Electronic Spectra of Thiocyanate, Selenocyanate, and Azide Complexes of Manganese, Vanadium, and Indium

H.-H. SCHMIDTKE

Institute of Physical Chemistry, University of Francfort, Germany,
and Cyanamid European Research Institute, Cologny, Geneva, Switzerland

and D. GARTHOFF

Cyanamid European Research Institute, Cologny, Geneva, Switzerland

(Z. Naturforsch. **24 a**, 126—133 [1969]; received 12 October 1968)

The anions $Mn(NCS)_4{}^{2-}$, $Mn(NCS)_6{}^{4-}$, $Mn(NCSe)_4{}^{2-}$, $Mn(NCSe)_6{}^{4-}$, $Mn(N_3)_4{}^{2-}$, $V(NCS)_6{}^{3-}$, $V(NCSe)_6{}^{3-}$, $V(N_3)_6{}^{3-}$, $VO(NCS)_5{}^{3-}$, $VO(NCSe)_4{}^{2-}$, $VO(N_3)_4{}^{2-}$, and $In(NCS)_6{}^{3-}$ have been prepared and crystallized with large organic cations. The complexes are characterized by elementary analyses, diffuse reflectance spectra in the visible and ultraviolet region, and by infrared spectroscopy. Ligand field and charge transfer bands of electronic transitions are interpreted by usual theoretical procedures. The parameters of semiempirical theories are calculated. From the charge transfer spectra the values $x(Mn^{II}) = 1.9$; $x(V^{III}) = 1.8$; $x(VO^{2+}) = 1.5$; $x(In^{III}) = 1.2$ are determined for the optical orbital energy parameters.

Introduction

Recently the preparation, the ligand field, and charge transfer spectra of various thiocyanate, selenocyanate and azide complexes of transition group ions have been reported[1–3]. These pseudohalides show spectrophotometric properties which are characteristic for halide complexes, i. e. their electronic spectra in the visible and ultraviolet region can be interpreted in the same way as in halide complexes. The bands in the absorption and diffuse reflectance spectra are classified into ligand field (d-d) and charge transfer transitions and the assignment to energy states in the term scheme is carried out on the basis of ligand field or molecular orbital theory. In either case the molecular ligand is considered as a "one-center ligand" which is approximated in the respective model by a point charge or electric dipole or by atomic orbitals located at the atom which is attached to the central metal. This model, of course, is immediately applicable to halide ligands, however, for molecular ligands, in particular for molecules with an internal π-electron system which may interfere with the chromophore ML_n, this approximation needs additional justification. This is obtained from the electronic spectra which allow a unified interpretation for both, halide and pseudohalide complexes.

Various questions have been discussed which are important for the theory[3]. In particular the interpretation of the very intense bands in the spectra of thiocyanate complexes has been clarified which earlier have been assigned to internal $\pi - \pi^*$ transitions of the ligand[4]. A large majority of these bands is now identified as charge transfer transitions from the ligand to the central ion[3]. This is true for N- and S-(Se) bonded thiocyanate and selenocyanate 1 : 4 and 1 : 6 complexes of various symmetries. The "optical electronegativity" parameters have different values for different ligand linkages. They also have been found in reverse order to the Pauling values of electronegativity. This indicates a drastic change in the electronic structure of the molecule compared to the isolated atoms.

In the present paper the spectra of complexes are reported which previously have not been investigated thoroughly. In some cases new preparative methods are proposed in order to obtain materials which give the spectra of the complex ions only. The coordination compounds are precipitated, if possible, by cations which do not absorb light in the regions of interest or supply clean and better crystallized substances. Some complex compounds are described for the first time. Also the infrared spectra are recorded in order to support the characterization and demonstrate the purity of the compounds.

---

[1] H.-H. SCHMIDTKE and D. GARTHOFF, J. Amer. Chem. Soc. **89**, 1317 [1967].

[2] H.-H. SCHMIDTKE and D. GARTHOFF, Helv. Chim. Acta **50**, 1631 [1967].

[3] H.-H. SCHMIDTKE, Ber. Bunsenges. Physik. Chem. **71**, 1138 [1967].

[4] C. K. JØRGENSEN, Absorption Spectra and Chemical Bonding in Complexes, Pergamon Press, Oxford 1962.

Experimental Section

(a) Materials. $[(CH_3)_4N]_4[Mn(NCS)_6]$. To a solution of $Mn(NO_3)_2 \cdot 4\,H_2O$ (0.5 g) in 3 ml of dried methanol a solution of KSCN (0.387 g) in methanol (3 ml) is added (2 moles SCN^- to 1 mole complex) at room temperature. After removing precipitated KNO_3 the filtrate is reacted with a solution of $(CH_3)_4N \cdot SCN$(1.16 g) in 10 ml of methanol (4.4 moles). A fine colourless precipitate is formed which dissolves on heating to boiling temperature. After cooling pale pink crystals are obtained which become less coloured on drying over silica gel. Analysis see Table 1. The preparation in ethanol yields products which analyse less accurately and have poorly resolved spectra.

