*Contribution from the *Cyanamid European Research Institute, 1223 Cologny, Geneva, Switzerland. **Institut für physikalische Chemie der Universität, 6 Frankfurt/Main 1, Germany.*

The Magnetic Properties of Transition Metal Pseudohalide Complexes. The Significance of the Orbital Reduction Factor k

J. J. Salzmann* and H. H. Schmidtke**

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The temperature dependence of the magnetic susceptibilities of some pseudohalide (SCN^-, $SeCN^-$, N_3^-) complexes of transition metals has been measured. The data together with others reported in the recent literature are interpreted by the theory of Lewis and Figgis. The physical significance of the orbital reduction factor is discussed. The variation of this factor due to chemical bonding and its relation to electron repulsion and spin-orbit coupling parameters is investigated.

Introduction

In systematic studies of the electronic structure of transition metal complexes magnetic data are used[1,2] to support the results of spectroscopic investigations. When the parameters of semi-empirical theories are not accessible by spectroscopic methods magnetic measurements can serve as a complement for the determination of these parameters. The study of the magnetic properties of 4:1 and 6:1 pseudohalide complexes ML_4, ML_6 ($L = NCO^-, NCS^-, NCSe^-, N_3^-$) is extended to an investigation of the temperature dependence of the paramagnetic susceptibility of totally 36 compounds. Since only very few magnetic data of pseudohalide complexes have been interpreted so far by the theory of Figgis and Lewis,[1,2] the present paper reports some parameters of this theory for these compounds. For A- and E-ground terms the orbital reduction factor k is determined by a formula which is derived from an intermixing of the ground state with excited states by spin-orbit coupling. For T-terms also components of low symmetry ligand fields Δ and the spin-orbit coupling parameters λ can be determined if experimental temperature curves are compared with curves calculated from theory.[3-5] Conclusions are drawn from these parameters on the electronic and molecular structure of paramagnetic pseudohalide complexes. In particular the significance of the orbital reduction factor (« electron delocalization parameter ») k is investigated and related to the nephelauxetic effect which is derived from spectroscopic data indicating also electron delocalization effects in coordination compounds.[6]

Experimental Section

Materials. The compounds have been prepared according to methods given in the literature;[7-11] they have been analyzed and their uv/vis- and/or ir-spectra have been recorded.

All V^{III}-complexes, $[(CH_3)_4N]_3Mo(NCSe)_6$, and $[(C_4H_9)_4N]_3Ru(N_3)_6$ had to be handled and measured in a nitrogen atmosphere. $[(C_4H_9)_4N]_3V(N_3)_6$ crystallized with a variable amount of NaN_3. The magnetic and analytical data of this compound have been measured on the same day using the same sample so that variations are excluded as far as possible.

Magnetic susceptibility measurements. The measurements have been carried out by the Gouy-method using a magnet (V-4004, VARIAN) with 1.5 inches conical poles and a current stabilisator (V-2301 A, VARIAN). The forces on the sample were measured by a servo-balance system. Calibrations were made with $CuSO_4 . 5H_2O$[12] and $HgCo(NCS)_4$.[13] The measurements were taken at different magnetic field strengths varying from 3200 to 11000 oersted. The temperature from 90 to 300°K could be stabilized within 0.1° over the whole range. The accuracy of the magnetic susceptibility values is about 2%

The experimental magnetic data are presented in Table I, and Figure 1-4, together with some data taken from recent literature which are necessary for calculating various parameters of the theory. Values of the magnetic moment μ_{eff} were calculated from the expression $\mu_{eff} = 2.84(\chi_M{}^c . T)^{1/2}$ where $\chi_M{}^c$ is the molar susceptibility corrected by diamagnetic contributions using the data of Landolt-Börn-

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* New address: Sandoz A. G., Basel, Switzerland.

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(2) B. N. Figgis, Introduction to Ligand Fields, Interscience Publishers, New York, 1966.

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stein,[14,15] and T is the temperatures in °K. The Weiss-constant Θ was determined graphically ($1/\chi_M^c = f(T)$), the magnetic moment $\mu(\Theta)$ was calculated by the Curie-Weiss formula $\mu(\Theta) = 2.84[\chi_M^c(T-\Theta)]^{1/2}$.

