In the strong-field limit, $\mu = -\beta/2$. However, as pointed out by Griffith,[87] the $^1T_2(t_{2g}^5e_g)$ state of low-spin d^6 ions is subject to extensive configuration interaction. We have therefore evaluated μ in the intermediate-field situation, diagonalizing the whole (7 × 7) $^1T_{2g}$ matrix[88] for a range of Δ and B values. The results show that μ increases uniformly as Δ decreases and B increases (*i.e.*, as configuration interaction increases), being $+0.57\beta$ for $\Delta = 18{,}000$ cm^{-1}, $B = 600$ cm^{-1}, $+0.95\beta$ for $\Delta = 18{,}000$ cm^{-1}, $B = 800$ cm^{-1}, and $+0.45\beta$ for $\Delta = 20{,}000$ cm^{-1}, $B = 600$ cm^{-1}. For $Co(ox)_3^{3-}$ $\Delta \sim 18{,}000$ cm^{-1}, $B \sim 540$ cm^{-1},[89] and hence the calculated μ value is close to that observed experimentally ($+0.48\beta$). The sensitivity of μ to configuration interaction is noteworthy. The effects of the D_3 perturbation on the wave functions are hard to evaluate but should be small.

The calculation of A/D for a spin-allowed $A_2 \rightarrow E$ transition in D_3 symmetry follows that above for $A_1 \rightarrow E$. Defining $\mu = i\langle E||\mu||E\rangle = i\langle E_x|\mu_z|E_y\rangle$, $A/D = -\mu/2$. For the $^4A_2 \rightarrow {}^1E_a$ transition of Cr(III), assuming ^4E_a to be unperturbed linear combinations of $^4T_{2g}$ O_h states (which are not subject to configuration interaction), we find $\mu = -\beta/2$, whence $A/D = \beta/4$.

(87) Reference 43, Section 11.6.1, pp 312–313.

(88) Reference 43, Table A29, p 412.

(89) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press Ltd., Oxford, 1962, Table 11, pp 110–111.

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Electronic and Infrared Spectral Study of Chromium(III) Derivatives of the Type $[Cr(NCS)_4\cdot(ligand)_2]^-$

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A series of complexes of the type $R^+[Cr(NCS)_4L_2]^-$ [$R^+ = K^+$, NH_4^+, $(C_2H_5)_4N^+$, cholinium$^+$, $(CH_3)_3PH^+$, $(C_2H_5)_3PH^+$, $(n\text{-}C_4H_9)_3PH^+$, $(CH_3)_2(C_6H_5)PH^+$, or $(C_2H_5)_2(C_6H_5)PH^+$; L = NH_3, pyridine, $^1/_2$(2,2′-bipyridyl), $^1/_2$(*o*-phenylenebisdimethylarsine), $(CH_3)_3P$, $(C_2H_5)_3P$, $(n\text{-}C_4H_9)_3P$, $(CH_3)_2(C_6H_5)P$, $(C_2H_5)_2(C_6H_5)P$, or $(C_2H_5)(C_6H_5)_2P$] have been prepared, several for the first time, and studied in the 10,000–40,000- and the 4000–70-cm^{-1} regions. From the position of the $^4T_{2g} \leftarrow {}^4A_{2g}$ transition in the electronic spectra of these complexes, the relative positions of the ligands (L) in the spectrochemical series have been deduced. In general, tertiary phosphines have slightly higher ligand field strengths than nitrogen-donor ligands. Methylphosphines have higher ligand field strengths than other alkylphosphines, whereas phenyl substituents lower the ligand field strengths of phosphines. The complex anions are all believed to have *trans*-octahedral structures, with the exceptions of the pyridine, 2,2′-bipyridyl, phenyldiethylphosphine, and *o*-phenylenebisdimethylarsine complexes, which have *cis*-octahedral structures. Assignments for the CN, CS, CrN, and CrL stretching vibrations and for the NCS bending vibration are given. In the case of the salts of the type $R^+[Cr(NCS)_4(NH_3)_2]^-$ the fully deuterated species were also studied in order to differentiate between the Cr–NH$_3$ stretching mode and the NCS bending mode. Metal–phosphorus stretching vibrations are believed to lie near 300 cm^{-1} in the case of trimethyl- and triethylphosphine derivatives. Assignments of the skeletal bending modes in the above complexes and in those of the type $M(NCS)_6^{3-}$ (M = V, Cr, or Fe) are also given.

Introduction

In an attempt to obtain more information about the factors influencing ligand field strengths, we have studied a series of complexes containing the octahedral anions $[Cr(NCS)_4L_2]^-$, where L is an amine, a tertiary phosphine, or (in one case) a tertiary arsine. It is of interest to establish how Dq varies with the nature of the substituent on the ligand atom. Chromium(III) complexes are particularly suited to such a study (a) because the first spin-allowed ligand field band $^4T_{2g} \leftarrow {}^4A_{2g}$ is a direct measure of the ligand field splitting parameter ($10Dq$) and (b) because although, in principle, this band should be resolved into two or three components in ligand fields lower than octahedral, the magnitude of this splitting is not usually large enough to observe without the use of polarized radiation. Where the ligand field strengths of the coordinated ligands are widely disparate, as for ammonia and halide ions, the $^4T_{2g}$ term *is* clearly split, but in the present series of complexes using ligands of comparable ligand field strengths, this is not the case.

The infrared spectra of the anions have been recorded down to 70 cm^{-1} in order to locate low-lying skeletal modes.

The above anions could, of course, exist as two possible stereochemical isomers, *i.e.*, *cis* or *trans* forms. The different selection rules pertaining to the vibrational modes of the two isomers usually permit the establishment of the isomeric form which crystallizes out. Moreover, in the case where L = NH_3, three salts of the anion $[Cr(NCS)_4L_2]^-$ have been the subject of full X-ray analyses;[1] in all three cases, the anion has the *trans*-octahedral structure, the thiocyanate group being nitrogen bonded. In the ammonium and pyridinium salts, the thiocyanate groups are coplanar

(1) Y. Takéuchi and Y. Saito, *Bull. Chem. Soc. Japan*, **29**, 319 (1957).

with the $Cr(N_{cs})_4$ plane, but in the cholinium salt the CrNC bond angle is reduced to 155.5°. The molecular symmetries and crystallographic details on these salts are given in Table I. In the case of the cholinium salt, the molecular symmetry is C_{2h}.