The compounds

$[(C_6H_5)_4As]_2[Mn(NCS)_4]$, $[(CH_3)_4N]_4[Mn(NCSe)_6]$,

and cat [*] $[Mn(NCSe)_4]$ are prepared accordingly using the methods given in the literature [5, 6]. Also precipitations with other cations have been tried. In all these cases, however, the analyses and the spectra are less accurate.

The azide, $[(C_2H_5)_4N]_2[Mn(N_3)_4]$, was described by Beck et al. [7] as a greyish powder. Colourless products with a good analysis are obtained by precipitating the n-cetyltrimethylammonium salt from aqueous solution.

The most appropriate starting material for the preparation of thiocyanate and selenocyanate complexes of V^{III} is $[V(urea)_6](ClO_4)_3$. In earlier procedures VCl_3 was used [8] which in usual grade contains some VO^{2+} which most conveniently is detected by the absorption at 950 – 1000 cm^{-1} in the infrared spectrum. Samples of VCl_3 show also acid reaction in aqueous solution which precipitates Se from selenocyanate solutions. Moreover starting from VCl_3-solutions the reaction was found considerably more sensitive to air oxidation than starting from the urea complex.

$[V(urea)_6](ClO_4)_3$ was first prepared by reducing an acid V_2O_5-solution [9]. A more convenient procedure starts from V^{III} salts. The chloride, VCl_3, is dissolved in water together with a small excess of urea. Impurities are removed from the green solution by filtration. On addition of solid $NaClO_4$ crystals are formed with high yield. After 20 min the product is collected on a glass filter, washed with ethanol and petrol ether. Bright grass green crystals which according to the infrared spectrum do not contain vanadyl salts. Analysis see Table 1.

$[(n\text{-}C_4H_9)_4N]_3[V(NCS)_6]$. The potassium salt described in the literature [8] is not sufficiently pure for recording spectra. It is not stable against air oxidation. Tetra-n-butyl-ammonium salts precipitated from aqueous solutions of the potassium salt yield materials which also contain substantial amounts of the oxidized product (vanadyl). To avoid air oxidation the reaction starting from the urea complex must be carried out under nitrogen atmosphere in a closed system with ground joints using oxygen free solvents.

The complex, $[V(urea)_6](ClO_4)_3$ (1 g), and KSCN (2.2 g) are dissolved in 10 ml of water (16 mole SCN^- to 1 mole complex). The precipitate formed is some $KClO_4$. The reaction mixture is warmed for 15 min at 40 °C and is extracted by 15 ml ethylacetate. The ethylacetate fraction is separated and evaporated at ca. 30 °C in vacuo. The dry residue is dissolved in water and an aqueous solution of $(n\text{-}C_4H_9)_4N \cdot Br$ (1 g) is added. Pale greenish yellow crystals are formed which are collected on a filter frit, washed with water and dried in vacuo at 10^{-2} Torr during 6 hrs. Recrystallization from any solvent is accompanied by appreciable

Compound	Mp[°C]	Calculated in %					Found in %				
		metal	S(Se)	C	H	N	metal	S(Se)	C	H	N
$[(CH_3)_4N]_4[Mn(NCS)_6]$	>280[a]	7.85	27.48	37.75	6.91	20.01	7.85	27.29	37.62	6.94	19.73
$[(C_6H_5)_4As]_2[Mn(NCS)_4]$	213	5.21	12.17	59.26	3.83	5.32	5.00	12.22	59.25	3.96	5.49
					As:	14.22				As:	14.30
$[(CH_3)_4N]_4[Mn(NCSe)_6]$	250[a]/279	5.60	48.27	26.93	4.93	14.27	5.80	47.93	26.91	5.28	14.15
cat[b]$[Mn(NCSe)_4]$	224	4.98	28.62	52.24	3.47	5.08	4.87	28.45	52.44	3.45	5.20
					P:	5.61				P:	5.41
$[C_{16}H_{33}(CH_3)_3N]_2[Mn(N_3)_4]$		6.93	—	57.62	10.69	24.76	7.00	—	57.47	10.50	24.85
$[V(urea)_6](ClO_4)_3$		7.18	—	10.15	3.41	23.69	7.31	—	10.29	3.30	23.66
					Cl:	11.99				Cl:	15.23
$[(C_4H_9)_4N]_3[V(NCS)_6]$	155	4.52	17.07	57.56	9.66	11.19	4.66	16.93	57.44	9.89	11.35
$[(C_4H_9)_4N]_3[V(NCSe)_6]$	114[a]/120	3.62	33.64	46.06	7.73	8.95	3.73	34.00	45.98	7.80	8.90
$[(CH_3)_4N]_3[VO(NCS)_5]$		8.79	27.65	35.22	6.26	19.33	9.32	27.74	34.60	5.92	19.27
$[(CH_3)_4N]_3[In(NCS)_6]$		16.74	28.06	31.53	5.29	18.38	16.85	27.92	31.64	5.39	18.18

[a] Beginning decomposition, [b] cat = $[(C_6H_5)_3P \cdot CH_2 \cdot C_6H_4 \cdot CH_2 \cdot P(C_6H_5)_3]^{2+}$.

Table 1. Elementary analyses.

