The Electronic Spectra of Some Noble Metal Azide Complexes

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Abstract: Some 6:1 azide complexes of Ru(III), Rh(III), Ir(III), and Pt(IV) and 4:1 complexes of Pd(II), Pt(II), and Au(III) have been prepared with large organic cations which do not absorb in the near-ultraviolet region. Ligand-field and charge-transfer bands in the absorption and reflectance spectra have been assigned to the electronic energy levels on the basis of usual theoretical procedures. The interpretation of the spectra allows a determination of the spectrochemical properties of the azide ligand to be made. Accordingly, azide is classified in the spectrochemical series between S-bonded SCN$^-$ and diethyldithiophosphate and in the nephelauxetic series between bromide and diethyldithiophosphate. For the optical electronegativity parameter the value $x(N_3^-) = 2.8$ has been determined. The infrared spectrum and conductance measurements serve to characterize the new compounds.

Recently the chemistry of azido complexes has become a field of rising interest. The identification of numerous azido compounds of transition group ions in aqueous or nonaqueous solution has been reported.[1-3] The stepwise formation of azido complexes strongly depends on the nature of the applied solvent and the azide concentration used. It was also possible to precipitate a number of 1:4 and 1:6 complexes by the addition of large organic cations.[4-8] These materials proved to be remarkably stable compared with the simple heavy metal azides. The scope of the work performed until now was confined to the preparation and identification of azide compounds using primarily infrared or Raman spectra for their characterization.

Little information, however, is available on the electronic spectra of azide complexes in the visible and ultraviolet regions. Except for the investigation of the azide complexes in solution,[1-3] which cannot give reliable results on the spectrochemical properties of the azide ligand, only the ligand-field spectrum of tetrahedral $[Co(N_3)_4]^{2-}$ has been measured.[9] It is the object of this work to record the visible and near-ultraviolet absorption and reflection spectra of some of the recently prepared precious metal azide compounds and to extend this group of compounds by preparing and characterizing new azide complexes of the platinum group. The assignment of the measured bands together with the usual theoretical procedures developed for coordination compounds allow the position of the azide ligand in the spectrochemical and nephelauxetic series to be found. The charge-transfer bands determine the value of the optical electronegativity for the azide ion. These results then supply some evidence of theoretical interest concerning bond properties and the electron distribution in the bonding region.

Experimental Section

(a) Materials. **Tetra-*n*-butylammonium Hexaazidoruthenium(III).** To a warm (35–40°) solution of NaN_3 (13.3 g) in a 2:1 mixture of water and ethanol (60 ml), crystals of $K_2[Ru^{IV}Cl_6]$ (0.2 g) are added. The excess of azide ion in this solution amounts to 400:1 compared to ruthenium. The reaction starts immediately with the formation of nitrogen due to the reduction of Ru(IV) with N_3^-. Such a reduction of Ru(IV) complexes was also observed with thiocyanate.[10] The color changes within 15 min from orange-yellow to red. After filtration, an aqueous solution of tetrabutylammonium bromide (4 g) is added to the reaction mixture. After evaporating almost all of the alcohol, the resulting red crystals are collected in a glass filter frit and washed with water. Brick-red crystals which are fairly stable in the absence of light are obtained in good yield.

Anal. Calcd for $C_{48}H_{108}N_{21}Ru$: C, 53.40; H, 10.04; N, 27.21; Ru, 9.35. Found: C, 53.29; H, 9.86; N, 27.00; Ru, 9.10.

The product is soluble in C_2H_5OH, CH_2Cl_2, acetone, and dimethylformamide. However, the orange-red solutions quickly change their colors to bluish green and after some 30 min to pale red, even when an excess of azide ion is present. In the absorption spectra a band near 600 mμ is formed which then disappears again. The band at 450 mμ decreases rapidly.

Tetra-*n*-butylammonium Hexaazidorhodium(III). The chloride, $Na_3[RhCl_6] \cdot 12H_2O$ (0.2 g), is dissolved in water (25 ml) and a solution of NaN_3 (1.51 g) in water (50 ml) is added (azide excess 70:1). The mixture is gently heated (40°) for 1 hr, and the product is precipitated by the addition of an excess of tetrabutylammonium bromide (*ca.* 1 g). The tiny pale red crystals are collected on a filter and washed with alcohol. The product is dissolved in CH_2Cl_2 and precipitated by the addition of ether.