Table I

X-Ray Data on the Reineckate Salts

$R^+[Cr(NCS)_4(NH_3)_2]^-$

Cation	Symmetry of anion	Bond lengths, A				Bond angles, deg	
		CrN_{cs}	NC	CS	$CrNH_3$	NCS	CrNC
NH_4^+	4/mmm = D_{4h}	2.05	1.14	1.80	2.15	180	180
$C_5H_6NH^+$	4/mmm = D_{4h}	1.95	1.15	1.76	2.11	180	180
$C_5H_{13}NOH^+$	2/m = C_{2h}	1.94	1.27	1.64	2.12	180	155.5

Experimental Section

Preparation of Compounds.—The compounds of the type $R^+[Cr(NCS)_4L_2]^-$, where L = NH_3,[2] C_5H_5N,[3] $(C_2H_5)_3P$,[4] and $(n\text{-}C_4H_9)_3P$,[4] were prepared according to literature methods, the analytical data being given in Table II. The other derivatives are reported for the first time.

Deuterated Reineckate Salts.—The deuterated reineckate salts were prepared by recrystallizing ammonium reineckate in D_2O to exchange the water of crystallization. The salt was then recrystallized three times from dilute solutions of KOD in D_2O, the solution being maintained at 40° for several hours to facilitate the exchange. The extent of deuteration, as judged from the infrared spectra, was at least 90% complete.

$K[Cr(NCS)_4dipy]$.—A solution of 0.3 g (0.0019 mole) of 2,2′-dipyridyl (dipy) in 20 ml of absolute ethanol was added to a solution of 1.3 g (0.0025 mole) of $K_3[Cr(NCS)_6]$ in 20 ml of absolute ethanol. The solution was warmed for 2 hr at 50°, a pink precipitate being formed. The solution was then refluxed on a water bath for 2 hr and allowed to cool; it was then filtered and the precipitate was washed with ethanol and dried *in vacuo* at 80°. The yield was ~90%. The initial equivalent conductance of the compound is 170 cm² ohm^{-1} mole^{-1} at 1.3 × 10^{-3} *M* in acetone, in agreement with that expected for a 1:1 electrolyte in this solvent. However the compound slowly decomposes in acetone, being half decomposed after about 15 min. It is only sparingly soluble in methanol and in ethanol. The compound has a magnetic moment of ~3.6 BM at room temperature, slightly lower than that typically found for d^3 complexes.

$(C_2H_5)_4N[Cr(NCS)_4diars]$.—*o*-Phenylenebis(dimethylarsine) (diars) (1.6 g, 0.006 mole) was refluxed for 8 hr under nitrogen with an ethanolic solution of 3.2 g (0.006 mole) of $K_3[Cr(NCS)_6]$. A solution of tetraethylammonium chloride in water was then added, followed by sufficient water to precipitate all of the chromium complexes from solution. The precipitate, which contains essentially the complexes $[(C_2H_5)_4N]_3[Cr(NCS)_6]$ and $(C_2H_5)_4N[Cr(NCS)_4diars]$, was filtered, washed with distilled water, and dried. The diarsine complex can be extracted with cold ethanol and isolated in low yield as blue crystals. The compound is soluble with some decomposition in alcohols and in acetone. Its magnetic moment at room temperature is 3.9 BM.

$(CH_3)_3PH[Cr(NCS)_4[(CH_3)_3P]_2]$.—Anhydrous $K_3[Cr(NCS)_6]$ (1.3 g, 0.0025 mole) and 0.75 g (0.01 mole) of trimethylphosphine (prepared by gentle heating of the silver iodide complex)[5] were heated in 10 ml of 2-propanol under nitrogen in a sealed tube at 80° for 2 hr. On addition of the resulting solution, under nitrogen, to a solution of 2 ml of concentrated HCl and 2 ml of water, a pink precipitate of the required complex was formed in about 80% yield. The equivalent conductance of the compound in acetone is 120 cm² ohm^{-1} mole^{-1} at a concentration of 0.9 × 10^{-3} *M*, consistent with that expected for a 1:1 electrolyte. The compound is also soluble in methanol, ethanol, and acetonitrile, but insoluble in ether, tetrahydrofuran, dichloromethane, benzene, and petroleum.

Table II

Analytical Data

Complex	% C	% H	% N
$(C_2H_5)_3PH[V(NCS)_6]$[a]	38.5 (38.1)[f]	6.2 (6.4)	10.6 (11.1)
$K_3[Cr(NCS)_6]$	13.6 (13.8)	0.2 (0.0)	. . .
$(C_2H_5)_4N[Cr(NCS)_6]$	45.2 (45.5)	7.5 (7.6)	. . .
$NH_4[Cr(NCS)_4(NH_3)_2]$	14.0 (13.6)	3.4 (3.4)	. . .
$pyH[Cr(NCS)_4(NH_3)_2]$	27.8 (27.3)	3.3 (3.1)	. . .
$chol[Cr(NCS)_4(NH_3)_2]$	25.2 (25.6)	4.9 (4.8)	. . .
$K[Cr(NCS)_4(py)_2]$	34.95 (34.95)	2.7 (2.1)	17.0 (17.4)
$(C_2H_5)_4N[Cr(NCS)_4(py)_2]$	46.0 (46.1)	5.4 (5.3)	. . .
$K[Cr(NCS)_4dipy]$	34.7 (35.1)	2.0 (1.7)	17.6 (17.5)
$(C_2H_5)_4N[Cr(NCS)_4diars]$	38.5 (37.7)	5.4 (5.2)	10.4 (10.0)
$(CH_3)_3PH[Cr(NCS)_4((CH_3)_3P)_2]$	30.4 (30.4)	5.5 (5.5)	11.0 (10.9)
$(C_2H_5)_4N[Cr(NCS)_4((CH_3)_3P)_2]$[b]	38.0 (38.1)	6.8 (6.8)	12.2 (12.4)
$(C_2H_5)_3PH[Cr(NCS)_4((C_2H_5)_3P)_2]$[c]	41.3 (41.2)	7.4 (7.2)	8.6 (8.7)
$(C_2H_5)_4N[Cr(NCS)_4((C_2H_5)_3P)_2]$[d]	44.5 (44.3)	8.1 (7.7)	10.8 (10.8)
$(n\text{-}C_4H_9)_3PH[Cr(NCS)_4((n\text{-}C_4H_9)_3P)_2]$	53.4 (53.9)	9.3 (9.2)	6.0 (6.3)
$(C_6H_5)P(CH_3)_2H[Cr(NCS)_4(C_6H_5P(CH_3)_2)_2]$	48.2 (48.1)	5.0 (4.9)	7.9 (8.0)
$(C_6H_5)P(C_2H_5)_2H[Cr(NCS)_4(C_6H_5P(C_2H_5)_2)_2]$[e]	52.0 (52.1)	5.9 (5.9)	7.9 (7.2)
$K[Cr(NCS)_4(C_6H_5P(C_2H_5)_2)_2]$	48.1 (48.4)	4.9 (5.0)	11.1 (11.8)
$(C_2H_5)_4N[Cr(NCS)_4(C_6H_5)_2P(C_2H_5)]$	55.1 (57.0)	6.0 (6.0)	. . .