---

[*] p-xylylene-bis(triphenylphosphonium).

[5] D. Forster and D. M. L. Goodgame, Inorg. Chem. **4**, 1712 [1965].

[6] D. Forster and D. M. L. Goodgame, J. Chem. Soc. **1965**, 268.

[7] W. Beck, W. P. Fehlhammer, P. Pöllmann, E. Schuierer, and K. Feldl, Chem. Ber. **100**, 2335 [1967].

[8] A. Rosenheim, E. Hilzheimer, and J. Wolff, Z. anorg. allg. Chem. **201**, 162 [1931].

[9] G. A. Barbieri, Atti Accad. naz. Lincei (5) **24**, 435 [1915].

decomposition. The product is stored under nitrogen. The crystals keep only few hours on air exposure.

$[(n\text{-}C_4H_9)_4N]_3[V(NCSe)_6]$. The preparation follows that for the corresponding thiocyanate complex. Here the urea compound, $[V(urea)_6](ClO_4)_3$ (0.5 g), and KSeCN (1.22 g) are dissolved in 10 ml of water. The mixture is extracted with 20 ml ethylacetate. The precipitation with $(n\text{-}C_4H_9)_4N \cdot Br$ yields an oil which solidifies after few minutes. Red crystals which decompose when being exposed to air.

The tetraphenylarsonium salts crystallize better than the corresponding tetrabutylammonium compounds, and do not show any infrared absorptions due to VO^{2+} stretching modes. However, they are less suitable for recording electronic spectra because of the strong cation absorption in the near ultraviolet (see e. g. Fig. 1). The preparation of, e. g., $[(C_6H_5)_4As]_3$ $[V(NCSe)_6]$ is different from that of the tetrabutylammonium salt. To a suspension of the urea complex (0.5 g) and KSeCN (0.68 g) in CH_2Cl_2 (30 ml) solid $(C_6H_5)_4AsCl$ (0.7 g, i. e. 80% of the theoretical amount) is added. The solution turns red and is stirred at room temperature for 40 min. After removing some residue the solution is treated with petrol ether which produces bright red crystals. The corresponding thiocyanate is yellow.

$[(n\text{-}C_4H_9)_4N]_3$ $[V(N_3)_6]$. A solution of NaN_3 (5.9 g) in water (15 ml) is reacted in nitrogen atmosphere with VCl_3 (0.2 g) under stirring. A dark brown suspension is formed immediately which transforms quickly to an orange solution while the evolution of a gas can be observed. After filtration the solution is reacted with $(n\text{-}C_4H_9)_4N \cdot Br$ (1.5 g in 5 ml of H_2O). Pink or light brown crystals are formed which are collected in a glass filter. The product decomposes on recrystallization. Therefore coprecipitated amounts of NaN_3 or $(n\text{-}C_4H_9)_4N \cdot N_3$ cannot be removed. However, these residues do not seriously interfere when recording the reflectance spectrum. Exposure to water or air yields green decomposition products. Freshly prepared materials show hardly any vanadyl absorptions in the infrared. The decomposed green substances display electronic absorption spectra which are identical with BECK's[7] $[VO(N_3)_4]^{2-}$ compound.

The vanadyl-thiocyanate, selenocyanate, and azide complexes are prepared except for minor variations according to methods given in the literature[7, 10, 11]. The azido complex freshly precipitated with n-cetyltrimethylammonium shows a light green colour which changes to dark green when it is dried. This colour is reported for this compound[7].

$[(CH_3)_4N]_3$ $[In(NCS)_6]$. The preparation follows common procedures given for thiocyanate complexes[2, 6]. A typical process starts from an ethanol solution of $InCl_3 \cdot 4\,H_2O$ (0.5 g) and KSCN (0.5 g). After removing KCl the filtrate is poured into a hot solution of $(CH_3)_4N \cdot SCN$. The white crystalline product is collected in a glass filter, washed with ethanol and dried over silica gel.

(b) Electronic spectra. Absorption spectra are recorded at room temperature on a Cary spectrophotometer, Model 14. The solutions had molar concentrations between 10^{-2} and 10^{-5} in various inert solvents. Reflectance spectra are taken on a manual instrument, Beckman DU, Model G 2400. As reference $BaSO_4$ of analytical grade is used in all cases. Samples sensitive to air exposure are measured in purified nitrogen atmosphere.

(c) Infrared spectra. The infrared spectra in nujol suspension or in KBr disks are recorded on a Perkin-Elmer grating infrared spectrophotometer, Model 521.

(d) Analyses. The analyses have been carried out at the Laboratoire Microchimique, Dr. Eder, Ecole de Chimie, University of Geneva.

Results and Discussions

In Table 2 the positions and assignments of the bands in the diffuse reflectance spectra for the visible, near infrared, and ultraviolet region are listed. The assignments are made by comparison with the spectra of other Mn^{II}- and V^{III}-complexes[4, 12] which have been interpreted on the basis of crystal field or molecular orbital calculations. The states in the energy level scheme are classified according to tetrahedral and octahedral group theoretical symbols, respectively, because these symmetries are usually realized in 4 : 1 and 6 : 1 complexes of Mn^{II} and V^{III}. Since furthermore the TANABE and SUGANO diagrams[13] are symmetric for octahedral and tetrahedral d^5 systems the level scheme for Mn^{II} complexes is identical for both symmetries except for the lack of parity in the tetrahedral case. The assignment of the charge transfer bands follows the newly established orbital energy order given by SCHATZ et al.[14] for low spin Fe^{III} complexes which agrees with that derived theoretically from pure topological considerations[15, 16].