Anal. Calcd for $C_{48}H_{108}N_{21}Rh$: C, 53.25; H, 10.07; N, 27.20; Rh, 9.50. Found: C, 52.91; H, 10.2; N, 27.20; Rh, 9.68.

The product is soluble in C_2H_5OH, CH_2Cl_2, acetone, and dimethylformamide, and the solutions do not change color within 1 day. (The intensities of the absorption bands are only slightly decreased within 15 min.) The tetraphenylarsonium salt which is only slightly soluble in alcohol and acetone is precipitated in a similar fashion.

Tetra-*n*-butylammonium Hexaazidoiridium(III). In a 2:1 mixture of water and ethanol (40 ml), NaN_3 (7.48 g) and $Na_3[IrCl_6] \cdot 12H_2O$ (0.2 g) are dissolved. The excess of azide is 400:1 compared to the iridium complex. The yellow-green solution is gently heated (40°) for about 1 hr under mechanical stirring. An excess of $(n\text{-}C_4H_9)_4NBr$ (*ca.* 1 g) dissolved in water is added in such a way that no precipitate is formed, and the solution is evaporated until crystals of NaN_3 are formed. These are dissolved again by adding some drops of water, and the reaction mixture is then left for some days. The color turns slowly to brown-red under the formation of shiny transparent crystals of the same color. After 1 week the product is collected on a filter, washed with water, and dried over silica gel. When powdered, the crystals have a greenish yellow color.

Anal. Calcd for $C_{48}H_{108}N_{21}Ir$: C, 49.15; H, 9.30; N, 25.15; Ir, 16.4. Found: C, 49.26; H, 9.49; N, 25.19; Ir, 16.8.

The crystals are soluble in C_2H_5OH, CH_2Cl_2, acetone, and di-

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(1) F. G. Sherif and W. M. Oraby, *J. Inorg. Nucl. Chem.*, **17**, 152 (1961).

(2) F. G. Sherif and K. F. Michail, *ibid.*, **25**, 999 (1963), and further references therein.

(3) V. Gutmann and O. Leitmann, *Monatsh. Chem.*, **97**, 926 (1966).

(4) F. Kröhnke and B. Sander, *Z. Anorg. Allgem. Chem.*, **334**, 66 (1964).

(5) W. Beck, K. Feldl, and E. Schuierer, *Angew. Chem.*, **77**, 458 (1965).

(6) W. Beck, E. Schuierer, and K. Feldl, *ibid.*, **78**, 267 (1966).

(7) W. Beck, E. Schuierer, P. Pöllmann, and W. P. Fehlhammer, *Z. Naturforsch.*, **21b**, 811 (1966).

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(9) F. A. Cotton and M. Goodgame, *J. Am. Chem. Soc.*, **83**, 1777 (1961).

(10) H.-H. Schmidtke, *J. Inorg. Nucl. Chem.*, **28**, 1735 (1966).

methylformamide. The color of the solution changes quickly to an intense blue, corresponding to a band at 630 mμ in the visible spectrum.

n-Cetyltrimethylammonium Tetraazidoplatinum(II). The chloride, $K_2[PtCl_4]$ (0.1 g), and NaN_3 (1.56 g) are dissolved[6] in 10 ml of water (excess azide 100:1) and heated (40°) for 10 min. An excess of n-cetyltrimethylammonium bromide in aqueous ethanol is added to the solution which produces pale yellow, silky shining crystals in almost 100% yield after a slow addition of water. The product is recrystallized from alcohol. The crystals decompose already after some hours.

Anal. Calcd for $C_{38}H_{84}N_{14}Pt$: C, 48.98; H, 9.08; N, 21.02; Pt, 20.93. Found: C, 49.23; H, 9.11; N, 21.15; Pt, 20.55.

The product is soluble in the solvents mentioned earlier and decomposes also in a relatively short time. The tetraphenylarsonium salt is prepared in the same way.[6]

n-Cetyltrimethylammonium Hexaazidoplatinum(IV). The acid, $H_2[PtCl_6]$ (0.1 g), and NaN_3 (2.65 g) are dissolved in 20 ml of H_2O and left for 1 hr at 40–50°. The precipitation of the product follows the same procedure as described for the Pt(II) complex. The stable orange crystals are also soluble in the above-mentioned organic solvents.