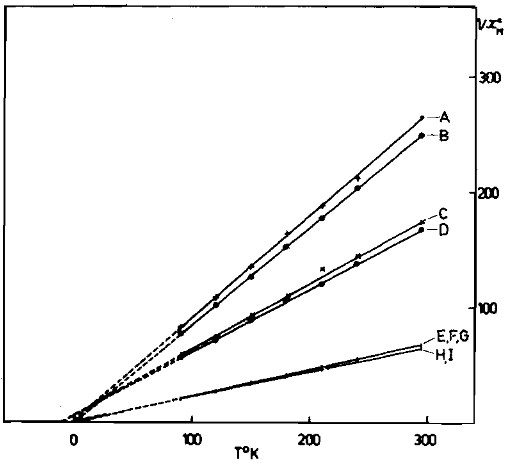

Figure 1. Plots of $1/\chi_M^c$ against temperature for complexes with A-ground terms

in Figure 1 and 2:

A. $[(CH_3)_4N]_4Ni(NCSe)_6$
B. $[(CH_3)_4N]_4Ni(NCS)_6$
C. $[(CH_3)_4N]_3Mo(NCSe)_6$
D. $[(C_4H_9)_4N]_3Cr(N_3)_6$
E. $[(CH_3)_4N]_4Mn(NCS)_6$
F. $[(CH_3)_4N]_4Mn(NCSe)_6$
G. $[(CH_3)_4N]_4Fe(NCS)_6$
H. $(Ph_4As)_2Mn(NCS)_4$
I. $[(Ph_3P{-}CH_2)_2C_6H_4]Mn(NCSe)_4$

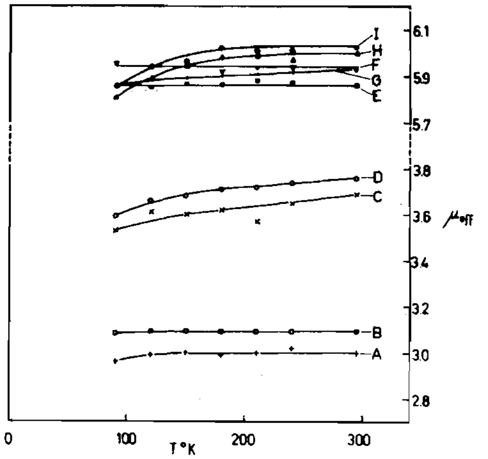

Figure 2. Plots of μ_{eff} against temperature for complexes with A-ground terms.

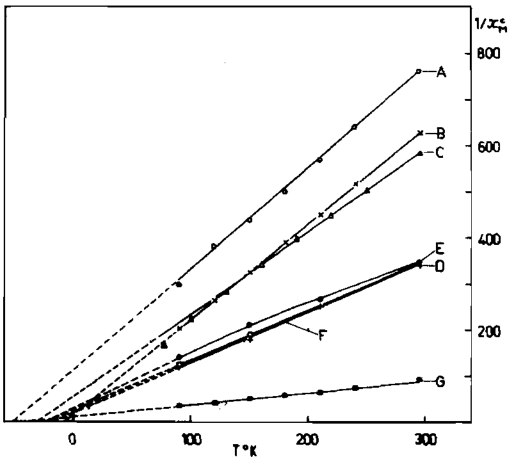

Figure 3. Plots of $1/\chi_M^c$ against temperature for complexes with T-ground terms

in Figure 3 and 4:

A. $[(C_4H_9)_4N]_3Os(NCS)_6$
B. $[(C_4H_9)_4N]_3Ru(N_3)_6$
C. $[(C_4H_9)_4N]_3Ru(NCS)_6$
D. $(Ph_4As)_3V(NCS)_6$
E. $(Ph_4As)_3V(NCSe)_6$
F. $[(C_4H_9)_4N]_3V(N_3)_6$
G. $[(CH_3)_4N]_4Co(NCSe)_6$

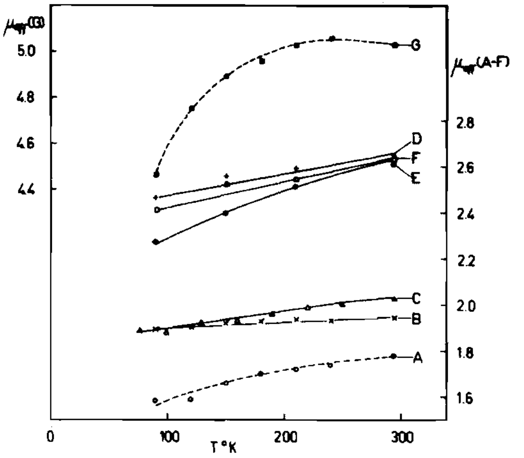

Figure 4. Plots of μ_{eff} against temperature for complexes with T-ground terms (solid lines are theoretically calculated curves).

Parameters calculated from the data listed in Table I are compiled in Table II A and II B. If magnetic data of one and the same ion but with different cations are reported, a mean value of those compounds was taken as basis for the calculation which guarantee a sufficient magnetic dilution of the paramagnetic species. For complexes with A- or E-ground terms (Table II A), the orbital reduction factor k has been calculated from[2]

$$\chi_M^c = \chi_o\left(1 - \frac{\alpha\lambda_o k^2}{|10Dq|}\right) + \frac{\alpha N\beta^2 k^2}{|10Dq|} \qquad (1)$$

which considers the mixing of higher terms into the ground term by spin-orbit coupling and the second order Zeeman effect. The symbols of this formula are explained by: χ_M^c the corrected experimental molar susceptibility; χ_o the spin-only value of the susceptibility for the same temperature; λ_o the spin-orbit coupling constant of the free ion; 10Dq d-orbital energy difference in cubic symmetry; $N\beta^2$ is 0.261; $\alpha = 4$ for E-terms, $= 8$ for A-terms.