For vanadyl complexes symbols of irreducible representations of the C_{4v} group are used although the symmetry of VOL_4 is indeed lower. This is justified by the fact that both types of complexes, VOL_5 and VOL_4, have very similar spectra, in general show-

---

[10] J. L. BURMEISTER and L. E. WILLIAMS, J. Inorg. Nucl. Chem. **29**, 839 [1967].

[11] J. SELBIN, Coordin. Chem. Rev. **1**, 293 [1966].

[12] C. K. JØRGENSEN, Structure and Bonding **1**, 3 [1966].

[13] Y. TANABE and S. SUGANO, J. Phys. Soc. Japan **9**, 766 [1954].

[14] P. N. SCHATZ, A. J. MCCAFFERY, W. SUETAKA, G. N. HENNIG, and A. B. RITCHIE, J. Chem. Phys. **45**, 722 [1966].

[15] H.-H. SCHMIDTKE, J. Chem. Phys. **45**, 3920 [1966].

[16] H.-H. SCHMIDTKE, Coordin. Chem. Rev. **2**, 3 [1967].

Complex	Type of transition mechanism[a]	Assignment (excited state)	Band maxima	Comments
$[(CH_3)_4N]_4[Mn(NCS)_6]$	lf	$^4T_{1g}(G)$	17.0	
		doublet ?	18.9	
		$^4T_{2g}(G)$	21.1	
		$^4A_{1g}$, $^4E_g(G)$	24.0	
		$^4T_{2g}(D)$	26.4	
		$^4E_g(D)$, $^4T_{1g}(P)$	(29)[b]; 31.2	
	ctf	$t_{1u} \rightarrow t_{2g}$	37.2; 39.0	
$[(C_6H_5)_4As]_2[Mn(NCS)_4]$	lf		15.7	Co^{II} impurity ?
		doublet ?	(18.5)	
		$^4T_1(G)$	(19.5)	
		$^4T_2(G)$	21.65	
		$^4A_1$, $^4E(G)$	22.7	
		$^4T_2(D)$	25.0	
		$^4E(D)$	27.0	
	ctf	$t_1 \rightarrow e$	(35)	
			$\sim$ 37	cation absorption
$[(CH_3)_4N]_4[Mn(NCSe)_6]$	lf	$^4T_{1g}(G)$	(16); 17.9	Co^{II} impurity ?
		doublet ?	19.5	
		$^4T_{2g}(G)$	21.9	
		$^4A_{1g}$, $^4E_g(G)$	23.8	
		$^4T_{2g}(D)$	26.3	
		$^4E_g(D)$, $^4T_{1g}(P)$	(29); (32)	
	ctf	$t_{1u} \rightarrow t_{2g}$	(36)	
cat$[Mn(NCSe)_4]$	lf		16.8	Co^{II} impurity
		$^4T_1(G)$	20.2	
		$^4T_2(G)$	21.75	
		$^4A_1$, $^4E(G)$	22.7	
		$^4T_2(D)$	25	
		$^4E(D)$	27	
	ctf	$t_1 \rightarrow e$	33.0; 34	
			37	cation absorption
$[(C_{16}H_{33})(CH_3)_3N]_2[Mn(N_3)_4]$	lf	$^4T_1(G)$	(20.5)	spectrum only poorly resolved
		$^4T_2(G)$	22	
		$^4A_1$, $^4E(G)$	23.3	
		$^4T_2(D)$	(25)	
	ctf	$t_1 \rightarrow e$	41.6	
$[(C_4H_9)_4N]_3[V(NCS)_6]$	lf	singlets ?	(12)	VO^{2+} complex ?
		$^3T_{2g}(F)$	16.5	
	ctf	$t_{1u} \rightarrow t_{2g}$	24.4	
		$t_{2u} \rightarrow t_{2g}$	32.4	
	lf ?	$^3A_{2g}(F)$?	37	
$[(C_4H_9)_4N]_3[V(NCSe)_6]$			13.3	VO^{2+} complex
	ctf	$t_{1u} \rightarrow t_{2g}$	20.6	
		$t_{2u} \rightarrow t_{2g}$	29.2	
			$>$ 40 ?	
$[(C_6H_5)_4As]_3[V(NCSe)_6]$		singlets ?	($\sim$ 12.5)	
	ctf	$t_{1u} \rightarrow t_{2g}$	20.2	
		$t_{2u} \rightarrow t_{2g}$	28.6	
$[(C_4H_9)_4N]_3[V(N_3)_6]$	lf	^1E_g, $^1T_{2g}(D)$	9.2; (10)	
		$^3T_{2g}(F)$	13.3	
		$^3T_{1g}(P)$	19.4	
	ctf	$t_{1u} \rightarrow t_{2g}$	26.4	
		$t_{2u} \rightarrow t_{2g}$	36	
$[(CH_3)_4N]_3[VO(NCS)_5]$	lf	^2E	12.5	
		$^2B_1$	17.3	
		$^2A_1$	24.3	
	ctf	π (NCS) $\rightarrow b_2$	30	
			(36)	
$[(C_4H_9)_4N]_2[VO(NCSe)_4]$	lf	^2E	14.5	
		$^2B_1$	17.5	
		$^2A_1$	(23)	
	ctf	π (NCSe) $\rightarrow b_2$	27.6	
			34	
$[(C_{16}H_{33})(CH_3)_3N]_2[VO(N_3)_4]$	lf	^2E	12.0	
		$^2B_1$	14.8	
		$^2A_1$	(25)	
	ctf	π $(N_3) \rightarrow b_2$	($\sim$ 31); (34)	
$[(CH_3)_4N]_3[In(NCS)_6]$	ctf	$t_{1u} \rightarrow a_{1g}(5s)$	41.4	