Anal. Calcd for $C_{38}H_{84}N_{20}Pt$: C, 44.9; H, 8.33; N, 27.6; Pt, 19.2. Found: C, 45.4; H, 8.51; N, 27.92; Pt, 19.2.

The tetraphenylarsonium[6] and tetraethylammonium salts are prepared in the same way.

Tetraethylammonium Tetraazidogold(III). The preparative procedure follows the course as described for the Pt(II) compound. A 40:1 excess of azide ion is used. The orange crystals decompose after a few days. The solutions turn to colorless within 24 hr. The tetraphenylarsonium salt is prepared in the same way.[6]

Anal. Calcd for $C_{24}H_{20}N_{12}AsAu$: C, 38.56; H, 2.69; N, 22.42; As, 10.01; Au, 26.32. Found: C, 38.0; H, 3.02; N, 22.63; As, 10.26; Au, 26.00.

The preparation of the Pd(II) complex follows the description given for the Pt(II) complex. The precipitation with cetyltrimethylammonium bromide yields a mononuclear compound in contrast to Beck's[6] bridged tetraphenylarsonium complex. The solutions are remarkably stable and the solid does not decompose during several days.

Anal. Calcd for $C_{38}H_{84}N_{14}Pd$: C, 54.10; H, 10.03; N, 23.24; Pd, 12.62. Found: C, 54.36; H, 10.20; N, 23.15; Pd, 12.74.

Efforts to prepare a 1:6 azide complex of Os(III) or Os(IV) following similar procedures led to an orange-yellow product. The tetraphenylarsonium salt is highly explosive when heated, so that a complete analysis could not be made. Analysis of the product gave 23.9% N and 10.3–10.6% As. The spectrum in CH_2Cl_2 shows an absorption at 427 mμ with an extinction coefficient of $\epsilon \sim 1500$. This product was not further identified.

(b) **Electronic Spectra.** The absorption spectra in the visible and ultraviolet regions were recorded at room temperature or at −10° using a Cary spectrophotometer, Model 14. The solutions had molar concentrations between 10^{-3} and 10^{-5} in CH_2Cl_2 or H_2O. The reflectance spectra were taken on a manual instrument, Beckman DU Model G 2400.

(c) **Infrared Spectra.** The infrared spectra of the solids in KBr or KI pellets and in acetone or chloroform solution were measured on a Perkin-Elmer grating infrared spectrophotometer, Model 521.

(d) **Conductance Measurements.** Conductivities were determined on a conductivity bridge, Philips Model GH 4249, at a frequency of 1000 cps.

(e) **Analyses.** The analyses were carried out at the Laboratoire Microchimique, Dr. Eder, Ecole de Chimie, University of Geneva.

Spectra

In Table I are listed the positions, the molar extinction coefficients, and the assignments of the absorption bands in the visible and ultraviolet regions of some azide complexes in methylene chloride. The assignments are made on the basis of theoretical results obtained from crystal field or molecular orbital theory[11] and by comparison with the spectra of other noble metal complexes of identical symmetry.[12] Since we expect the structure of some of the investigated complexes to be square-planar (Pd(II), Pt(II), Au(III)) and octahedral or nearly octahedral (Ru(III), Rh(III), Ir(III), Pt(IV)), the multiplets and the terms in the orbital energy scheme are classified according to these symmetries. The spectra of the less stable compounds were taken at temperatures below 0° within 2 min of recording time. Under these conditions the absorption spectra do not differ from the diffuse reflectance spectra, so that decomposition of the complex is considered to be small during the time necessary to record the spectra.

