH_3)_5(SCN)](ClO_4)_2$: as above. Found: C, 2.16; H, 3.02; N, 15.76; S, 6.17; Cl, 13.17; Ir, 35.7.

The corresponding chlorides have also been prepared by exchanging the perchlorates on an ion-exchange resin.

(b) **Preparation of Formiatopentaammineiridium(III) Perchlorate.**—The chloride $[Ir(NH_3)_5Cl]Cl_2$ was dissolved in a solution of sodium hydroxide (33 ml of a 1 *M* solution) and refluxed for 8 hr. Thereafter the solution was acidified with concentrated formic acid (15 ml) and evaporated almost to dryness on a steam bath. Some decomposition products formed. After further addition of concentrated formic acid (10 ml) the solution was heated another hour on the steam bath. Water (25 ml) was added and the decomposition products removed by filtration. The light yellow filtrate was cooled to 0°, and a white product was precipitated by a dropwise addition of cold 60% perchloric acid (3 ml). The crystals were collected on a filter, washed with alcohol and ether, and dried *in vacuo* (yield 76%). *Anal.* Calcd for $[Ir(NH_3)_5(OOCH)](ClO_4)_2$: C, 2.30; H, 3.10; N, 13.43; Cl, 13.6; Ir, 36.83. Found: C, 2.43; H, 3.15; N, 13.49; Cl, 13.54; Ir, 37.13.

(c) **Preparation of Azidopentaammineiridium(III) Azide.**—The perchlorate $[Ir(NH_3)_5H_2O](ClO_4)_3$ (0.5 g) and sodium azide (0.55 g, a tenfold excess of azide) were dissolved in water (35 ml) and refluxed for 4 hr. The solution was reduced to a volume of about 5 ml by evaporation on a steam bath and cooled below 0°. Brown-yellow crystals formed, which were collected on a filter and washed with ethanol and acetone. The salt crystallized with appreciable amounts of perchlorate as anion. For recrystallization the product was dissolved in water (2 ml), and a concentrated aqueous solution of tetra-*n*-butylammonium azide was added. The voluminous precipitate of tetrabutylammonium perchlorate was removed by filtration, and the product was precipitated as pale yellow crystals from the filtrate by ethanol (yield 35%). *Anal.* Calcd for $[Ir(NH_3)_5(N_3)](N_3)_2$: H, 3.75; N, 48.6; Ir, 47.6. Found: H, 3.93; N, 48.05; Ir, 47.1. Attempts to prepare perchlorate salts yielded only mixed salts of the aquo and azido complexes.

(d) **Preparation of Iodopentaammineiridium(III) Chloride.**—The iodide $[Ir(NH_3)_5I]I_2$ was prepared according to the method of Palmaer.[7] The corresponding chloride was precipitated by adding an excess of concentrated hydrochloric acid to a hot solution of the iodide. Slow cooling to 0° increased the yield. The yellow well-formed crystals were dried over KOH. *Anal.* Calcd for $[Ir(NH_3)_5I]Cl_2$: H, 3.18; N, 14.74; Cl, 14.92; I, 26.71; Ir, 40.45. Found: H, 3.32; N, 14.59; Cl, 15.13; I, 26.82; Ir, 40.53.

(e) **Preparation of Nitratopentaammineiridium(III) Chloride.**—The nitrate $[Ir(NH_3)_5(H_2O)](NO_3)_3$ was prepared according to Palmaer[7] and heated for some hours at 105° in a drybox. The product $[Ir(NH_3)_5(NO_3)](NO_3)_2$ was dissolved in water and the perchlorate precipitated by perchloric acid. The perchlorate (0.2 g) was dissolved in hot water (20 ml), and after cooling to room temperature the solution was passed through a 30-cm column of the chloride form of an anion exchanger (Dowex 1×4). The solution was evaporated under reduced pressure and the product precipitated by addition of a few milliliters of concentrated hydrochloric acid. The white crystals were washed with alcohol and acetone and purified by repeated precipitation with hydrochloric acid. *Anal.* Calcd for $[Ir(NH_3)_5(NO_3)]Cl_2$: H, 3.68; N, 20.47; Cl, 17.28; Ir, 46.80. Found: H, 3.76; N, 20.53; Cl, 17.43; Ir, 46.93.