[a] lf, ligand field transitions; ctf, charge transfer transitions.

[b] Wave numbers in parantheses indicate only inflections; accurate positions of these transitions are uncertain.

Table 2. Maxima (in kilokaysers: 1 kK = 1000 cm^{-1}) and assignment of the bands in the diffuse reflectance spectra. Charge transfer spectra are recorded for samples diluted with $BaSO_4$.

ing three bands in the region 10 – 30 kK which are characteristic for numerous vanadyl complexes[17].

In Figs. 1 – 4 the diffuse reflectance spectra of particular significance are presented in detail. Various inflections can be detected which are not listed in Table 2. Their origin is uncertain; they can, however, be reproduced and may be considered as real.

Mn^{II} compounds. The ligand field spectra of tetrahedral Mn^{II} thiocyanate and selenocyanate have been measured also by FORSTER and GOODGAME[5, 6]. The spectra of the present work essentially agree with theirs. Small absorptions are also found at 15.7 and 16.8 kK, respectively, which probably are due to impurities of Co^{II}. The corresponding Co^{II} thiocyanate

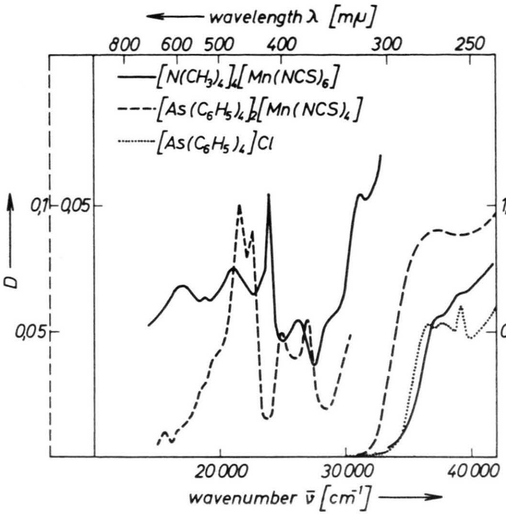

Fig. 1. Diffuse reflectance spectra of Mn(II) thiocyanate complexes, in the visible from pure compounds, in the ultraviolet from dilutions with BaSO$_4$.

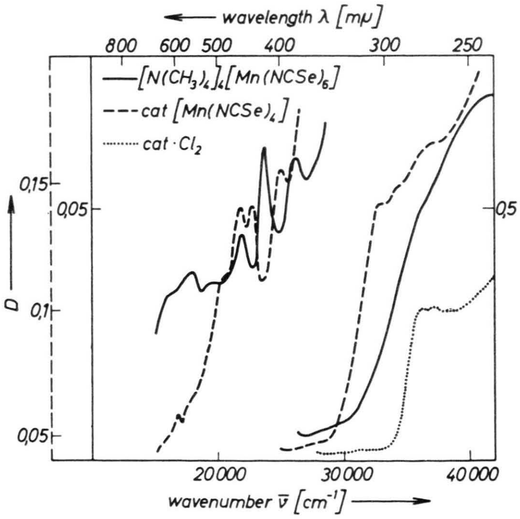

Fig. 2. Diffuse reflectance spectra of Mn(II) selenocyanate complexes. The materials are diluted as described in legend Fig. 1.

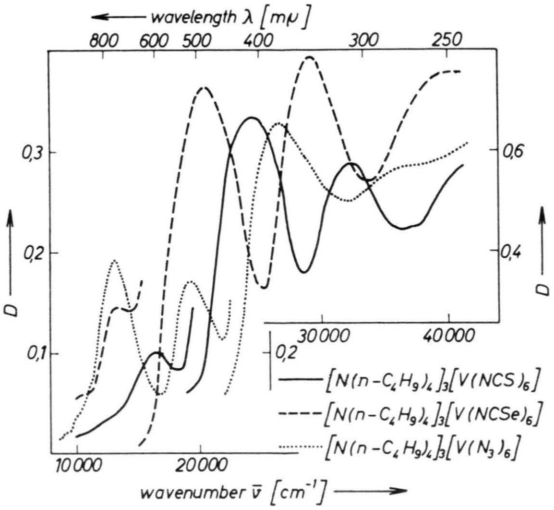

Fig. 3. Diffuse reflectance spectra of V(III) complexes, in the near infrared from pure compounds, in the visible and near ultraviolet from dilutions with BaSO$_4$.