Table I. Maxima (in kilokaisers: 1 kK = 1000 cm^{-1}), Extinction Coefficients, and Assignments of Absorption Bands for Some Azide Complexes in CH_2Cl_2 at −10 or 20°

Complex	Type of transition mechanism[a]	Assignment	Band max	Extinction coeff
$(n\text{-}Bu_4N)_3[Ru(N_3)_6]$	lf	$^2T_{2g} \rightarrow {}^2\Gamma, {}^4\Gamma$	(16.5)[b]	195
	ctf	$t_{1u}(\pi) \rightarrow t_{2g}$	22.3	2,540
	ctf	$t_{1u}(\pi) \rightarrow e_g$ (or $t_{2u}(\pi) \rightarrow t_{2g}$)	35.7	20,300
	ctf		(39) (?)	18,600
$(n\text{-}Bu_4N)_3[Rh(N_3)_6]$	lf	$^1A_{1g} \rightarrow {}^1T_{1g}$	20.5	893
	lf	$^1A_{1g} \rightarrow {}^1T_{2g}$	24.5	1,145
	ctf	$t_{1u}(\pi) \rightarrow e_g$	32.6	28,700
	ctf	$t_{2u}(\pi) \rightarrow e_g$	42.0	15,450
$(n\text{-}Bu_4N)_3[Ir(N_3)_6]$	lf	$^1A_{1g} \rightarrow {}^3T_{1g}$	(15.4)	57
	lf	$^1A_{1g} \rightarrow {}^3T_{2g}$	19.4	232
	lf	$^1A_{1g} \rightarrow {}^1T_{1g}$	25.0	935
	lf	$^1A_{1g} \rightarrow {}^1T_{2g}$	27.6	1,050
	ctf	$t_{1u}(\pi) \rightarrow e_g$	38.3	19,900
$(Et_4N)_2[Pt(N_3)_6]$	lf	$^1A_{1g} \rightarrow {}^3T_{1g}, {}^3T_{2g}$	(20.4)	248
	ctf	$t_{1u}(\pi) \rightarrow e_g$	32.6	37,000
$[(n\text{-cetyl})Me_3N]_2\text{-}[Pd(N_3)_4]$	lf	$^1A_{1g} \rightarrow {}^1A_{2g}$	(20)	458
	lf	$^1A_{1g} \rightarrow {}^1E_g$	(24.2)	1,730
	ctf	$b_{2u}(\pi) \rightarrow b_{1g}$	30.8	15,350
	ctf	$e_u(\sigma,\pi) \rightarrow b_{1g}$	41.9	17,000
$[(n\text{-cetyl})Me_3N]_2\text{-}[Pt(N_3)_4]$	lf	$^1A_{1g} \rightarrow {}^3A_{2g}$	20.4	92
	lf	$^1A_{1g} \rightarrow {}^3E_g$	(22.7)	138
	lf	$^1A_{1g} \rightarrow {}^1A_{2g}$	26.7	755
	lf	$^1A_{1g} \rightarrow {}^1E_g$	(30.3)	820
	ctf	$b_{2u}(\pi) \rightarrow b_{1g}$	40.5	19,800
$(Et_4N)[Au(N_3)_4]$	lf	$^1A_{1g} \rightarrow {}^1A_{2g}$ (?)	(20.6)	258
	ctf	$b_{2u}(\pi) \rightarrow b_{1g}$	30.0	31,300
	ctf	$e_u(\sigma, \pi) \rightarrow b_{1g}$	45.2[c]	15,530

[a] lf is a ligand field and ctf a charge-transfer transition. [b] Wave numbers in parentheses indicate only inflections; the actual positions of these transitions are uncertain. [c] In aqueous solution.

In Table II the diffuse reflectance spectra of those complex azides which prove to be very unstable in solution are compiled. The optical density units listed in this table are arbitrary. The materials used for recording the reflectance spectra were diluted with $BaSO_4$ and thoroughly ground to obtain maximal reflection conditions. In the reference sample also $BaSO_4$ of analytical grade was used. In Figures 1–3 some absorption and reflectance spectra of particular significance are presented in full, showing the domination by the charge-transfer bands in these complexes covering in some cases the ligand-field bands which in general have smaller intensities.

For characterization, the infrared spectra of the compounds in the solid state or in solution are presented in Table III. The absorption frequencies are

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(11) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, 1962, and other literature therein.

(12) C. K. Jørgensen, *Advan. Chem. Phys.*, **5**, 33 (1963).