[a] % P, 11.8 (12.3). [b] % Cr, 9.1 (9.2). [c] % Cr, 8.2 (8.1); % P, 14.5 (14.6); % S, 20.0 (19.8). [d] % P, 9.4 (9.5). [e] % P, 11.7 (11.8).
[f] The experimentally found values are followed in parentheses by the calculated values.

$(C_2H_5)_4N[Cr(NCS)_4[(CH_3)_3P]_2]$.—Anhydrous $K_3[Cr(NCS)_6]$ (1.3 g) and 0.75 g of trimethylphosphine were heated in 10 ml of 2-propanol under nitrogen in a sealed tube at 80° for 2 hr. On addition of the resulting solution under nitrogen, to an alcoholic solution of tetraethylammonium chloride, there was an immediate precipitation of the required complex as a red powder. It is only slightly soluble in most polar solvents and insoluble in nonpolar ones, and in water.

$(C_2H_5)_2(C_6H_5)PH[Cr(NCS)_4[(C_2H_5)_2(C_6H_5)P]_2]$ and $K[Cr(NCS)_4[(C_2H_5)_2(C_6H_5)P]_2]$.—Anhydrous $K_3[Cr(NCS)_6]$ (5.2 g, 0.010 mole) was heated with 5 g (0.030 mole) of phenyldiethylphosphine in 25 ml of 2-propanol in a sealed tube for 6 hr at 110°. White needles of potassium thiocyanate, together with an orange-

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[2] A. Reinecke, *Ann. Chem.*, **126**, 113 (1863).
[3] P. Pfeiffer and W. Ossan, *Chem. Ber.*, **39**, 2115 (1906).
[4] K. Issleib and A. Tzschach, *Z. Anorg. Allgem. Chem.*, **297**, 121 (1958).
[5] F. G. Mann and A. F. Wells, *J. Chem. Soc.*, 720 (1938).

red compound, were precipitated. The solution was filtered from the crystalline material, and 10 ml of 50% HCl was added. The resulting orange-red precipitate was washed with 100 ml of distilled water and dried on a vacuum line for 5 hr. This compound is the phosphonium salt. It is soluble in methanol, ethanol, acetone, and acetonitrile, but insoluble in water, dichloromethane, and nonpolar solvents. Its magnetic moment at room temperature is 3.9 BM.

Treatment of the original orange-red mixture with water to remove the potassium thiocyanate leaves the pure potassium salt $K[Cr(NCS)_4[(C_2H_5)_2(C_6H_5)P]_2]$. This salt is insoluble in water, methanol, acetone, and acetonitrile. From a study of the infrared spectra of this salt in the Cr–NCS stretching region, it appears, surprisingly, that the complex has the *cis* configuration, whereas the corresponding phosphonium derivative has the *trans* configuration.

$(CH_3)_2(C_6H_5)PH[Cr(NCS)_4[(CH_3)_2(C_6H_5)P]_2]$.—The preparation of this salt is similar to that of the phenyldiethylphosphonium salt except that the corresponding potassium salt is not precipitated. It has closely similar properties to the phenyldiethyl complex, and it is red-brown.

$(C_2H_5)_4N[Cr(NCS)_4[(C_2H_5)(C_6H_5)_2P]_2]$.—Anhydrous $K_3[Cr(NCS)_6]$ (2.5 g, 0.005 mole) and 2.25 g (0.010 mole) of diphenylethylphosphine were heated for 12 hr at 110° in a sealed tube with 10 ml of 2-propanol. A very small amount of potassium thiocyanate was formed. The solution was filtered under nitrogen into a solution of 2.5 g of tetraethylammonium chloride in ethanol, to produce a purple-red precipitate (largely unreacted hexaisothiocyanate). This precipitate was extracted with hot methanol containing some diphenylethylphosphine to leave 0.15 g of the red-brown complex $(C_2H_5)_4N[Cr(NCS)_4[(C_2H_5)(C_6H_5)_2P]_2]$. The complex is insoluble in all solvents tried.

Diphenylmethylphosphonium Complex.—Attempts to prepare the corresponding diphenylmethylphosphonium complex were unsuccessful. On heating together 2.5 g of $K_3[Cr(NCS)_6]$ and 3.3 g of diphenylmethylphosphine in the way described above for the diphenylethyl complex, white needles of potassium thiocyanate were again produced. On addition of tetraethylammonium chloride to the reaction mixture, a mixed product precipitated. This material contained coordinated diphenylmethylphosphine (infrared evidence), but all attempts to isolate the pure phosphine complex were unsuccessful.

Attempts to isolate the anion with the $(CH_3)(C_6H_5)_2PH^+$ cation yielded only the salt $[(CH_3)(C_6H_5)_2PH]_3[Cr(NCS)_6]$. *Anal.* Calcd for $[(CH_3)(C_6H_5)_2PH]_3[Cr(NCS)_6]$: C, 55.1; H, 4.6. Found: C, 55.3; H, 4.7.