(f) **Preparation of Hydroxopentaammineiridium(III) Perchlorate.**—The procedure follows essentially the method by Dixon[8] except that it starts from the perchlorate. Fine white crystals separated over a period of 15 hr; they were collected in a narrow glass filter frit G4, washed with alcohol, and dried in a desiccator over potassium hydroxide. *Anal.* Calcd for $[Ir(NH_3)_5(OH)](ClO_4)_2$: H, 3.27; N, 14.2; Cl, 14.37; Ir, 38.98. Found: H, 3.14; N, 14.37; Cl, 14.44; Ir, 38.96.

The other compounds were prepared according to prescriptions given in the literature.[5,7,9]

Electronic Absorption Spectra.—Spectra were recorded at room temperature using a Cary Model 14 spectrophotometer for 10^{-2}–10^{-3} *M* aqueous solutions in quartz cells of 1 or 2 cm thickness.

Conductance Measurements.—Conductivities were determined on a Philips Model GH 4249 conductivity bridge at a frequency of 1000 cps. The measuring cell contained two platinum electrodes coated with platinum chloride.

Molecular Weight Determinations.—Molarities were determined by a Mechrolab, Inc., Model 301A vapor pressure osmometer.

Infrared Spectra.—The infrared spectra of samples in KBr disks were measured on a Perkin-Elmer Model 521 grating infrared spectrophotometer.

Analyses.—The analyses were carried out at the Laboratoire Microchimique, Ecole de Chimie, Dr. K. Eder, Geneva.

Discussion of Absorption Spectra and Bonding Properties

In Figures 1–4 the visible and ultraviolet absorption spectra in aqueous solution are shown for these compounds. When comparing these spectra with those of the corresponding rhodium compounds[1] we find a general shift of the bands toward shorter wavelength. This is expected from the spectrochemical series of central ions.[10] According to this series, homologous complexes of higher transition group ions should absorb further in the ultraviolet so that we expect, for instance, in the series Co(III), Rh(III), and Ir(III) an increasing blue shift of cor-

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[7] W. Palmaer, *Z. Anorg. Allgem. Chem.*, **10**, 320 (1895).

[8] B. E. Dixon, *J. Chem. Soc.*, 34 (1934).

[9] F. Basolo and G. S. Hammaker, *Inorg. Chem.*, **1**, 1 (1962).

[10] C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Ltd., Oxford, 1962, p 114.

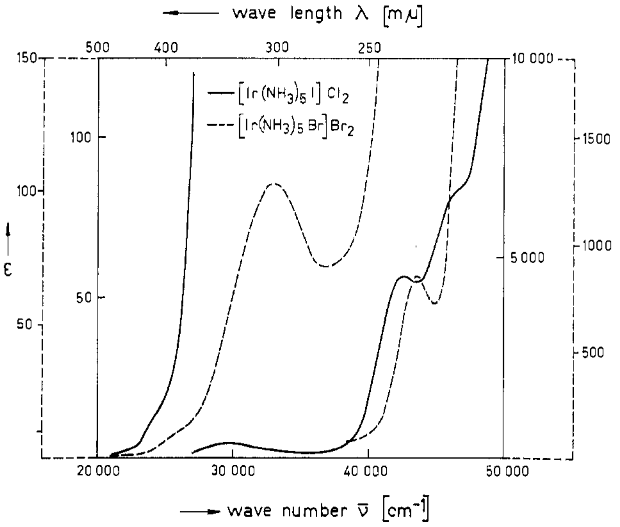

Figure 1.—Absorption spectra of the iodo and bromo complexes in aqueous solution. ε is the molar extinction coefficient.