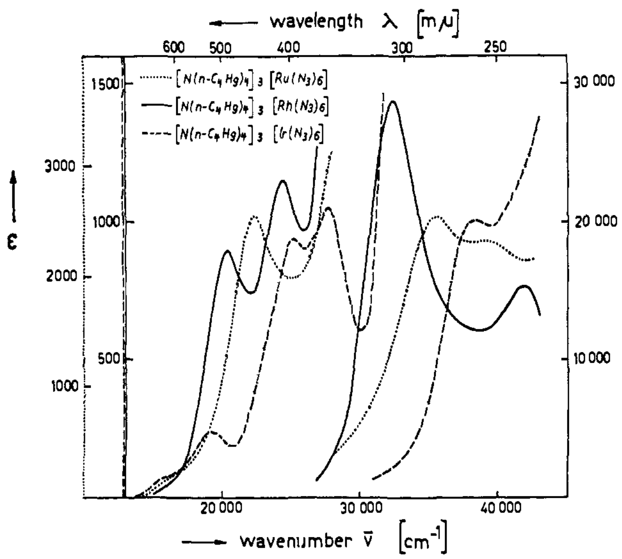

Figure 1. Absorption spectra of 6:1 azide complexes in CH_2Cl_2 at −10°.

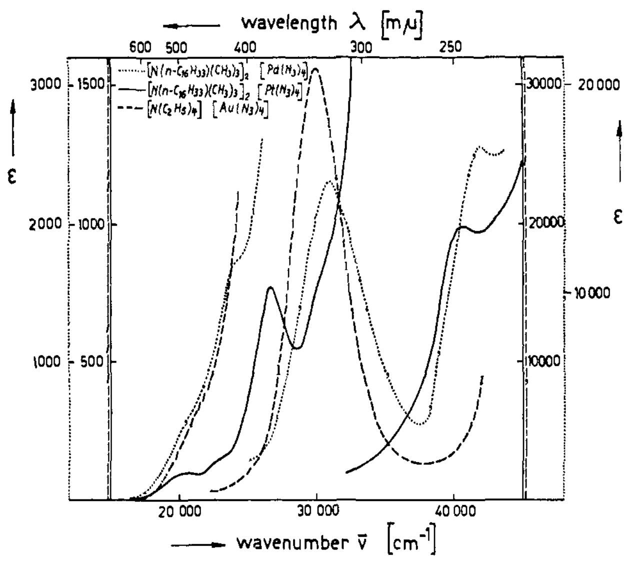

Figure 2. Absorption spectra of 4:1 azide complexes in CH_2Cl_2 at 20°.

found in the expected regions according to the notation and assignment given in the literature.[8,13]

Table II. Maxima (in kilokaisers) and Optical Densities in Arbitrary Units of Diffuse Reflectance Spectra

Complex	Type of transition mechanism	Band max, kK	Opt density
$(n\text{-}Bu_4N)_3[Ru(N_3)_6]$	lf	(18.6)	0.355
	ctf	22.0	0.565
	ctf	35.7	0.55
$(n\text{-}Bu_4N)_3[Ir(N_3)_6]$	lf	16.0	0.3
	lf	19.4	0.4
	lf	24.3	0.55
	lf	27.2	0.54
		(33)	0.6
	ctf	37.6	0.84
$(Me_4N)_2Na[Fe(N_3)_6]$[a]	ctf[b]	20.7	0.615
	ctf	28.2	0.51
	ctf	39.0	0.42

[a] Prepared according to ref 4. [b] The ctf bands are assigned to t_{1u}, t_{2u}, and $t_{1u} \rightarrow t_{2g}$ orbital transitions as in the corresponding cyanide compound; see P. J. Stephens, *Inorg. Chem.*, **4**, 1690 (1965); P. N. Schatz, A. J. McCaffery, W. Suetaka, G. N. Hennig, and A. B. Ritchie, *J. Chem. Phys.*, **45**, 722 (1966).

Conductance Measurements

Molar conductivities serve as a means of determining the ionization of the salts in solution. In Table IV the conductivities as measured in dimethylformamide are listed. The values fall in those regions which are expected for salts dissociated into two, three, or four ions, respectively. The molar conductivity of the osmium compound, however, does not agree with any of the corresponding regions, indicating that the formula given in the table cannot be the correct one.