Decomposition of the Complexes—The dipyridyl and diarsine complexes tended to decompose slowly in organic solvents. In daylight, solutions of the phosphine complexes decomposed slowly, but decomposition was much more rapid when the solutions were exposed to a fluorescent lamp. After 100 hr of such exposure of an ethanolic solution of the complex $(C_2H_5)_3PH[Cr(NCS)_4[(C_2H_5)_3P]_2]$, absorption bands appeared at 23,200 (ϵ 100) and 17,400 (ϵ 95) cm^{-1}. The solution, which smelled of triethylphosphine, presumably then contained an ethanol-chromium(III) species such as $[Cr(NCS)_4(C_2H_5OH)_2]^-$.

Tertiary Arsine Derivatives.—Attempts to make the corresponding trimethyl- and triethylarsine complexes were unsuccessful. While there is little doubt that the arsines coordinate to chromium(III), the resulting complexes could not be obtained pure. Clearly the Cr^{III}–As bond is weaker than the Cr^{III}–P bond.

Physical Measurements.—Electronic spectra were recorded using Unicam SP500 and Cary 14 instruments. Infrared spectra were recorded on Perkin-Elmer 337 (4000–400 cm^{-1}) and Grubb-Parsons Models D.M.2 (450–200 cm^{-1}) and GM 3 (200–65 cm^{-1}) instruments. In the region of the CN stretching vibrations ($\sim$2000 cm^{-1}), an expanded-scale pen recorder was fitted to the Perkin-Elmer instrument. Sodium chloride, potassium bromide, or polythene mulls were used where appropriate. Magnetic susceptibilities were determined by the Gouy method using a permanent magnet of $\sim$5000 gauss.

Results and Discussion

Electronic Spectra.—Both alcoholic solution and diffuse reflectance spectra of the complexes have been recorded and the close similarity between the results using the two techniques indicates that no structural change occurs on dissolution. The electronic spectrum of only one of the complexes has been obtained previously, that of $NH_4[Cr(NCS)_4(NH_3)_2]$ in aqueous solution.[6a] The band maxima are in almost the same place as those reported here for ethanolic solution. Adamson has also reported the spectrum of the reineckate ion in a number of organic media.[6b,c]

Chromium(III) complexes typically possess two spin-allowed ligand field bands in the visible region, assigned as ${}^4T_{2g} \leftarrow {}^4A_{2g}$ (lower energy) and ${}^4T_{1g}(F) \leftarrow {}^4A_{2g}$ (higher energy). The first band is a direct measure of the ligand field splitting parameter $10Dq$, whereas the second depends on Dq and the Racah parameter B. Unfortunately, only in the case of some of the nitrogen-donor complexes (*e.g.*, the reineckate salts) could the ${}^4T_{1g}(F) \leftarrow {}^4A_{2g}$ transition be located; for the phosphine complexes, very much more intense charge-transfer bands occur from about 25,000 cm^{-1} and upward in energy and effectively obscure the ligand field bands. It has therefore not been possible to establish the position of the phosphines in the nephelauxetic series. The spectral data are given in Table III.

The complexes possess symmetries which closely approximate to D_{4h} (*trans*) and C_{2v} (*cis*). However, all of the ligands lie in the high-energy part of the spectrochemical series, and hence no splitting of the ${}^4T_{2g} \leftarrow {}^4A_{2g}$ transition was observed in any case.

The data indicate that nitrogen-donor ligands in general tend to have slightly lower ligand field strengths than tertiary phosphines. The spectrochemical series derived from the data is: $H_2O < NCS^- <$ [diars] $< (C_2H_5)(C_6H_5)_2P \sim$ [py] $<$ [dipy] $< (C_2H_5)_2(C_6H_5)P \sim NH_3 < (CH_3)_2(C_6H_5)P \sim (n\text{-}C_4H_9)_3P \sim (C_2H_5)_3P < (CH_3)_3P < CN^-$. The ligands in brackets are believed to form complexes $[Cr(NCS)_4L_2]^-$ with a *cis* configuration, on the basis of infrared work. The above spectrochemical series is to be compared with that derived by Chatt, Gamlen, and Orgel[7] from the energy of the $d_{xy} \rightarrow d_{x^2-y^2}$ transition of square-planar platinum(II) complexes of the type *trans*-[L(piperidine)$PtCl_2$]. Their order of the ligands (L) is: $(C_2H_5)_2Te < (C_2H_5)_2Se < (C_2H_5)_2S < (n\text{-}C_3H_7)_3As <$ piperidine $< (n\text{-}C_3H_7)_3P < P(OCH_3)_3$. Cotton and co-workers[8] have also placed two tertiary phosphines in the spectrochemical series, on the basis of an analysis of the electronic spectra and magnetism of tetrahedral cobalt(II) complexes of the type CoX_2Y_2. Their spectrochemical series is: $I^- < Br^- < Cl^- < (C_6H_5)_3PO < C_7H_9N \sim (C_6H_5)_3P \sim (c\text{-}C_6H_{11})_3P \sim N_3^- \sim NCO^- \sim NCS^-$.

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[6] (a) R. Tsuchida, *Bull. Chem. Soc. Japan*, **13**, 436 (1938); (b) A. W. Adamson, *J. Am. Chem. Soc.*, **80**, 3183 (1958); (c) A. W. Adamson, *J. Inorg. Nucl. Chem.*, **28**, 1955 (1966).

[7] J. Chatt, G. A. Gamlen, and L. E. Orgel, *J. Chem. Soc.*, 1047 (1959).

[8] F. A. Cotton, O. D. Faut, D. M. L. Goodgame, and R. H. Holm, *J. Am. Chem. Soc.*, **83**, 1780 (1961).