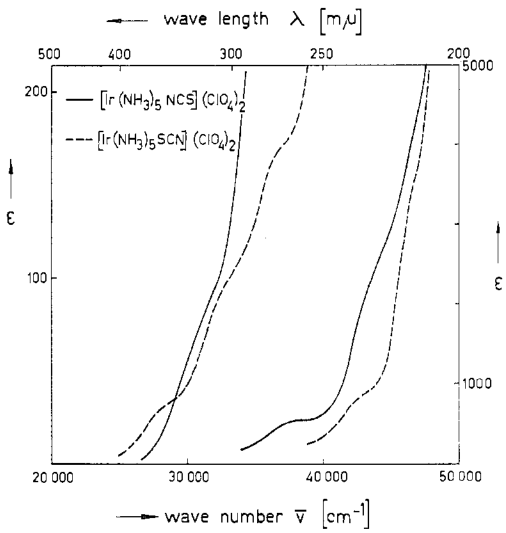

Figure 2.—Absorption spectra of the linkage isomers of the thiocyanato complexes in aqueous solution.

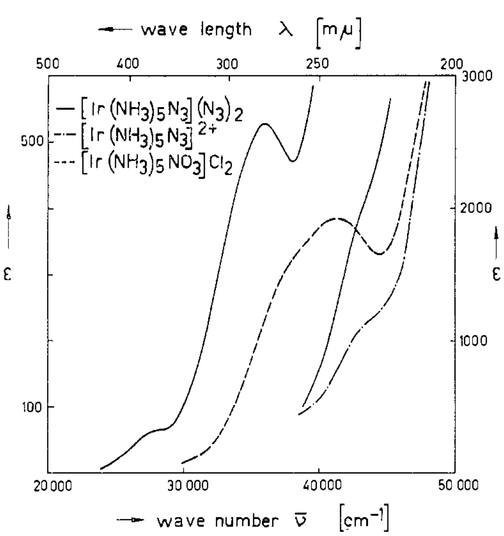

Figure 3.—Absorption spectra of the nitrato and azido complexes in aqueous solution. The spectrum of the azido complex cation is gained by a deduction of the spectrum of $2N_3^-$.

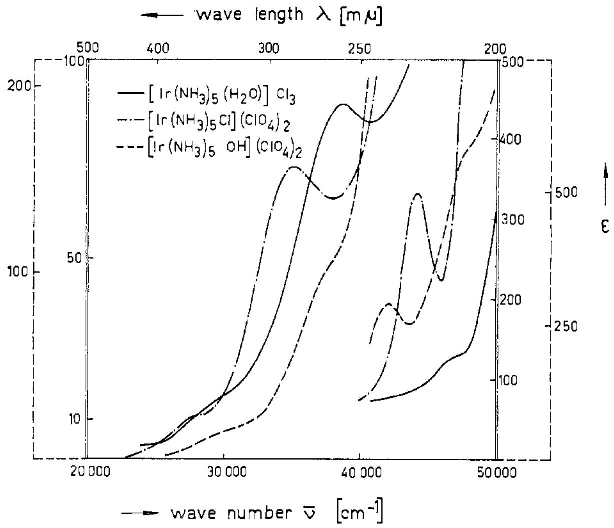

Figure 4.—Absorption spectra of the aquo, hydroxo, and chloro complexes in aqueous solution. The spectrum of the hydroxo complex is identical with that of the aquo complex in 0.1 *M* NH_3 solution.

responding bands. Furthermore, we observe that for the iridium complexes the bands are not so clearly resolved as are those of the rhodium complexes. The transitions appearing in the spectra of the iridium complexes are in some cases only shoulders on other strong bands located further in the violet. This might be explained by an intermixing of the d–d (ligand field) transitions with other transition mechanisms (charge-transfer processes or internal ligand transitions) which have much higher transition probabilities. This intermixing is more probable for higher transition group elements since for these complexes the excited ligand field states become closer in the energy scheme to the charge-transfer state or some excited states of the ligands.[11]

In Table I are listed the position, the molar absorption coefficients, and the assignments of the bands which are observed in the visible and near-ultraviolet regions of some $[Ir(NH_3)_5X]^{n+}$ type complexes. The compounds are ordered according to the spectrochemical series[2,12] of the ligand X. It is seen that the observed absorptions follow the spectrochemical series for the singlet–triplet transitions and for the first spin-allowed transition as well. The assignments are made by comparison with the spectra of the corresponding Co(III) and Rh(III) compounds, whose spectra are known and interpreted.[1,3,13] We observe in the spectrum ligand field (d–d) transitions and charge-transfer transitions from the ligand to the partly filled d shell. If we assume octahedral microsymmetry for the complex cation, two triplets ($^3T_{1g}$, $^3T_{2g}$) and two singlets ($^1T_{1g}$, $^1T_{2g}$) arise from the $t_{2g}{}^5e_g$ excited configuration. The weak spin-forbidden transitions from the ground state $t_{2g}{}^6$ ($^1A_{1g}$) are found in the spectra of the iridium complexes more frequently than for the corresponding rhodium compounds.