In all calculations the second order Zeeman effect has been also accounted for. The accuracy of the k-values is some ±5% if an upper error limit of ±10% is assumed for the differences $\chi_M^c - \chi_o$. Howe-

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(14) Landolt-Börnstein, Numerical data, New Series, II/2, Springer, Berlin, 1966.

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Table I. Magnetic data

Compound	Lit.	T°K	$\chi_M^c \times 10^6$	μ_{eff}	Θ	$\mu(\Theta)$	diam.corr.$\times 10^6$
$(NH_4)Ti(NCS)_4$	16	293	420	0,99			
$K_3V(NCS)_6 . 4H_2O$	17	292.6	2980	2.64			
		181.0	4309	2.50			
		82.2	8049	2.30			
$(Ph_4As)_3V(NCS)_6$		295	2929	2.64	—18	2.72	—856
		210	3968	2.59		2.70	
		150	5587	2.59		2.74	
		90	8337	2.46		2.70	
$(Ph_4As)_3V(NCSe)_6$		295	2863	2.61	—21	2.70	—916
		210	3717	2.51		2.63	
		150	4739	2.39		2.55	
		90	7087	2.27		2.52	
$[(C_4H_9)_4N]_3V(N_3)_6$		295	2885	2.62	—23	2.72	—709
		150	5249	2.52		2.70	
		90	8001	2.41		2.70	
$K_3Cr(NCS)_6 . 4H_2O$	18	295.2	6046	3.79	—2		
		197.9	8949	3.78			
		82.1	21110	3.74			
$[(C_4H_9)_4N]_3Cr(N_3)_6$		295	5961	3.76	—12	3.84	—710
		240	7246	3.74		3.84	
		210	8251	3.72		3.84	
		180	9455	3.71		3.83	
		150	11187	3.68		3.83	
		120	13825	3.66		3.84	
		90	17789	3.59		3.82	
$K_3Mo(NCS)_6 . 4H_2O$	18	297.5	5971	3.78	—3		
		193.1	9059	3.76			
		79.8	21500	3.72			
$(NH_4)_3Mo(NCS)_6 . 4H_2O$	19	295		3.70			
$(NH_4)_3Mo(NCS)_6 . EtOH, H_2O$	19	295		3.80			
$(pyH)_3Mo(NCS)_6$	20	297		3.86			
$(pyH)_2Mo(NCS)_6$	20	297		2.45			
$[(CH_3)_4N]_3Mo(NCSe)_6$		295	5714	3.69	—12	3.76	—450
		240	6887	3.65		3.75	
		210	7507	3.57		3.68	
		180	8993	3.62		3.74	
		150	10718	3.60		3.75	
		120	13477	3.61		3.79	
		90	17094	3.53		3.76	
$K_4Mn(NCS)_6 . 3H_2O$	21	291		6.06			
$[(CH_3)_4N]_4Mn(NCS)_6$		295	14719	5.93	0		—432
		240	18248	5.94			
		210	20747	5.94			
		180	24096	5.92			
		150	29239	5.94			
		120	36496	5.94			
		90	48780	5.95			
$[(CH_3)_4N]_4Mn(NCSe)_6$		295	14432	5.86	0		—492
		240	17825	5.88			
		210	20398	5.88			
		180	23697	5.86			
		150	28425	5.86			
		120	35413	5.85			
		90	47170	5.85			
$[(C_2H_5)_4N]_2Mn(NCO)_4$	22	296		5.98			
$(Bu^nPh_3P)_2Mn(NCS)_4$	10	296	14660	5.92			
$(Ph_4As)_2Mn(NCS)_4$		295	15129	6.00	—4	6.04	—578
		240	18446	5.97		6.02	
		210	21098	5.98		6.03	
		180	24625	5.98		6.04	
		150	29207	5.94		6.02	
		120	35840	5.89		5.98	
		90	46276	5.80		5.92	
$(cat^{2+})Mn(NCSe)_4$	11	298		6.07			
		118		6.07			
$[(Ph_3PCH_2)_2C_6H_4]Mn(NCSe)_4$		295	15291	6.03	—6	6.09	—583
		240	18580	6.00		6.07	
		210	21339	6.01		6.09	
		180	24951	6.02		6.11	
		150	29407	5.96		6.08	
		120	36444	5.94		6.08	
		90	47115	5.85		6.03	