Table III

Electronic Spectra of the Complexes (cm^{-1})[a]

Complex	Solvent or diffuse refl (D)	Ligand field bands $^4T_{2g} \leftarrow {}^4A_{2g}$	Ligand field bands $^4T_{1g} \leftarrow {}^4A_{2g}$	Charge-transfer bands		
$NH_4[Cr(NCS)_4(NH_3)_2]$	C_2H_5OH	19,150 (105)	25,250 (83)		32,300 (3.4×10^4), ~36,600	
	D	19,900	25,500		nm	
chol$[Cr(NCS)_4(NH_3)_2]$	D	19,100	25,100		nm	
pyH$[Cr(NCS)_4(NH_3)_2]$	D	19,150	25,100		nm	
$K[Cr(NCS)_4(py)_2]$	C_2H_5OH	18,450 (150)	~23,500 (sh)		30,500 (1.3×10^4)	
	D	18,350	~23,200 (sh)		nm	
$K[Cr(NCS)_4$dipy$]$	CH_3OH	18,600 (137)	...	29,300 (0.9×10^4)	[30,200, 31,400, 32,700] (1.2×10^4)	
	D	18,700	...		nm	
$(C_2H_5)_4N[Cr(NCS)_4$diars$]$	CH_3OH	18,000 (d)	nm (d)		nm (d)	
	D	18,000	23,650	26,300 (sh)	29,700	a
$(CH_3)_3PH[Cr(NCS)_4((CH_3)_3P)_2]$	C_2H_5OH	19,950 (180)	...	26,000 (1.4×10^4)	31,700 (1.6×10^4), 42,000 (1.0×10^4)	
	D	20,150	...		nm	
$(C_2H_5)_4N[Cr(NCS)_4((CH_3)_3P)_2]$	CH_3OH	19,950 (180)	...	26,000 (1.4×10^4)	31,700 (1.6×10^4), 42,000 (1.0×10^4)	
$(C_2H_5)_3PH[Cr(NCS)_4((C_2H_5)_3P)_2]$	C_2H_5OH	19,500 (200)	...	25,700 (1.9×10^4)	31,350 (3.2×10^4), 41,800 (2.2×10^4)	
	D	19,450	...		nm	
$(C_2H_5)_4N[Cr(NCS)_4((C_2H_5)_3P)_2]$	CH_3OH	19,400 (200)	...		nm	
$(n\text{-}C_4H_9)_3PH[Cr(NCS)_4((n\text{-}C_4H_9)_3P)_2]$	C_2H_5OH	19,400 (240)	...	25,600 (2.3×10^4)	31,350 (2.7×10^4)	
	D	19,400	...		nm	
$C_6H_5P(CH_3)_2H[Cr(NCS)_4(C_6H_5P(CH_3)_2)_2]$	CH_3OH	19,400 (230)	...	25,600 (0.9×10^4)	31,100 (1.9×10^4)	a
	D	19,400	...	25,600	31,900	a
$C_6H_5P(C_2H_5)_2H[Cr(NCS)_4(C_6H_5P(C_2H_5)_2)_2]$	CH_3OH	19,050 (255)	...	25,500 (1.0×10^4)	30,600 (2.0×10^4)	a
	D	19,050	...	25,400		a
$(C_2H_5)_4N[Cr(NCS)_4((C_6H_5)_2PC_2H_5)_2]$	D	~18,400 (sh)	...	26,300 (sh)	29,700	a

[a] Extinction coefficients are given in parentheses following the band maxima: d, decomposes in solution; sh, shoulder; nm, not measured; a, complicated absorption in this region.

The present result on the position of an arsine in the spectrochemical series is in agreement with that inferred from the electronic spectra of chromium(III) complexes of the type $[CrCl_3TAS]$, where TAS represents a triarsine.[9] However, diarsine exerts a slightly higher ligand field strength where it is part of a spin-paired cobalt(III) system, *e.g.*, in *cis-* and *trans-*[Co(diars)$_2$X$_2$]ClO$_4$ (X = Cl or Br).[10] In this case, the metal atom has the t_{2g}^6 configuration, in which the opportunities for π-bond back donation (which is known to increase *Dq*) are greatest.

Of particular interest is the relative order of the tertiary phosphines themselves in the spectrochemical series: $(CH_3)_3P > (C_2H_5)_3P \sim (n\text{-}C_4H_9)_3P \sim C_6H_5(CH_3)_2P > C_6H_5(C_2H_5)_2P$. The effect of phenyl substitution in lowering the ligand field strength of a tertiary phosphine can be correlated with the accompanying decrease in base strength and hence with poorer σ-donor capacity; *e.g.*, the pK_a values for $(C_2H_5)_3P$ and $C_6H_5(C_2H_5)_2P$ in nitromethane are 8.69 and 6.25, respectively.[11a] There may also be steric hindrance to coordination by phenyl-substituted tertiary phosphines, as shown by the failure to prepare both triphenylphosphine *and* tricyclohexylphosphine complexes of the type $[Cr(PR_3)_2(NCS)_4]^-$,[4] despite the high basicity of the aliphatic ligand.

It is less easy to see why methyl-substituted tertiary phosphines should have significantly higher ligand field strengths than their ethyl analogs, since their base strengths are almost identical; *e.g.*, the pK_a values for $(CH_3)_3P$ and $(C_2H_5)_3P$ in nitromethane are 8.65 and 8.69, respectively;[11a] in ethanol–water solutions, the respective values are 7.20 and 6.68.[11b] However, it is an oversimplification to relate the complexing of polarizable ligands such as tertiary phosphines with transition metals to their basicity. Henderson and Buckler[12] have shown that the order of nucleophilicity of alkylphosphines is $(C_2H_5)_3P < (CH_3)_3P < (C_2H_5)_2CH_3P < C_2H_5(CH_3)_2P$ and have suggested that there are two competing effects: (1) increasing the size of the alkyl group leads to an increase in the C–P–C bond angle, hence a closer approach to sp^3 hybridization, and an increase in nucleophilicity; (2) on the other hand, steric hindrance to the attacking group is increased with larger alkyl groups. Nucleophilicity has been related to both basicity and polarizability,[13] and the latter factor may well be significant in stabilizing phosphine complexes of transition metals.