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[11] R. Englman, *Mol. Phys.*, **3**, 48 (1960).

[12] See ref 10, p 109.

[13] C. K. Jørgensen, *Advan. Chem. Phys.*, **5**, 33 (1963).

TABLE I

POSITION (1 kK = 1000 CM^{-1}) AND ASSIGNMENT OF BANDS IN THE VISIBLE AND ULTRAVIOLET SPECTRA OF SOME Ir(III) PENTAAMMINE COMPLEXES[a]

$[Ir(NH_3)_5X]^{n+}$, X =	Singlet-triplet transitions	$^1A_{1g} \rightarrow {}^1T_{1g}$	$^1A_{1g} \rightarrow {}^1T_{2g}$	Ctf[b]
I^-	24 (14) sh[c]	29.7 (372)		π: 42.7 (4600) 46.5 (6700)
Br^-	26 (10) sh	33.0 (100)		π: 43.5(800)
Cl^-	27.4 (10.2)	35.0 (73)	44.1 (333)	
SCN^-	27.8 (28) sh	32.8 (100) sh 36.4 (165) sh	42.5 (820)	
N_3^-	27.8 (64)	36.0 (528)	43 (1100) sh	
ONO^-		36.5 (1210)	41 (1090) sh	
$^-OOCCH_3$ } ^-OOCH }	30 (20) sh	38.2 (128)		
OH^-	30 (16) sh	37 (95) sh (?) 42.0 (293)	47.6 (570)	
ONO_2^-		37.8 (1590) sh 41.2 (1920)		
H_2O	30 (12) sh	38.8 (86)	47 (128)	
NCS^-	30 (60) sh	38.5 (560)	43.5 (2260) sh (?)	
NH_3[d]	31.8 (14) sh	39.8 (92)	46.8 (160)	
NO_2^-	31.5 (190) sh	39.8 (1050)		48.8 (4380)

[a] The molar extinction coefficients are given in parentheses. The ligand X is attached to the central ion by the atom first listed in each case. [b] Ctf is a charge-transfer transition from the σ- or π-bonded ligand to the partly filled shell of the central atom. [c] sh, the absorption is visible in the spectrum only by a shoulder so that its location could not be accurately determined. [d] See H.-H. Schmidtke, *J. Mol. Spectry.*, **11**, 483 (1963).

This is explained by the larger spin–orbit coupling constant (Landé parameter) for higher transition group elements, which makes spin-forbidden transitions more intense and causes increasing breakdown of the Russell–Saunders coupling scheme. We notice that the first spin-allowed transitions for some compounds are split into two bands, as was also observed for some pentaammine–cobalt(III)complexes.[3] This splitting may be attributed to the low symmetry field component C_{4v} which splits the octahedral terms by[4]

$$^1T_{1g} \longrightarrow {}^1A_2 + {}^1E$$

$$^1T_{2g} \longrightarrow {}^1B_2 + {}^1E$$

The deviation from octahedral symmetry could only be observed for the first spin-allowed band because the second one is contaminated by other heavy absorptions further in the violet. There is some doubt about the assignment for the hydroxopentaammine complexes because of the large separation (5 kK) of the band components in the first spin-allowed band. The second transition also could be due to a transition from the ground state to the $^1T_{2g}$ state or one of its low symmetry components.