Discussion

Both ligand-field and charge-transfer bands were observed and readily classified, although strong covalent bonding between the metal and azide could have led to a breakdown of this classification.[14] The ligand-field bands are assigned to molecular electronic states of octahedral or square-planar symmetry. In the octahedral case low-spin d^5 (Ru(III)) and d^6 (Rh(III), Ir(III), Pt(IV)) central atoms have $^2T_{2g}$ ($t_{2g}{}^5$) and $^1A_{1g}$ ($t_{2g}{}^6$) ground states, respectively. The excited configuration $t_{2g}{}^4e_g$ gives rise to $^4T_{1g}$, $^4T_{2g}$, $^2A_{2g}$, and additional states which are in general strongly mixed with other subshell configurations. An assignment of the 16.5-kK transition in the ruthenium complex is therefore not possible. For the $t_{2g}{}^5e_g$ excited configuration two triplet ($^3T_{1g}$, $^3T_{2g}$) and two singlet ($^1T_{1g}$, $^1T_{2g}$) states are expected, and these are actually observed in some of the d^6 azide complexes. The 20.4-kK band of the Pt(IV) complex is assigned to the spin-forbidden transitions on the basis of the spectrochemical series for central metals. In this series isoelectronic central ions with higher ionic charges have larger crystal-field

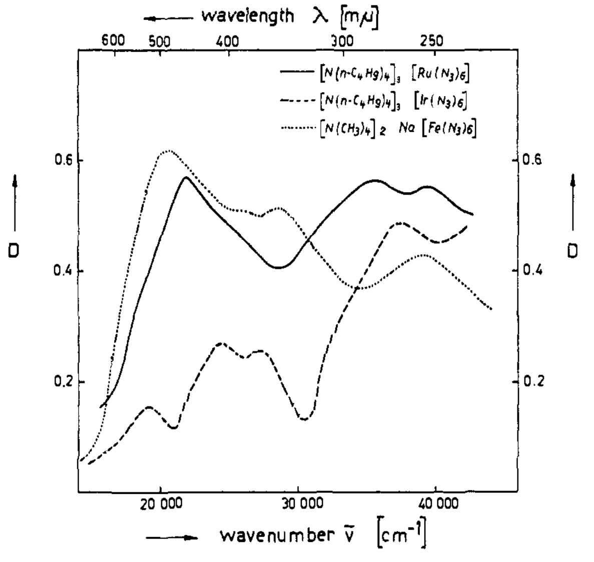

Figure 3. Diffuse reflectance spectra of azide complex diluted in $BaSO_4$. Optical density units are arbitrary.

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(13) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963.

(14) H.-H. Schmidtke, *Inorg. Chem.*, **5**, 1682 (1966).

Table III. Maxima (in cm^{-1}) of Absorptions in the Infrared Region[a]

Compound	Overtone $\nu_1 + \nu_3$	ν_3 (asym str)	ν_1 (sym str)	ν_2 (def)	M–N_3 str	Medium or solvent
$(Me_4N)_2Na[Fe(N_3)_6]$	3317 w	2057 s; 2017 s, sp	1280 m	633 s; 604 m	~325 s	KI
$(n\text{-}Bu_4N)_3[Ru(N_3)_6]$	3320 w	2083 sh; 2030 sh; 2018 s	1285 s	670 m; 636 w; 591 w	364 s	KI
$(Ph_4As)_3[Rh(N_3)_6]$	3278 w	2042 sh; 2002 s	1288 s	582 w	373 s; 365 s	KBr
$(n\text{-}Bu_4N)_3[Rh(N_3)_6]$	3305 w	2045 s; 2016 m	1291 s; 1262 s	681 m; 592 m; 530 m	380 s	KBr
		2060 sh; 2008 s			380 s	$CHCl_3$
$(n\text{-}Bu_4N)_3[Ir(N_3)_6]$	3312 w	2062 s; 2027 w	1290 s	680 m; 581 m; 530 m	372 m; 352 m	KI
$(Et_4N)_2[Pt(N_3)_6]$	3277 m	2020 s	1268 s	693 m; 580 m	402 s	KBr
$[(cetyl)Me_3N]_2[Pt(N_3)_6]$	3277 m	2030 s; 2014 s	1270 m; 1260 s	693 m; 580 m	410 sh; 400 s	KBr
$[(cetyl)Me_3N]_2[Pd(N_3)_4]$	3270 w	2030 m, sp; 2010 s	1278 s	670 w; 582 w	408 w; 385 m	KBr
		2062 m; 2010 s				Acetone
$(Ph_4As)_2[Pt(N_3)_4]$	3280 w	2060 m; 2020 s	1277 s	575 w	387 m	KBr
		2060 sh; 2023 s				Acetone
$[(cetyl)Me_3N]_2[Pt(N_3)_4]$	3283 w	2030 sh; 2020 s	1288 m, sp; 1278 s	686 w; 578 w	408 w; 394 m, sp	KBr
$(Ph_4As)[Au(N_3)_4]$	3280 m	2023 s	1261 s	693 m (?); 579 m	433 s; 426 s	KBr
		2031 s				Acetone
$(Et_4N)[Au(N_3)_4]$	3277 m	2012 s	1262 s	696 m; 573 m	437 s	KBr