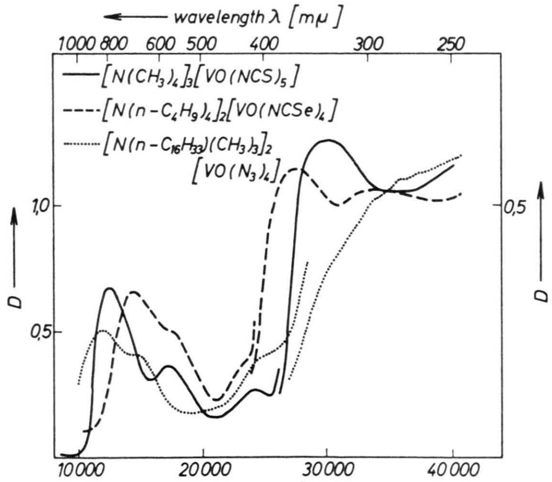

Fig. 4. Diffuse reflectance spectra of vanadyl complexes. The materials are diluted as described in legend Fig. 1.

---

[17] J. SELBIN, Chem. Rev. **65**, 153 [1965].

absorbs strongly (molar extinction coefficients $\varepsilon = 1800$) in this region[18]. The ligand field spectra of these compounds are distinctly different from those of their hexacoordinated counterparts. The latter are characteristic for octahedral high spin d^5 complexes, e. g., the number of bands and their relative intensities are identical with the spectrum of $Mn(H_2O)_6^{++}$ (cf. [4]). Each spectrum is dominated by a sharp, intense band at 24 kK due to the states $^4A_{1g}$ and ^4E_g which in ligand field theory are accidentally degenerate. Since these states and the ground state $^6A_{1g}$ arise from the same subshell configuration, the position of this band is expressed in terms of this theory by parameters of electronic repulsion (Racah parameters) only. This band is therefore a direct measure of the nephelauxetic effect. Indeed, the corresponding transition of the fluoride complex occurs at higher wave numbers (25.3 kK [18]) which indicates a smaller nephelauxetic effect for this ligand. The position of this band in the thiocyanate and selenocyanate spectra is more comparable to that of the chloro complex (23.7 kK). This agrees with the nephelauxetic series where these ligands occupy similar positions. Smaller wave numbers for this transition found in the tetrahedral Mn^{II} complexes, indicate a larger nephelauxetic effect for this molecular symmetry. The octahedral ligand field parameters calculated from Jørgensen's approximative formulae[18] by the use of the better resolved $^4T_{2g}$ bands yield 10.1 kK for the thiocyanate and 8.5 kK for the selenocyanate complex. The corresponding tetrahedral ligand field parameters are smaller. Their actual value cannot be calculated sufficiently accurately by the above approximation. The ligand field spectrum of the Mn^{II} azide complex is only poorly resolved. The assignment is not reliable enough in order to calculate any parameter from this spectrum.

$[(CH_3)_4N]_4[Mn(NCS)_6]$	36.3	(a) 2260	(b) 2300
	37.7	3280	3400
$[(C_6H_5)_4As]_2[Mn(NCS)_4]$	(36)	1650	2000
$[(CH_3)_4N]_4[Mn(NCSe)_6]$	(35)	2500	3450
cat $[Mn(NCSe)_4]$	(34.5)	1600	2900

Table 3. Charge transfer absorption spectra (in kK) of 10^{-3} molar complex solutions. Extinction coefficients are given (a) in pure CH_3CN and (b) in presence of $1.5 \cdot 10^{-2}$ KSCN. Wave numbers in brackets indicate shoulders.

The charge transfer spectra of the tetrahedral thiocyanate and selenocyanate complex are contaminated by large cation absorptions. These transitions are only observed as shoulders or inflections in the spectral curves. Therefore it was tried to measure also solution spectra. Acetonitrile has been found as an appropriate solvent. However, also in this solvent a partial decomposition of the compounds is observed forming equilibria with solvolyzed products. In Table 3 solution spectra are presented of either pure complexes or together with ligand ions added in order to avoid decomposition. The band positions are found withtin the usual limits identical with those measured by diffuse reflectance. The small change of the extinction coefficient for the hexathiocyanate complex on addition of KSCN shows a remarkable stability of this complex in the present solvent. The large variations for the 4 : 1 complexes when adding KSCN or KSeCN, of course, are due to the formation of the hexacoordinated species. Since charge transfer bands of tetrahedral and octahedral high spin d^5 complexes are expected to occur at almost identical positions in the spectrum, all these bands despite of their poor appearance can be considered as genuine in both symmetries. If these transitions are interpreted by a charge transfer from the ligand to the lower subshell of the central ion which is only partially filled by d-electrons, the position of the corresponding bands does not depend on the ligand field parameter[3]. Using Jørgensen's charge transfer formula[19, 20], these charge transfer bands can be calculated in good agreement with the experiment listed in Table 2. The x-parameter ("optical electronegativity") for Mn^{II} used in this calculation is $x(Mn^{II}) = 1.9$ which compares well with other divalent ions of the first transition series[3, 19].