Pure electron-transfer transitions are observed only in the iodopentaammine complex. Here two transitions from ligand orbitals to the empty e_g orbital state can be seen. Using Jørgensen's method[14] for calculating electron-transfer bands from optical electronegativities, a band at 35.5 kK for a transition from the π orbital and another at 50.5 kK from the σ-bonded orbital state are predicted (assuming a ligand field parameter Δ = 31 kK and the parameter of spin-pairing energy D = 3 kK). The observed splitting (3.8 kK) of the charge-transfer band is therefore probably due to spin–orbit coupling effects on the π-bonding orbitals of the iodide ligand. The corresponding band in the spectrum of the bromo compound cannot be assigned to a pure charge-transfer process. From reasons mentioned earlier we expect for these compounds an essential intermixing of the d–d transitions with other transition mechanisms. Therefore we assign the 43.5-kK transition to a joint d–d and electron-transfer transition. This conclusion arises from the larger extinction coefficient (ε 800) and from a much too high separation of the two spin-allowed transitions if both stronger bands are assigned to pure ligand field transitions. For such an assignment the electron repulsion (Racah) parameter as calculated from the spectrum would become $B = 0.74$ (with $\Delta =$ 34.6), leading to a nephelauxetic ratio[15] $\beta = B_{\text{compl}}/B_{\text{free ion}}$ larger than 1.

The limitation of the usual band assignment into d–d and electron-transfer transitions is illustrated by the spectra of some pentaammine complexes of iridium (Table II), showing the successive breakdown of this classification in a series of ligands with rising polarizabilities.

TABLE II

LIGAND FIELD AND CHARGE-TRANSFER BANDS OF $[Ir(NH_3)_5X]^{n+}$ IN kK

	X				
	H_2O	NH_3	Cl^-	Br^-	I^-
$^1T_{1g}$	38.8	39.8	35.0	33.0	29.7
$^1T_{2g}$	47	46.8 }	44.1	43.5	
CtfX→Ir		}			42.7, 46.5
β[a]	0.84	0.71	(0.95)	(1.12)	

[a] β is the nephelauxetic ratio.

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(14) C. K. Jørgensen, "Essays in Coordination Chemistry," W. Schneider, Ed., Birkhäuser Verlag, Basel, 1964, p 98.

(15) C. E. Schäffer and C. K. Jørgensen, *J. Inorg. Nucl. Chem.*, **8**, 143 (1958).

While the hexaammine and aquopentaammine complexes have two weak absorptions undoubtedly assigned to d–d transitions (with $\Delta = 41.2$ kK and $B = 0.47$ kK for $[Ir(NH_3)_6]^{3+}$ and $\Delta = 40.4$ kK and $B = 0.55$ kK for $[Ir(NH_3)_5H_2O]^{3+}$), a classification of the second band for the chloro and bromo complexes is not possible. This is explained by the increasing delocalization of the electrons in the central atom so that a distinct partition of the electronic system into a central atom and a ligand part becomes impossible. As is also seen from Table I an assignment of the linkage isomers is possible on the basis of their ultraviolet spectra. Although the bands in the spectra of both isomers are poorly resolved it nevertheless can be seen that one component which we assign to the sulfur-bonded complex absorbs at longer wavelengths. According to the spectrochemical series the positions of corresponding bands are found for the sulfur-bonded (thiocyanato) complex near those of the chloro complex, while the nitrogen-bonded (isothiocyanato) compound has its absorptions near those of the hexaammine or nitropentaammine complex.

This assignment is supported by infrared measurements. According to Turco and Pecile[16] and Tramer,[17] the position of the C–S stretching frequency serves as a criterion for the linkage properties. Their results indicate that isothiocyanate compounds absorb between 780 and 860 cm^{-1} while thiocyanato compounds absorb between 690 and about 760 cm^{-1}.

In Table III the infrared frequencies due to the SCN group of some thiocyanato complexes of Ir and Rh are listed. The C–S stretching bands are for this assignment of the linkage isomers within the regions given by Turco and Pecile[16] and Tramer.[17] They do not represent overtones of the NCS deformation mode,[18] since no bands are found at positions which correspond to one-half the energy of those bands. These bands are very well distinguished from the NH_3 rocking bands which appear at higher wavenumbers (850–870 cm^{-1}). Also the SCN bending vibrations support these assignments. According to Sabatini and Bertini[19] the N-bonded group absorbs at frequencies near 475 cm^{-1}, while the S-bonded group has several bands at lower frequencies. However, the C–N stretching frequency does not fit into the infrared data which are available at present. In general this band is found for S-bonded complexes at higher wavenumbers than for N-bonded compounds.[16–19] High frequencies such as 2140 and 2145 cm^{-1}, which are observed in our N-bonded pentaammines, were only found for complexes with SCN bridges.[20] It appears that a binuclear Ir complex with two SCN bridges would have an analysis similar to the nonbridged species. The assumption that the N-bonded isomer is indeed a bridged complex can be ruled out by several arguments. A substitution of one ammonia in $[Ir(NH_3)_5(SCN)]^{2+}$ by a $(NCS)Ir(NH_3)_4$ group would shift the ultraviolet absorption bands further to the visible region. This arises from the fact that, even though the ligand field strength of isothiocyanate is enhanced[21] when acting as a bridged ligand, it never surpasses ammonia in the spectrochemical series.