Small differences in the complexes of methyl- and ethylphosphines have been noted previously. The C–O stretching frequencies of $Mo(CO)_{6-x}(PR_3)_x$ (x = 1, 2, or 3)[14a] are always slightly higher (~5 cm^{-1}) for R = CH_3 than for R = C_2H_5, and the same trend is evident from comparison[14b] of the C–O stretching frequencies of $Ni(CO)_2[o\text{-}C_6H_4(PR_2)_2]$ (R = CH_3 or C_2H_5). Moreover, methyl-substituted ligands $o\text{-}C_6H_4[E(CH_3)_2]_2$ (E = P or As) give eight-coordinate complexes of the formula $TiCl_4(chelate)_2$, whereas the corresponding ethyl-substituted ligands give six-coordinate complexes of the formula $TiCl_4$(chelate).[15]

The infrared data on C–O frequencies suggest that

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TABLE IV

INFRARED SPECTRA OF COMPLEXES IN THE SOLID STATE (CM^{-1})^a

Complex	Symmetry of anion	ν C–N	ν C–S	ν M–NCS	δ NCS	ν M–L	δ L–M–L	Other bands
$(C_2H_5)_3PH[V(NCS)_6]$	O_h	2074 vs	840? vw	340 s	485 s	...		93 m, br
$K_3[Cr(NCS)_6]$	O_h	2058 vs	820 vw	358 s	474 s	...		nm
		2098 vs						
		2118 s						
$((C_2H_5)_4N)_3[Cr(NCS)_6]$	O_h	2082 vs	820 vw		481 s	...		98 m, br
$((C_2H_5)_4N)_3[Fe(NCS)_6]$	O_h	2080 vs	823 vw	270 s, br	479 s	...		98 m, br
$NH_4[Cr(NCS)_4(NH_3)_2]$	D_{4h}	2057 vs	827 m	342 s	467 s	501 s		
		2127 s						
$ND_4[Cr(NCS)_4(ND_3)_2]$	D_{4h}	2057 vs	827 m	342 s	467 s	487 s		
		2127 s						
$pyH[Cr(NCS)_4(NH_3)_2]$	D_{4h}	2094 vs	837 m	345 s, br	489 s	466 vw^b	257 w	~180 s, br, 102 m, br, 90 m, br
$pyH[Cr(NCS)_4(ND_3)_2]$	D_{4h}	2094 vs	837 m	343 s, br	488 s	452 vw^b	248 w	~180 s, br
$chol[Cr(NCS)_4(NH_3)_2]$	C_{2h}	2085 vs	840 w	346 s	490 s	466 vw^b	258 w	184 s, 102 m, br, 87 m, br
$chol[Cr(NCS)_4(ND_3)_2]$	C_{2h}	2085 vs	840 w	346 s	481 s	451 mw^b	249 w	165.5 s, 102 m, br, 87 m, br
$K[Cr(NCS)_4(py)_2]$	C_{2v}	2074 vs	840 vw	382 s	484 s	213 w^b		
				362 s		225 w^b		
				335 s				
$(C_2H_5)_4N[Cr(NCS)_4(py)_2]$	C_{2v}	2077 vs	848 w	382 s	488 s	212 w^b		
				362 s	485.5 s			
				334 s	483 s	226 w^b		
$K[Cr(NCS)_4dipy]$	C_{2v}	2110 vs	847 vw	382 s	478 s	...		
		2092 vs		360 s				
		2080 vs			485 s	...		
$(C_2H_5)_4N[Cr(NCS)_4diars]$	C_{2v}	2051 vs	na	358 s	486 s	...		
		2069 vs						
		2090 vs		341 s		...		
$(CH_3)_3PH[Cr(NCS)_4((CH_3)_3P)_2]$	D_{4h}	2067 vs	846 m	368 s	480 s	275 m		178 m, 149 m, 88 s
$(C_2H_5)_4N[Cr(NCS)_4((CH_3)_3P)_2]$	D_{4h}	2070 vs	846 m	367 s	480 s	276 m		178 m, 149 m, 88 s
$(C_2H_5)_3PH[Cr(NCS)_4((C_2H_5)_3P)_2]$	D_{4h}	2066 vs	846 sh	362 s	482 s	305 m		181 m, br, 141–83 s, v br
$(C_2H_5)_4N[Cr(NCS)_4((C_2H_5)_3P)_2]$	D_{4h}	2083 vs	848 sh	357 s	482 s	304 m		
		2070 vs						
$(n\text{-}C_4H_9)_3PH[Cr(NCS)_4((n\text{-}C_4H_9)_3P)_2]$	D_{4h}	2068 vs	846 m	362 s	482 s	296 m		
$C_6H_5P(CH_3)_2H[Cr(NCS)_4(C_6H_5P(CH_3)_2)_2]$	D_{4h}	2068 vs	845 sh^b	365 s	481 s	na		
$C_6H_5P(C_2H_5)_2H[Cr(NCS)_4(C_6H_5P(C_2H_5)_2)_2]$	D_{4h}	2073 vs	855?^{b}	365 s	484 s	na		
		2055 vs						
$K[Cr(NCS)_4(C_6H_5P(C_2H_5)_2)_2]$	C_{2v}	2045 vs	na	361 s	484 s	na		
				342 m				
$(C_2H_5)_4N[Cr(NCS)_4((C_6H_5)_2PC_2H_5)_2]$	?	2050 vs	na	348 s^b	478 s	na		
				356 s				
				362 s, sh				

[a] dipy = 2,2′-dipyridyl; diars = *o*-phenylenebis(dimethylarsine). vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; br, broad; nm, not measured; na, not assigned because of ligand absorption in the region; vbr, very broad. [b] Assignments uncertain because of ligand absorption in this region.

the methyl-substituted ligands are slightly poorer σ donors (or slightly better π acceptors) than the ethyl-substituted ligands, and the infrared data (see later) on Cr–PR$_3$ vibrations suggest that, in chromium(III) complexes, the Cr–P(CH$_3$)$_3$ bond is weaker than the Cr–P(C$_2$H$_5$)$_3$ bond. These results appear to be incompatible with the order of ligand field strengths, which might be expected to parallel σ-donor ability, and at present we can offer no explanation of the discrepancy.

The charge-transfer bands have not been assigned, except that the strong band near 30,000 cm^{-1} is commonly assigned as an internal transition of the thiocyanate ion.[16]

Infrared Spectra.—Many previous studies have been made of the infrared spectra of inorganic thiocyanates, mainly to obtain information about the mode of bonding of the thiocyanate group.[17] More recently, studies of thiocyanate complexes in the 450–200-cm^{-1} region have also been made in order to assign some of the metal–ligand vibrational frequencies.[18] In the present complexes, the thiocyanate group is nitrogen bonded, as evidenced by the X-ray results on the reinecke salts (Table I) and the internal vibrational frequencies of the thiocyanate group.