V^{III} compounds. The long wave length region of the thiocyanate and selenocyanate complex is perturbed by absorptions due to the corresponding vanadyl complexes. An oxidation of the tetrabutylammonium salts could not be completely avoided despite various precautions which have been undertaken as described in the experimental section. The 13.3 kK band of the selenocyanate certainly originates from the vanadyl complex. The corresponding

---

[18] C. K. Jørgensen, Advan. Chem. Phys. **5**, 33 [1963].

[19] C. K. Jørgensen, Orbitals in Atoms and Molecules, Academic Press, London 1962.

[20] H.-H. Schmidtke, Electronic Absorption Spectroscopy in Physical Methods in Advanced Inorganic Chemistry, Ed. by H. A. O. Hill and P. Day, Interscience, London etc. 1968, p. 107.

tetraphenylarsonium salt, however, has only a weak inflection in this region because of its higher stability with respect to air oxidation. The infrared spectra (Table 4) show identical results. While in tetrabutylammonium salts distinct V – O stretches are detected, no such oxidation products are present in the tetraphenylarsonium compounds. Other ligand field bands are assigned in a straightforward way following usual procedures which are common to all octahedral d^2 complexes. The parameters of the semiempirical theory can be calculated only for the azide complex. Using calculated energy levels from GRIFFITH[21] a ligand field parameter $\Delta = 14.3$ kK is obtained, the Racah parameter is $B = 0.47$ kK.

More important, however, are the charge transfer transitions which dominate the near ultraviolet regions of these spectra. In all cases two such absorptions are found. The first parity allowed electron transfer transition is well explained by JØRGENSEN's formula[19, 20] if for V^{III} a x-parameter $x(V^{III}) = 1.8$ is adopted. As it was found earlier[3], in all selenocyanates these transitions occur at longer wave lengths than in corresponding thiocyanates. The second charge transfer transition is found at wave numbers 8 – 10 kK higher than the first. This number is noticeable smaller than the ligand field parameters of these compounds. Therefore the origin of the second band cannot be explained by a transition to a higher d-orbital component. A more likely explanation is a parity allowed transition from lower lying ligand orbitals t_{2u} as it has been proposed by FARADAY measurements in other octahedral complex ions with cyanide ligands[14].

VO^{2+} compounds. An assignment of bands in the electronic spectrum of vanadyl complexes is not yet unambiguously obtained[22, 23]. The ligand field transitions are explained by molecular orbital or crystal field calculations carried out for the aquo ion, $VO(H_2O)_5^{2+}$ (cf. [24, 25]). Solution and crystal spectra of the pentathiocyanate complex are reported earlier[22, 26]. The diffuse reflectance spectrum in addition is recorded by us for the sake of completeness. The results vary only little for different recording techniques. More interesting again are the charge transfer bands. The 30 kK band in the spectrum of the thiocyanate is assigned to a charge transfer transition from the π-bonded thiocyanate ligand to the central metal. The corresponding transition for the selenocyanate is also found at somewhat longer wave lengths. These transitions compare well with the 36.8 kK band which is reported[26] for the cyanide, $VO(CN)_5^{3-}$. A shift by about 6 kK is expected from the difference in the x-parameters which are for the two ligands $x(NCS) = 2.6$ and $x(CN) = 2.8$. Complexes with even higher ligand x-values, e. g. $VO(H_2O)_5^{2+}$ or VOF_5^{3-}, absorb only at 41.7 and 43.0 kK, respectively[17, 24]. These transitions may be due to a promotion of an electron from the oxygen π-orbital to the non-bonding b_2 d-orbital state of V^{IV}. Such an internal vanadyl transition has been recently proposed[23] to occur already in the region at 16 – 17 kK, however, this needs further experimental verification.

If the charge transfer formula[19, 20] is applied to the present vanadyl complexes, an "optical electronegativity" parameter of $x = 1.5$ must be used for V^{IV} to explain the results. This value, however, compares badly with the parameter determined for the V^{III} ion, i. e. $x(V^{III}) = 1.8$. Usually a red shift is observed for such charge transfer transitions if the ionic charge of the central ion is increased. This is expressed in the above formula by a larger x-value for higher oxidized ions. A straightforward explanation for the reverse order is obtained if the vanadyl ion is considered as an entity such that the electron is transferred to a molecular orbital essentially belonging to the "vanadyl molecule" which bears only two formal charges. A theoretical treatment of $VOL_4^{n\pm}$ complexes by a procedure which would be equivalent to the method "molecules in molecules" was already carried out by SELBIN, HOLMES and MCGLYNN[27]. This explanation suggests that the x-parameters should be called "optical orbital energy parameters" rather than electronegativities. The notation is also evident from the interpretation of the charge transfer bands in thiocyanate complexes[28].

---

[21] J. S. GRIFFITH, The Theory of Transition-Metal Ions. Cambridge University Press, 1961.