TABLE III

INFRARED FREQUENCIES (CM^{-1}) OF THE SCN GROUP OF COMPLEX CHLORIDES OR PERCHLORATES IN KBr DISKS[a]

Complex	SCN bending[b]	C–S stretch	C–N stretch
$[Ir(NH_3)_5(NCS)]^{2+}$	485 w, b	825 s	2140 s, b
$[Ir(NH_3)_5(SCN)]^{2+}$	420, 440, 475 m	700 m	2110 s, sp
$[Rh(NH_3)_5(NCS)]^{2+}$	485 w	815 s	2145 s, b
$[Rh(NH_3)_5(SCN)]^{2+}$	430 w, 460 m	730 w, b	2115 s, sp
$K_3[Rh(SCN)_6]$	420, 440, 450, 465 m, sp	710 m, sp	2095 s, b

[a] See H.-H. Schmidtke, *J. Am. Chem. Soc.*, **87,** 2522 (1965). [b] In this region also metal–ligand stretching frequencies are expected, so that the assignment of these bands is uncertain. Abbreviations: s, strong; m, medium; w, weak; b, broad; sp, sharp.

Conductance measurements performed in aqueous solutions are presented in Table IV.

TABLE IV

CONDUCTANCE DATA (CM^2 OHM^{-1} MOLE^{-1}) FOR Ir COMPLEXES AT 25° IN 2×10^{-3} *M* AQUEOUS SOLUTIONS

Compound	Conductivity	Compound	Conductivity
$[Ir(NH_3)_5Cl]Cl_2$	253	$[Ir(NH_3)_5(NCS)](ClO_4)_2$	217
$[Ir(NH_3)_5Cl](ClO_4)_2$	236	$[Ir(NH_3)_5(SCN)](ClO_4)_2$	219

The molar conductivities of the two isomers are essentially identical and similar to those of the analogous chloro complex. From these values we conclude that at least in aqueous solution the presence of a binuclear complex is improbable. If such a complex existed in the crystalline form, the compound would have to react in a quite complicated way to change from a binuclear compound having two bridges to the mononuclear species. This is also quite improbable for an Ir(III) complex compound, whose reactions are generally kinetically controlled. The equivalent conductances of these compounds indicate an almost complete ionic dissociation. It is therefore possible to get some information from molecular weight determinations by the vapor pressure method. In Table V the results are listed which were obtained for the two linkage isomers. They also cannot be interpreted by the presence of a binuclear species, because evidently the true molecular weight has to lie between the two limiting values for the non- and completely dissociated molecule. This is, however, in our case only fulfilled if mononuclear species are assumed for both isomers. The dissociation constants for these salts at the given concentrations are calculated from these results for the N-bonded compound as $\alpha = 0.91$, and for the S-bonded as $\alpha = 0.89$.

Further evidence regarding bond properties could

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(16) A. Turco and C. Pecile, *Nature*, **191,** 66 (1961).

(17) A. Tramer, *J. Chim. Phys.*, **59,** 232 (1962).

(18) A. Sabatini and I. Bertini, *Inorg. Chem.*, **4,** 1665 (1965).

(19) A. Sabatini and I. Bertini, *ibid.*, **4,** 959 (1965).

(20) P. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, 1912 (1960).

(21) C. E. Schäffer, Abstracts of International Conference on Coordination Chemistry, London, 1959, p 153; Special Publication No. 13, The Chemical Society, London.