The band maxima in the infrared region are listed in Table IV together with the assignments, and the symmetry species of the various vibrational modes are given in Table V. In the *trans*-octahedral complexes, only one CN, CS, CrN, or CrL stretching vibration is infrared active, whereas in the *cis*-octahedral complexes, all four CN, CS, and CrN stretching vibrations are allowed in the infrared region and so are both of the CrL stretching vibrations. However, in some cases where the complexes must have the *cis*-octahedral arrangement (*e.g.*, with the bidentate ligand 2,2′-dipyridyl) only a single CN stretching frequency is observed in the infrared region in solution (Table VI). Presumably the four infrared-active modes are accidentally degenerate. In solid-state spectra, the CN

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TABLE V

SPECIES OF THE VIBRATIONAL MODES OF COMPLEX IONS OF THE TYPE $[Cr(NCS)_4L_2]^-$ [a]

	Symmetry point group	$\nu(CN)$, $\nu(CS)$, or $\nu(CrN)$	$\delta(CrNC)_{ip}$ or $\delta(NCS)_{ip}$	$\delta(CrNC)_{op}$ or $\delta(NCS)_{op}$	$\nu(CrL)$	Skeletal bending modes
trans-$[Cr(NCS)_4L_2]^-$	D_{4h}	$a_{1g} + b_{1g} + \underline{e_u}$	$a_{2g} + b_{2g} + \underline{e_u}$	$\underline{a_{2u}} + b_{2u} + e_g$	$a_{1g} + \underline{a_{2u}}$	$b_{2g} + e_g + \underline{a_{2u}} + b_{2u} + \underline{2e_u}$
trans-$[Cr(NCS)_4L_2]^-$	C_{2h}	$a_g + b_g + \underline{a_u} + \underline{b_u}$	$2a_g + 2b_g + \underline{2a_u} + \underline{2b_u}$		$a_g + \underline{b_u}$	$2a_g + b_g + \underline{3a_u} + \underline{3b_u}$
cis-$[Cr(NCS)_4L_2]^-$	C_{2v}	$\underline{2a_1} + \underline{b_1} + \underline{b_2}$	$\underline{2a_1} + 2a_2 + \underline{2b_1} + \underline{2b_2}$		$\underline{a_1} + \underline{b_1}$	$\underline{3a_1} + 2a_2 + \underline{2b_1} + \underline{2b_2}$

[a] ip, in plane; op, out-of-plane. Vibrational species which are underlined are infrared active.

TABLE VI

CN STRETCHING VIBRATIONS OF THE THIOCYANATE COMPLEXES IN SOLUTION (CM^{-1})[a]

Complex	Solvent Acetone	 Chloroform
$K_3[Cr(NCS)_6]$	2089	. . .
$[(C_2H_5)_4N]_3[Cr(NCS)_6]$	2090	. . .
$NH_4[Cr(NCS)_4(NH_3)_2]$	2074	. . .
$(CH_3)_3PH[Cr(NCS)_4((CH_3)_3P)_2]$	2067	. . .
$(C_2H_5)_3PH[Cr(NCS)_4((C_2H_5)_3P)_2]$	2069	. . .
$(n\text{-}C_4H_9)_3PH[Cr(NCS)_4((n\text{-}C_4H_9)_3P)_2]$	2070	2075
$K[Cr(NCS)_4(py)_2]$	2068	. . .
$K[Cr(NCS)_4dipy]$	2068	. . .
$(C_2H_5)_4N[Cr(NCS)_4diars]$	. . .	2066, 2089 sh

[a] Measured on a Perkin-Elmer 337 instrument fitted with an expanded scale; measurements are believed to be accurate to ±2 cm^{-1}. The spectra in this region were calibrated by reference to the rotational spectrum of DCl.

stretching frequency is frequently split owing to site symmetry and other solid-state effects.

The NCS bending vibration at 480 cm^{-1} appears as a single band in the spectra of all of the complexes except the dipyridyl and one of the pyridine complexes, in which two or three bands are observed.

Metal-Ammonia Vibrational Frequencies.—The assignment of the metal-ammonia stretching vibrations in the reineckate salts is complicated because these are expected to occur in the same region as the NCS bending vibrations; *cf.* for $[Cr(NH_3)_6]Cl_3$, $\nu_3(t_{1u})$ occurs at 469 cm^{-1},[19] and for $[(C_2H_5)_4N]_3[Cr(NCS)_6]$, the $\delta(NCS)$ mode occurs at 481 cm^{-1}.

In order to assign the modes in the salts of the ion $[Cr(NCS)_4(NH_3)_2]^-$, it is necessary to study the deuterated derivatives. In ammonium reineckate two bands occur at 467 and 501 cm^{-1}; in the fully deuterated analog, the corresponding bands occur at 467 and 489 cm^{-1}. The band at 501 cm^{-1} is thus assigned as being essentially the Cr–NH_3 stretching mode, and the 467-cm^{-1} band, as the NCS bending mode. In the pyridinium salt, the band at 488 cm^{-1} is independent of deuteration, and accordingly is assigned as the NCS bending mode, whereas the very weak band at 466 cm^{-1} shifts to 452 cm^{-1} on deuteration. The latter is accordingly believed to be the Cr–NH_3 stretching mode. The apparent reversal in the relative order of the Cr–NH_3 stretching mode and the NCS bending mode in those two salts would not be expected from the bond length data.

Cholinium reineckate has C_{2h} rather than D_{4h} symmetry, and as a consequence two infrared-active CN, CS, or CrN_{cs} stretching vibrations are expected. In practice, however, only one of each type could be resolved. In the 450–500-cm^{-1} region, both observed bands move downward by 9–15 cm^{-1} on deuteration. From Table V it is seen that in D_{4h} symmetry, the CrL stretching vibration (a_{2u} species) can only couple with the out-of-plane NCS bending vibration, whereas in C_{2h} symmetry it can couple to both in-plane and out-of-plane NCS bending vibrations. Consequently, the coupling of vibrations in this region is much more extensive for the cholinium salt than for the other derivatives. Thus the separate identification of the Cr–NH_3 stretching vibration and the NCS bending vibration in this salt is not possible.

The deuteration data on the NH_3 symmetric and antisymmetric deformation modes and on the NH_3 rocking mode are given in Table VII.