Table I. (Continued)

Compound	Lit.	T°K	$\chi_M^c \times 10^6$	μ_{eff}	Θ	$\mu(\Theta)$	diam.corr. $\times 10^6$
$K_2Re(NCS)_6$	23	299	3550	2.93	−149	3.58	
		197	4690	2.73		3.61	
		78	7110	2.12		3.61	
$Ag_2Re(NCS)_6$	23	299	3700	2.99	−212	3.90	
		197	4680	2.73		4.02	
		78	6470	2.02		3.89	
$Tl_2Re(NCS)_6$	23	298	4510	3.29	−41	3.51	
		197	6740	3.27		3.57	
		78	13120	2.88		3.55	
$[(CH_3)_4N]_3Fe(NCS)_6$	10	295	14707	5.92			
		295	14787	5.93	0		−376
		240	18061	5.91			
		210	20632	5.91			
		180	23990	5.90			
		150	28693	5.89			
		120	35742	5.88			
		90	47035	5.85			
$Na[(CH_3)_4N]_2Fe(N_3)_6$	24	292	14058	5.85	−6	5.86	
		195	20710	5.84			
		77	51865	5.90			
$[(C_2H_5)_4N]_2Fe(NCS)_4$	10	294	12370	5.42	−15	5.54	
		100	33333	5.18		5.55	
$(cat^{2+})Fe(NCSe)_4$	11	290	12009	5.30	−7	5.36	
		98	33898	5.17		5.36	
$[(C_4H_9)_4N]_3Ru(NCS)_6$		296	1703	2.02	−32	2.12	−854
		250	1977	2.00		2.12	
		220	2222	1.99		2.12	
		190	2503	1.96		2.11	
		160	2889	1.93		2.11	
		130	3509	1.92		2.14	
		100	4370	1.88		2.15	
		77	5763	1.89		2.25	
$[(C_4H_9)_4N]_3Ru(N_3)_6$		295	1598	1.95	−8	1.97	−722
		240	1929	1.93		1.96	
		210	2219	1.94		1.97	
		180	2564	1.93		1.97	
		150	3073	1.92		1.98	
		120	3772	1.91		1.97	
		90	4921	1.89		1.97	
$[(C_4H_9)_4N]_3Os(NCS)_6$		295	1329	1.78	−51	1.93	−866
		240	1570	1.74		1.92	
		210	1745	1.72		1.92	
		180	1984	1.70		1.92	
		150	2273	1.66		1.92	
		120	2609	1.59		1.90	
		90	3443	1.58		1.98	
$(Ph_4As)_3Os(N_3)_6$?		295		1.11			
		90		0.97			
$[(CH_3)_4N]_4Co(NCSe)_6$		295	10644	5.03	−38	5.35	−490
		240	13238	5.06		5.45	
		210	14916	5.03		5.46	
		180	16919	4.96		5.45	
		150	19707	4.89		5.46	
		120	23277	4.75		5.44	
		90	27418	4.46		5.32	
$K_2Co(NCO)_4$	25	300	7509	4.26	−8	4.32	
		194	11340	4.22		4.30	
		72	28395	4.06		4.28	
$[(C_6H_5)_3(C_4H_9)P]_2Co(NCO)_4$	25	297	8034	4.38	−8	4.44	
		195	12120	4.36		4.45	
		73	30135	4.22		4.44	
$K_2Co(NCS)_4$	26	298.3	8142	4.43			
$K_2Co(NCS)_4 . 4H_2O$	26	297.8	8320	4.47	−3	4.49	
		194.6	13140	4.54		4.57	
		74.1	32180	4.39		4.48	
	27	295.3	8570	4.53			
		178.2	13670	4.43			
		78	29410	4.30			
$K_2Co(NCS)_4 . 4H_2O$	28	R.T.		4.96?			
$(NH_4)_2Co(NCS)_4 . 4H_2O$	29	R.T.		4.16?			
$[(CH_3)_4N]_2Co(NCS)_4$	30	297.9	7860	4.34	−7	4.40	
		194.6	11890	4.31		4.39	
		73.4	29812	4.20		4.40	

Table I. (Continued)