[a] Abbreviations: s, strong; m, medium; w, weak; sp, sharp; sh, shoulder.

Table IV. Conductivities in 2 × 10^{-3} *M* Dimethylformamide Solutions at 24°

Complex	c^a	$\Lambda^b \times 10^4$	$\Lambda_m{}^c$
$(Ph_4As)[Au(N_3)_4]$	1.497	1.242	62.1
$(Ph_4As)_2[Pt(N_3)_4]$	2.110	2.484	124.2
$[(cetyl)Me_3N]_2[Pt(N_3)_4]$	1.865	2.382	119.1
$[(cetyl)Me_3N]_2[Pd(N_3)_4]$	1.687	2.443	122.5
$[(cetyl)Me_3N]_2[Pt(N_3)_6]$	2.032	2.463	123.2
$(Ph_4As)_3[Rh(N_3)_6]$	3.010	3.088	154.4
$(Bu_4N)_3[Rh(N_3)_6]$	2.165	2.744	137.2
$(Bu_4N)_3[Ir(N_3)_6]$	2.344	2.834	141.7
$(Bu_4N)_3[Ru(N_3)_6]$	2.162	2.813	140.7
$(Ph_4As)_3[Os(N_3)_6]$ (?)	3.185	1.907	95.4[d]

[a] Concentration in g/l. [b] Conductivity in ohm^{-1} cm^2. [c] Molar conductivity in ohm^{-1} cm^2 mole^{-1}. [d] As calculated with the formula indicated.

parameters. Transitions in Pt(IV) compounds are consequently expected at higher wave numbers compared to the corresponding bands of Ir(III) compounds. The assignment of ligand-field transitions in square-planar compounds is made by comparison with that of the Pd(II) and Pt(II) chloro complexes. For the d^8 square-planar case, singlet and triplet ligand-field states of A_{2g}, B_{1g}, and E_g are expected. Following the Chatt–Gamlen–Orgel[15] band assignment, which was recently adopted[16] to be one of the most likely for the $[PtCl_4]^{2-}$ complex, the first four ligand-field transitions are due to ${}^1A_{1g} \rightarrow {}^3A_{2g}$, ${}^3E_g$, ${}^1A_{2g}$, ${}^1E_g$. The assignment of the first ligand-field band for the gold complex is doubtful. According to calculations of Basch and Gray,[17] the Δ_1 crystal-field parameter denoting the orbital energy difference of the b_{1g} and b_{2g} antibonding orbital state should be larger for Pt(II) than for Au(III). This parameter therefore does not follow the trend observed in octahedral complexes where larger crystal-field parameters result from higher ionic charges. When adopting Basch and Gray's suggestion, the 20.6-kK band measured in the azide complex should be assigned to the first spin-allowed transition. In this case the position of the first charge-transfer band, however, cannot be explained by Jørgensen's parameter set of optical electronegativities as will be discussed later.

The assignment of the bands in the octahedral complexes of Rh(III) and Ir(III) leads to a definite location of the azide ligand in the spectrochemical and the nephelauxetic series. Using the two spin-allowed transitions and the formulas of the semiempirical theory as they were used earlier,[18] the crystal-field parameters Δ and Racah parameters *B* are calculated as given in Table V. These results place the azide ligand in the spectrochemical series[11] between sulfur-bonded thiocyanate on the long-wavelength side and diethyldithiophosphate and fluoride on the side of higher Δ parameters. This classification agrees well with that of Shimura and Tsuchida, who located azide somewhere between chloride[19] and fluoride in this series. The azide ligand has therefore a weaker ligand-field strength as proposed by Staples and Tobe,[20] who put azide on the short-wavelength side of fluoride. The classification of a ligand in the nephelauxetic series is determined by its nephelauxetic quotient.[21] With the values given in Table V, azide is located between bromide and diethyldithiophosphate.[11] The parameter values indicate relatively low crystal fields and a very high nephelauxetic effect for the azide ligand. We conclude therefore that the metal–ligand bond is largely covalent with