TABLE VII

NH_3 DEFORMATION MODES IN REINECKATE SALTS (CM^{-1})

	Degen def	Sym def	Rock
$NH_4[Cr(NCS)_4(NH_3)_2]$	(1656, 1630, 1599) m	1257 s	706 vs
$ND_4[Cr(NCS)_4(ND_3)_2]$	1248 m, 1165 m	976 s	546 s
$pyH[Cr(NCS)_4(NH_3)_2]$	1628 m, 1602 m	1257 s	695 s
$pyH[Cr(NCS)_4(ND_3)_2]$	1244 m, 1160 m	965 s	532 s
$chol[Cr(NCS)_4(NH_3)_2]$	1655 w, 1594 w	1252 s	695 s
$chol[Cr(NCS)_4(ND_3)_2]$	1258 w, ~1168 w	972 s	542 s, br

Bands occurring at 258 cm^{-1} in the infrared spectra of the reineckate salts and at ~248 cm^{-1} in the spectra of the deuterated analogs are assigned as NH_3–Cr–NH_3 bending modes by analogy with the corresponding assignment for the complex $[Cr(NH_3)_6]Cl_3$.[19] Further bands in the spectra of the pyridinium and cholinium salts at ~180 cm^{-1} may also be bending vibrations. The spectrum of the ammonium salt below 200 cm^{-1} is badly resolved owing to the presence of librational modes associated with the molecule of water in the lattice.[1]

Metal–Isothiocyanate Vibrational Frequencies.—The metal–isothiocyanate stretching frequencies occur as strong bands in the 335–382-cm^{-1} region. They occur as single bands as expected in the spectra of the *trans* complexes (e_u species) but as two or three bands in the spectra of the *cis* complexes (four bands are symmetry allowed, 2 $a_1 + b_1 + b_2$ species). Their strength and frequency are probably the most characteristic feature of nitrogen-bonded thiocyanates. In the hexaisothiocyanates, the frequency order of this vibration (t_{1u} in O_h symmetry) is Cr > V > Fe, as might have been expected from the relative ligand field stabilization energies of the ions. The metal–isothiocyanate stretching frequencies for the three reineckate salts all lie at 344 ± 2 cm^{-1}, which suggests that the large Cr–NCS bond-

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(19) I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, **22**, 759 (1966).

length differences (0.11 A) reported for these salts are not real.

The assignment of the infrared-active (SCN)Cr(NCS) bending vibrations is more difficult. The (OC)Cr(CO) bending vibration of chromium hexacarbonyl (t_{1u} species in O_h symmetry) occurs at 90 cm^{-1} and the corresponding (NC)Cr(CN) bending vibration of the $Cr(CN)_6^{3-}$ ion is at 124 cm^{-1}.[20] However, very recent force constant calculations on the $Zn(NCX)_4^{2-}$ ions (X = O, S, or Se) indicate[21] that even in these ions, the (XCN)Zn(NCX) bending vibrations would be expected below 50 cm^{-1}. Hence the strong bands at $\sim$100 cm^{-1} in the infrared spectra of all of the complexes measured in this region are assigned as CrNC deformation modes. This assignment is to be compared with the corresponding band in the spectrum of the $Zn(NCS)_4^{2-}$ ion, which occurs at 168 cm^{-1}.

Metal-Phosphorus Vibrations.—The region of absorption corresponding to metal-phosphorus stretching vibrations has been discussed for several years, but few experimental data are available. The first assignment was based on the Raman spectrum of the complex $Ni(PF_3)_4$, in which the a_1 fundamental at 195 cm^{-1} was identified with the Ni-P symmetric stretching frequency.[22] Coates and Parkin[23] later assigned gold-phosphorus stretching vibrations in linear complexes of gold(I) of the type R_3PAuX ($X = CH_3$, $C{\equiv}CC_4H_9$, Cl, or Br; $R = CH_3$, C_2H_5, or C_6H_5) to medium-strong bands occurring in the 347-388-cm^{-1} region. Metal-phosphorus stretching vibrations in square-planar complexes of Au(III), Ni(II), Pd(II), and Pt(II) were believed to occur in a similar region. More recently, Goggin and Goodfellow[24] have assigned metal-phosphorus stretching vibrations in square-planar platinum(II) complexes of the type $(R_3P)_2PtX_2$ (X = Br or I; $R = CH_3$ or C_2H_5). They concluded that $Pt-P(CH_3)_3$ and $Pt-P(C_2H_5)_3$ stretching vibrations occur in the 348-400- and 409-441-cm^{-1} ranges, respectively. Other workers[25] have also assigned $Pt-P(C_2H_5)_3$ stretching frequencies in square-planar platinum(II) complexes to a similar frequency range, namely, 406-450 cm^{-1}. Metal-phosphorus stretching vibrations in tetrahedral complexes of the type $[(C_6H_5)_3P]_2MX_2$ (M = Zn, Cd, or Hg; X = Cl, Br, or I) have been assigned[26] to the absorption bands occurring in the following regions: Zn, 153-166; Cd, 133-136; Hg, 98-137 cm^{-1}. The wide range of the M-P stretching frequencies assigned so far probably arises because the complexes studied differ in coordination number, stereochemistry, and oxidation state, and all of these factors are known to affect metal-ligand stretching frequencies.[27]

In the spectra of the present trimethylphosphine and triethylphosphine complexes, it seems most reasonable to assign the $Cr-PR_3$ stretching vibrations to the medium bands occurring at $\sim$275 cm^{-1} ($R = CH_3$) and $\sim$304 cm^{-1} ($R = C_2H_5$). This assignment of $Cr-P(C_2H_5)_3 > Cr-P(CH_3)_3$ is in agreement with the similar results found for the square-planar platinum system.[24]

A possible complicating feature, however, is that trimethylphosphine itself is reported to absorb at 263 and 305 cm^{-1}; these bands have been assigned as the symmetric and antisymmetric CPC bending vibrations, respectively.[28]

Moreover, for triethylphosphine itself, bands in the Raman spectrum are reported at 410, 368, 333, 306, 278, and 249 cm^{-1} [29] and are assigned to CCP and CPC bending modes and methyl group torsional modes.[24] However, these internal ligand vibrations are usually much weaker than metal-ligand stretching vibrations,[24] and thus the assignments of metal-phosphorus stretching vibrations can be made with some confidence. The assignment of metal-phosphorus stretching vibrations in complexes containing mixed phosphines was not possible owing to the multitude of internal ligand vibrations in the 300-cm^{-1} region in these cases.

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