Compound	Lit.	T°K	$\chi_M^c \times 10^6$	μ_{eff}	Θ	$\mu(\Theta)$	diam.corr.$\times 10^6$
$[(C_2H_5)_4N]_2Co(NCS)_4$	31	298.2	8451	4.51			
$[(C_2H_5)_4N]_2Co(NCS)_4$	32	298	8720	4.58			
$(Ph_4As)_2Co(NCS)_4$	31	297.5	8429	4.50			
$[(CH_3)_4N]_2Co(NCSe)_4$	33	300	7970	4.39	−8	4.45	
		195	12120	4.36		4.45	
		77	28990	4.24		4.45	
$(Ph_4As)_2Co(NCSe)_4$	33	300	8305	4.48	−9	4.55	
		195	12580	4.44		4.55	
		77	29850	4.31		4.55	
$(Ph_4As)_2Co(NCSe)_4$	31	298.2	8418	4.50			
$[(C_2H_5)_4N]_2Co(NCSe)_4$	31	298.2	8077	4.41			
$(Ph_4As)_2Co(N_3)_4$	25	299	7987	4.39	−6	4.43	
		195	12365	4.40		4.48	
		72	31465	4.27		4.46	
$[(C_2H_5)_4N]_4Ni(NCS)_6$	34	292.5	4480	3.25			
$[(CH_3)_4N]_4Ni(NCS)_6$		295	4003	3.09	0		−429
		240	4917	3.09			
		210	5641	3.09			
		180	6578	3.09			
		150	7884	3.09			
		120	9837	3.09			
		90	13158	3.08			
$[(CH_3)_4N]_4Ni(NCSe)_6$		295	3774	3.00	−2		−489
		240	4715	3.02			
		210	5291	3.00			
		180	6142	2.99			
		150	7446	3.00			
		120	9237	2.99			
		90	12058	2.96			
$[(C_2H_5)_4N]_2Ni(NCO)_4$	22	296	5771	3.71			
		203	8137	3.65			
		89	15600	3.35			
$(Ph_4As)_2Ni(NCO)_4$	35	296	5750	3.69			−470
$[cat^{2+}]Ni(NCS)_4$	34	295.5	5510	3.62			
		182.1	8490	3.53			
		95.1	14770	3.37			
$[cat^{2+}]Ni(NCSe)_4$ [a]	11	290		3.17			
$[(C_2H_5)_4N]_2Cu(NCO)_4$	22	294	1653	1.98			
		121.9	3696	1.91			
$[cat^{2+}]Cu(NCS)_4$	34	297	1400	1.83			

[a] Six-coordinate, bridging NCSe-groups

ver, in some cases the error in k probably is still larger than 5% because of its critical dependence on various parameters (see discussion of k).

For complexes with T-ground states (Table II B), the parameters have been determined by comparing the experimental temperature curves with the calculated curves from the theory of Figgis and Lewis.[3-5] The parameter A adjusts the crystal field effect on the ground state wavefunctions: it is 1.5 for the weak field and 1.0 for the strong field limit, λ is the spin-orbit coupling constant in the complex, Δ describes the splitting of the T-term by low symmetry ligand field components. It has a positive sign when the orbital singlet is the lower term. The ratio Δ/λ is denoted by v.

Compounds of the type $MHg(NCS(Se))_4$ with M being also a transition metal ion have not been considered because of the bridging structure of the pseudohalide ligand.

Discussion of Experimental Data

1. *Complexes with A- and E-Ground Terms.*

a) d^3, $^4A_{2g}$: The magnetic moments of the octahedral

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Table II. Values of measured and calculated parameters for the pseudohalide complexes and others used for comparison. A.) Complexes with A_2— or E-ground terms; B.) Complexes with T-ground terms

A.)

Compound	Ground term	10Dq kK	μ B.M.	T°K	λ_o(cm^{-1})	k	TIP×10^6
$Cr(NCS)_6^{3-}$	$^4A_{2g}$	17.8	3.79	295	91	1.33	127
$Cr(N_3)_6^{3-}$		15.0	3.76	295		1.42	139
$Cr(CN)_6^{3-}$		26.7	3.87	295		0.25	78
$Cr(en)_3^{3+}$		21.9	3.83	302		1.12	95
$Cr(H_2O)_6^{3+}$		17.4	3.80	293		1.07	120
$Cr(NH_3)_6^{3+}$		21.6	3.83	293		1.08	97
$Mo(NCS)_6^{3-}$	$^4A_{2g}$	23.0	3.78	298	280	0.73	91
$Mo(NCSe)_6^{3-}$		23.0	3.76	295		0.84	91
$MoCl_6^{3-}$		19.4	3.79	300		0.64	108
$Re(NCS)_6^{2-}$	$^4A_{2g}$	30.0	3.51	298	1100	0.79	70
$Co(NCO)_4^{2-}$	$^4A_2$	4.15	4.38	297	−172	0.83	503
$Co(NCS)_4^{2-}$		4.55	4.49	298		0.96	459
$Co(NCSe)_4^{2-}$		4.72	4.45	300		0.93	443
$Co(N_3)_4^{2-}$		3.92	4.47	300		0.95	533
$CoCl_4^{2-}$		3.13	4.59	300		0.86	667
$CoBr_4^{2-}$		2.85	4.69	300		0.88	733
CoI_4^{2-}		2.65	4.77	300		0.89	789
$Ni(NCS)_6^{4-}$	$^3A_{2g}$	9.6	3.09	295	−315	0.76	218
$Ni(NCSe)_6^{4-}$		10.0	3.00	295		0.62	209
$Ni(H_2O)_6^{2+}$		8.5	3.24	300		0.92	246
$Ni(NH_3)_6^{2+}$		10.8	3.10	293		0.84	194
$Ni(dmso)_6^{2+}$		7.8	3.26	301		1.00	268
$Fe(NCS)_4^{2-}$	^5E	5.2	5.42	295	−102	1.51	201
$Fe(NCSe)_4^{2-}$		5.4	5.30	290		1.34	193
$FeCl_4^{2-}$		4.0	5.40	293		1.29	261
$FeBr_4^{2-}$		5.1	5.46	293		1.55	205

B.)