Table V. Spectrochemical Parameters

Compound	Δ^a	B^b	β^c
$[Rh(N_3)_6]^{3-}$	21.3	0.27	0.37
$[Ir(N_3)_6]^{3-}$	25.6	0.17	0.26

[a] Crystal-field parameter in kK. [b] Racah parameter in kK. [c] Nephelauxetic quotient calculated with the *B* parameters for the free ions $B_{Rh(III)} = 0.72$ and $B_{Ir(III)} = 0.66$.

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(15) J. Chatt, G. A. Gamlen, and L. E. Orgel, *J. Chem. Soc.*, 486 (1958).

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a relatively strong π-antibonding character which is not influenced very much by the empty π^* systems of the ligands.[22,23]

We now turn to the charge-transfer bands. The extinction coefficients are usually so large that in some cases the bands unfortunately cover those of the ligand field, the position of which would be of interest. The p_π functional system of the ligands gives rise to t_{1g}, t_{2g}, t_{1u}, and t_{2u} molecular orbitals for octahedral symmetry. Together with the t_{1u} state of the p_σ system, three parity-allowed orbital transitions from the ligand to the "gerade" d orbital states are possible. For Ru(III), where there is an electron hole in the t_{2g} subshell, the following charge-transfer transitions are predicted: $2t_{1u}, t_{2u} \rightarrow t_{2g}$, or e_g. Magneto optical rotatory dispersion (Faraday effect) measurements indicate[24,25] that in $[Fe(CN)_6]^{3-}$, which also represents an octahedral low-spin d^5 complex, the "ungerade" orbital states are in the following order: $t_{1u} < t_{2u} < t_{1u}$. This order can be explained theoretically[26] simply by applying topological properties to the octahedral nuclear framework. When adopting these results for the Ru(III) azide complex, we assign the first strong absorption at 22.3 kK to the $t_{1u} \rightarrow t_{2g}$ orbital transition, which corresponds to a ${}^2T_{2g} \rightarrow {}^2T_{1u}$ electron transition in the molecule. The extinction coefficient compares with those for equivalent transitions found[27] in the chloro and bromo complexes. The other band with a much higher oscillator strength is likely to be a transition from t_{1u} to the other d orbital component e_g. The reflectance spectrum of $[Fe(N_3)_6]^{3-}$ shows, as in the case of the cyanide complex, three bands (see Table II) which accordingly are assigned to the three parity-allowed orbital charge-transfer transitions. The band assignments for the other octahedral azides is then straightforward. Low-spin d^6 complexes have charge-transfer bands further in the ultraviolet because the electron is transferred to the higher e_g orbital state of the central ion. The assignment of the bands in square-planar complexes is made on the basis of topological arguments.[28]

The identification of the first parity-allowed charge-transfer transition enables the optical electronegativity coefficient defined by Jørgensen[29] to be determined. Using his method for describing charge-transfer bands in inorganic chromophores and the values of optical electronegativities given for Ru(III), Rh(III), Ir(III), and Pt(IV), a value of 2.8 for x_{opt} for the azide ligand is obtained. This value also agrees with the position of charge-transfer bands of square-planar azide complexes to within the usual limit of accuracy. However, the situation is not clear for the gold complex. If Jørgensen's value of $x_{opt} = 2.8$ for gold is taken to describe the 30.0-kK charge-transfer band of the azide complex, the Δ_1 ligand-field parameter must be larger than the corresponding parameter in the Pt(II) compound. This is in disagreement with the result of Basch and Gray,[17] who propose the opposite order. The only way to reconcile this result with the concept of optical electronegativity for the gold azide complex is to change the optical electronegativity parameter x_{opt} for Au(III) to a value in the neighborhood of 2.4.[30]

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[30] NOTE ADDED IN PROOF. W. Beck, private communication, has now also measured absorption spectra of azide complexes. His spectrochemical parameters agree well with those reported in this paper.