TABLE V

MOLECULAR WEIGHTS DETERMINED IN AQUEOUS SOLUTION

		Mol wt		
Compound	Concn, g/l.	Apparent[a] ($\alpha = 0$)	mono[b] ($\alpha = 1$)	Bi[c] ($\alpha = 1$)
$[Ir(NH_3)_5(NCS)](ClO_4)_2$	3.66	190	570	950
$[Ir(NH_3)_5(SCN)](ClO_4)_2$	4.08	192	576	960
Calcd[d] mol wt			534.4	1034.7

[a] Apparent molecular weight if no dissociation is assumed (molarity = 1). [b] For a complete dissociation of the mononuclear complex (three ions). [c] For a complete dissociation of the binuclear form (five ions). [d] Molecular weight calculated from the formulas of the mono- and binuclear $[Ir_2(NH_3)_8(NCS)_2](ClO_4)_4$ species.

be obtained by ^{14}N nuclear magnetic resonance spectroscopy;[22] however, the compounds prove to be insufficiently soluble in any common solvent for an application of this technique.

Our pair of isomers represents another example of an inorganic thiocyanate linkage isomerism, for which both components of one and the same compound are known. While for the planar Pd complexes of Burmeister and Basolo[23] the S-bonded component is rather unstable, rearranging even at room temperature to the N-bonded isomer, both of our iridium pentaammines prove to be stable for hours at 40°. At higher temperatures decomposition is observed so that kinetic runs could not be carried out. However, it may be concluded from the yields when preparing the two isomers and from the corresponding results we have gained from the rhodium compounds[24] that the N-bonded isomer is the more stable component. A prolonged boiling of the reaction mixture when preparing the thiocyanate compounds decreases the yield of the S-bonded isomer in favor of the N-bonded component. From this we conclude that the first step of the reaction is the formation of the thiocyanate isomer, followed by a rearrangement to the more stable linkage isomer. In general the S-bonded Ir(III) isomer is more easily available than the corresponding Rh(III) isomer, which can be understood from the increasing b character in the series Co(III), Rh(III), Ir(III) in the Chatt–Ahrland–Davies classification.[25,26]

Similar infrared evidence is gained for the nitro- and nitritopentaammine complexes. The spectra agree essentially with those given in the literature.[9] Since the nitritopentaammine–iridium complex is more stable in comparison with the rhodium compound, the ultraviolet spectrum was much easier to record than it was for the rhodium salt.

The infrared spectrum also serves to determine the bonding properties in the coordination sphere in the case of the azido and nitrato complexes.

The ultraviolet spectrum distinguishes, *e.g.*, between $[Ir(NH_3)_5(NO_3)](NO_3)_2$ and $[Ir(NH_3)_5(H_2O)](NO_3)_3$ only on the basis of higher absorption coefficients of the nitrato or azido complex in solution (*cf.* Table I). The positions of the d–d bands are for all compounds approximately the same, since the groups NO_3^- and N_3^- are close neighbors of H_2O in the spectrochemical series. The infrared spectrum, however, is able to distinguish between bonded and free NO_3^- or N_3^- groups, respectively. The doubly degenerate stretch (E′) of free NO_3^- at 1350–1400 cm^{-1} is split for the monodentate nitrato group.[27,28] Our experimentally found frequencies at 1280 and 1490 cm^{-1} are well within the region given for the split components.[27] For $[Ir(NH_3)N_3](N_3)_2$ we find an infrared band at 2030 cm^{-1} for the free anion and a series of others near 2060 cm^{-1} which are assigned to the coordinated group.[29] These conclusions drawn from the infrared spectra, of course, only hold for the crystalline state. Spectroscopical investigations in the ultraviolet region and the possibility of recrystallization of the products from aqueous solution guarantees that no aquotization in the solution takes place within a reasonable time.

The ultraviolet spectrum of the newly prepared formiatopentaammine complex is nearly identical with that of the corresponding acetato compound.[5] This finding is expected if two ligands have identical atoms attached to the central ion, provided that the electronic structure of this atom is not changed very much by other atomic groups in the ligand (*e.g.*, by internal π-bonding effects or by other electron-driving or -withdrawing groups).

Acknowledgments.—The author is indebted to Dr. C. K. Jørgensen for many helpful discussions and to Mr. D. Garthoff for his experimental assistance.

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