Compound	Ground term	λ_o(cm^{-1})	A	k	v	λ(cm^{-1})	Δ(cm^{-1})
$V(NCS)_6^{3-}$	$^3T_{1g}$	105	1.2	0.6	4	100	400
			1.2	0.5	2.0	95	190[17]
$V(NCSe)_6^{3-}$		105	1.2	0.6	2	100	200
$V(N_3)_6^{3-}$		105	1.3	0.6	4	100	400
$Ru(NCS)_6^{3-}$	$^2T_{2g}$	−1180		0.7	−2	−400	800
$Ru(N_3)_6^{3-}$		−1180		0.7	−3	−550	1650
$Ni(NCO)_4^{2-}$	$^3T_1$	−315	1.5	0.8	−3	−150	450
$Ni(NCS)_4^{2-}$		−315	1.5	0.8	−4	−150	600
$Cu(NCO)_4^{2-}$	$^2T_2$	−829		0.7	−3	−420	1260

d^3-compounds are reduced below the spin-only value by spin-orbit coupling effects. This reduction is small for Cr^{III}-complexes because of the small spin-orbit coupling constant, *i.e.* $\lambda_o = 91$ cm^{-1}. The calculated value of μ_{eff} for $Cr(N_3)_6^{3-}$ is 3.84 B.M., which agrees with the experimental value $\mu(\Theta)$ corrected by the Weiss constant. At low temperatures the experimental curve follows a Curie-Weiss law which probably indicates either small exchange interactions or low symmetry components of the ligand field.[36] These effects seem to be more important for $Mo(NCSe)_6^{3-}$, where the Curie-Weiss law is obeyed for the whole temperature range. The calculated value for μ_{eff}, taking 10Dq = 23 kK,[37] is 3.71 B.M. in good agreement with the experimental μ_{eff} = 3.69 B.M.

The Weiss constant of $Re(NCS)_6^{2-}$ is very large[23] so that a proper interpretation of the magnetic behaviour is problematic, although μ_{eff} is in the expected range when a reduction of some 20% of the spin-only moment is taken into account. The temperature dependence follows the Curie-Weiss law.

b) d^5, $^6A_{1(g)}$: Octahedral and tetrahedral high-spin d^5-complexes have susceptibilities with no contribution from the second order Zeeman effect and higher ligand field terms due to spin-orbit coupling effects can be neglected. Therefore magnetic moments are expected to be very close to the spin-only value and are independent of temperature. The experimental values of the mangetic moments for the octahedral Mn^{III}- and Fe^{III}-pseudohalide compounds are indeed

[36] B. N. Figgis, *Trans. Farad. Soc.*, *56*, 1553 (1960).

[37] H. H. Schmidtke, *Ber. Bunsenges. Phys. Chem.*, *71*, 1138 (1967).

very close to 5.92 B.M. and no temperature dependence is found for the magnetic moment. For tetrahedral $Mn(NCS)_4^{2-}$ and $Mn(NCSe)_4^{2-}$ the correct room-temperature magnetic moment is found; however, the expected temperature independence of the moment is not observed. Both complexes show a small departure from the Curie- and also from the Curie-Weiss law in the low temperature range, which cannot be explained by a low symmetry component of the ligand field since this does not affect the $^6A_1$ ground term.[36]

c) d^7, $^4A_2$: Considerable magnetic work on tetrahedral Co^{II}-complexes has been done by various authors.[25-33] The pseudohalide compounds show magnetic moments in the expected range. The free ion spin-orbit coupling constant must be reduced by 10-40% if spectral and magnetic data are to agrec. In these calculations the coupling constant for the complex is determined from a formula which also considers the second order Zeeman term $8N\beta^2/10Dq$, that is generally neglected by various authors. The temperature dependence for these pseudohalide complexes follows a Curie-Weiss law with a Weiss constant $|\Theta|$ smaller than 9°.