[22] H. A. KUSKA and M. T. ROGERS, Inorg. Chem. **5**, 313 [1966].

[23] J. SELBIN, G. MAUS, and D. L. JOHNSON, Proc. IX. I.C.C.C., St. Moritz, Ed. by W. SCHNEIDER, Verlag Helvetica Chimica Acta, Basel 1966, p. 130.

[24] C. J. BALLHAUSEN and H. B. GRAY, Inorg. Chem. **1**, 111 [1962].

[25] E. WENDLING, Bull. Soc. Chim. France **1968**, 35.

[26] J. R. WASSON, J. Inorg. Nucl. Chem. **30**, 171 [1968].

[27] J. SELBIN, L. H. HOLMES, JR., and S. P. MCGLYNN, J. Inorg. Nucl. Chem. **25**, 1359 [1963].

[28] H.-H. SCHMIDTKE, Proc. XI. I.C.C.C., Haifa, Ed. by M. CAIS, Elsevier Publishing Company, Amsterdam 1968, p. 509.

In^{III} compound. The only band found in the spectrum of the In^{III} thiocyanate is due to a charge transfer transition. Since all d-orbitals are occupied, the electron is promoted to a higher shell which may be assigned to the 5s state. From this band an optical orbital energy parameter for In^{III} is determined: $x(\mathrm{In^{III}}) = 1.2$. This parameter is in perfect agreement with the corresponding values [19] $x(\mathrm{Sn^{IV}}) = 1.5$ and $x(\mathrm{Sb^{V}}) = 1.8$ of isoelectronic ions. The parameters show a uniform increase for rising charges of the central ion.

In Table 4 principle bands in the infrared spectra are listed which are characteristic for the bonding properties of the thiocyanate and selenocyanate ligands. In all compounds C – N, C – S(Se) stretches and NCS(Se) deformation modes indicate that the ligands are attached to the central ion through their nitrogen atoms. This agrees well with the results obtained from the electronic spectra of these compounds. Linkage properties are accordingly determined from charge transfer transitions by different optical orbital energy parameters for N- and S(Se)-bonded thiocyanates (selenocyanates) [3]. The charge transfer bands of the present compounds are only correctly predicted if the parameter $x = 2.6$ is used for the two ligands. This value is characteristic for N-bonded, i. e. isothiocyanate and isoselenocyanate isomers.

VO stretching frequencies detected in V^{III} compounds demonstrate the purity of these compounds and their resistance to air oxidation. It is seen that tetrabutylammonium salts although all precautions have been made during the preparation, are in all cases contaminated by the vanadyl complex while tetraphenylarsonium compounds do not show signs of the oxidized product. For the azide complexes the internal ligand vibrations are also listed in the table.

Acknowledgements

The authors are grateful to Mr. B. Dusonchet for his experimental assistance and to Mr. M. P. Ruch for recording the infrared spectra. One of us (H.-H. S.) appreciates the financial support of the Deutsche Forschungsgemeinschaft.

Complex	C—N stretch	C—S(Se) stretch	NCS(Se) def.	V=O stretch	M—N stretch	Medium	Lit.
$[(C_4H_9)_4N]_3[V(NCS)_6]$	2120 mw, 2070 vs[a], 2065 vs	—[b]	480 m, sp	958 mw	330 s	KBr	
	2125 mw, 2085 sh, 2073 vs, 2062 vs	—[b]	482 m, sp, 472 vw	960 mw	340 s	nujol	
$[(C_6H_5)_4As]_3[V(NCS)_6]$	2058 vs		—[b]	—	342 s	nujol	
$[(C_4H_9)_4N]_3[V(NCSe)_6]$	2073 vs, 2059 vs	681 m, 664 m	442 m, sp	963 m	308 s	KBr	10
$[(C_6H_5)_4As]_3[V(NCSe)_6]$	2059 vs	—[b]	442 mw	—		nujol	
$[(CH_3)_4N]_3[VO(NCS)_5]$	2080 vs	820 vw	482 m	950 s	~ 340 s	KBr	26
$[(C_4H_9)_4N)_2[VO(NCSe)_4]$	2052 vs, 2071 vs	680 m, 600 s	495m, 485 sh, 450 w	1000 s		nujol	10
$[(CH_3)_4N]_3[In(NCS)_6]$	2085 vs, 2030 w	815 w	475 m, 451 w	—		KBr	
Azides	N_3: ν_3 (asym. str.)	ν_1 (sym. str.)	ν_2 (def.)	V=O stretch		Medium	Lit.
$[(C_4H_9)_4N]_3[V(N_3)_6]$	2095 w, 2040 s, br	1342 m, 1287 w	641 m, sp	970 w, br		nujol	
$[C_{16}H_{33}(CH_3)_3N]_2[VO(N_3)_4]$	2100 sh, 2070 vs, 2025 w	1345 s, 1292 m	655 w	965 s		nujol	7
$[C_{16}H_{33}(CH_3)_3N]_2[Mn(N_3)_4]$	2075 vs, 2060 vs, 2046 vs	1332 m	640 m, 617 m	—		nujol	7

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

[b] Covered by cation absorptions.

Table 4. Prominent infrared bands (in cm^{-1}).