d) d^8, $^3A_{2g}$: For $Ni(NCS)_6^{4-}$ ($10Dq = 9.6kK$) ana $Ni(NCSe)_6^{4-}$ ($10Dq = 10kK$) magnetic moments 3.25 B.M. and 3.24 B.M., respectively, are calculated, if the free ion spin-orbit coupling constant $\lambda_o = -315$ cm^{-1} is assumed. Experimental moments 3.09 and 3.00 B.M., respectively, are obtained which still are in the range expected for octahedral Ni^{II}-complexes. Obviously the free ion coupling constant must be reduced by a fairly large amount in order to obtain agreement between theory and experiment. The magnetic moments are rather independent of temperature, the Curie law is obeyed over the whole temperature range.

e) d^6, ^5E: Reported tetrahedral Fe^{II}-complexes with pseudohalide ligands[10,11] show magnetic moments which are considerably higher ($Fe(NCS)_4^{2-}$, 5.42 B. M.; $Fe(NCSe)_4^{2-}$, 5.30 B. M.) than the calculated values of 5.13 and 5.14 B. M., respectively. Also the expected Curie-law behaviour for the temperature dependence is not obtained. A departure from T_d-symmetry is a probable explanation for these results.

2. *Complexes with T- Ground Terms.*

a) d^2, $^3T_{1g}$: Octahedral V^{III}- complexes are expected to show at room temperature a magnetic moment which is slightly lower than the spin-only value. According to the theory for T-ground terms[4] the moments should exhibit a marked temperature dependence only at low temperatures. This behaviour predicted from the theory is found in all three complexes measured . The Weiss constants are large. Different cations of $V(NCS)_6^{3-}$ do not affect the room temperature moment, however, the temperature dependence is less pronounced for salts with large cations.[17] $(Ph_4As)_3$-$V(NCSe)_6$ shows a strong temperature dependence and no Curie-Weiss law is obtained. When examining the different parameters presented in Table II B it is noticed that in each case Δ is positive which indicates that $^3A_{2g}$ is the lowest split level. This is in agreement with other results on d^2-complexes.[17,38] The spin-orbit coupling constants λ do not vary much for all three pseudohalide complexes; the reduction compared to the free ion value is only small. For $V(NCS)_6^{3-}$ and $V(N_3)_6^{3-}$ higher values for Δ (400 cm^{-1}) are found than reported by Machin and Murray in VX_6^{3-} complexes (2-300 cm^{-1}).[17] Due to the larger cation in our compounds the crystal packing is different which by outer sphere effects may give rise to a larger splitting of the $^3T_{1g}$-term by the axial ligand field component.

b) d^5, $^2T_{2g}$: Because of high spin-orbit coupling effects the magnetic moments of Ru^{III}-complexes are expected to be very close to the spin-only value and practically independent on temperature.

It is therefore difficult to determine the low symmetry ligand field component Δ.[39,40] However, in both complexes studied, $Ru(NCS)_6^{3-}$ and $Ru(N_3)_6^{3-}$, a large splitting of the $^2T_{2g}$ ground term is probable such that the orbital singlet is lowest. The free ion spin-orbit coupling constant is essentially reduced. The magnetic moments are only slightly larger than the spin-only value, and for $Ru(N_3)_6^{3-}$ practically no change with temperature is observed in constrast to $Ru(NCS)_6^{3-}$ which also has a markedly larger Weiss constant than the azide complex.

Because of the high spin-orbit coupling constant of Os^{III} a very small ratio $kT/\lambda < 0.1$ is obtained which does not allow to determine any parameter from the calculated curves. The μ_{eff} of $Os(NCS)_6^{3-}$ is slightly larger than the spin-only value and a Curie-Weiss law is obeyed; however, the Weiss constant is so high that the significance of the parameters calculated from this curve is doubtful. The magnetic moment found for the Os^{III} azide complex represents a further indication that this compound cannot be formulated as $Os(N_3)_6^{3-}$, as was already concluded from molar conductivity measurements.[7] Structures with azide-bridges must be discussed for this compound.

c) d^7, $^4T_{1g}$: The complex, $Co(NCSe)_6^{4-}$, shows a magnetic moment at room temperature which is close to the calculated moment for a $^4T_{1g}$-ground term in the weak field limit. Also the predicted strong temperature dependence of the moment is experimentally found. The Weiss-constant is large, which seems to be a general feature for octahedral Co^{II}-complexes.[1] The Curie-Weis law holds over a large temperature range.

d) d^8, $^3T_1$: The experimental results of Forster and Goodgame[22] for $Ni(NCO)_4^{2-}$ and $Ni(NCS)_4^{2-}$ have been used to calculate the parameters presented in Table II B. They are slightly different from those calculated earlier[34] on the basis of data given by Figgis *et.al.*[41] which later have been revised.[4] For $Ni(NCO)_4^{2-}$ a completely different set of parameters than that given in Table II B can be

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(38) B. N. Figgis, J. Lewis, F. Mabbs, *J. Chem. Soc.*, 2480 (1960).
(39) B. N. Figgis, J. Lewis, F. E. Mabbs, G. A. Webb, *J. Chem. Soc.*, 422 (1966).
(40) A. Earnshaw, B. N. Figgis, J. Lewis, R. S. Nyholm, *Nature*, *179*, 1121 (1957).
(41) B. N. Figgis, J. Lewis, F. Mabbs, G. A. Webb, *Nature*, *203*, 1138 (1964).

determined from the experimental curves, i.e. A = 1.5, k = 1.0, v = –5, $\lambda = -215$ cm^{-1} and $\Delta = 1075$ cm^{-1}. However, the latter Δ-value seems to be too large compared to other NiX_4^{2-}-complexes.[4] Both pseudohalide complexes show a considerable reduction of the free ion spin-orbit coupling constant which agrees with other λ- values obtained for tetrahedral Ni^{II}-complexes. The low symmetry component parameter $\Delta = 450$ cm^{-1} for $Ni(NCO)_4^{2-}$ compared with $\Delta = 600$ cm^{-1} in $Ni(NCS)_4^{2-}$ is also in agreement with the larger distortion from T_d-symmetry as derived from electronic- and infrared-spectra for isothiocyanate complexes.[34]

e) d^9, $^2T_2$: The experimental data[22] of $Cu(NCO)_4^{2-}$ can be fitted to the calculated ones[3] by a parameter set presented in Table II B. The large value of Δ obviously is the main reason for the small room temperature magnetic moment which is decreased compared to the value for the pure tetrahedral symmetry.[42] Unfortunately no other temperature curves of the magnetic moment of tetrahedral Cu^{II}-pseudohalides have been reported in the literature.

The Significance of the Orbital Reduction Factor k

Introduction

Until now we omitted the discussion of the orbital reduction or orbital g-factor k[44,45] which has been introduced by Stevens[44] in his theory on the paramagentic properties of octahedral complexes. Later this factor was identified[2,3,38] with a parameter (π-electron delocalization factor) indicating a delocalization of t_{2g}- electrons if π-bonding effects are important. Moreover it has been argued[1-5] that since k allows for the loss of orbital angular momentum (the operator L is replaced by kL), any physically meaningful value of k should occur in the range $0<k\leqq 1$. For $k = 1$ the electrons of orbital type t_{2g} are pure d- electrons which are unperturbed by the neighborhood of the ligands and therefore entirely located on the central atom.

However, for A- and E-ground terms where k can be calculated directly, cf. Eq.(1), also k factors larger than one have been determined experimentally.[2] Such k-values are also found from the present data (Table II A) when applying the corresponding formulae of Lewis and Figgis. Obviously these large k-values cannot be explained by errors arising from poorly determined parameters of optical and magnetic measurements. Even if error limits for k are assumed which are twice as much as those resulting from the critical difference $\chi_M^c - \chi_o$ (see experimental section), the value of k cannot be reduced below one for all compounds investigated. Also, an introduction of spin-orbit coupling constant λ' for the complex substituting $k\lambda_o$ in Eq. (1) does not improve the results: the k-values become even larger. Evidently the small error limit of ±5% which is claimed[5,39] for T-terms is not generally valid. No such extreme values for k are determined for T-ground terms (cf. Table II B) since the parameters for these terms have been obtained in the present work by comparing the experimental curves with those calculated by Lewis and Figgis.

In his original paper, Stevens[44] concludes from molecular orbital theory that k will be less than unity if only π-bonding effects are important. In addition he mentions that no k values are found so far other than in the range lower than one. Also Griffith[43] does not exclude larger k values by saying « in practice they are less than unity ».

We believe that the theory of Lewis and Figgis, *i.e.* a first and second order perturbation on ligand field terms, is a sensible approach and we do not want to question the basic ideas. However, the treatment of covalent bonding and the introduction of the orbital reduction factor in this theory needs some more detailed investigation. Also, the effect of σ-bonding is included in an improved theory. Such σ-bonding modes are in general considered to have larger effects on the electronic structure than π-bonding effects. If a decreased angular momentum represents electron delocalization it should be possible to construct a connection between the parameter k and the nephelauxetic effect[6] which was introduced into ligand field theory to account for certain observations in the optical spectra. Since both theories claim to supply evidence for a delocalization of d-electrons in coordination compounds, corresponding results should be obtained if the concept of « electron delocalization » is of any physical significance in these theories.

Symmetry adapted k-values. Following the theory of Stevens,[44] matrix elements of the angular momentum operator l or of one of its components l_λ, applied on t_2- and e-orbitals which are not necessarily approximate d-orbitals, are represented by d-orbital matrix elements.[43] By the use of the replacement theorem it is obtained

$$\begin{aligned} <t_2\varkappa \mid l_\lambda \mid t_2\mu> &= k_t <d_{t2}\varkappa \mid l_\lambda \mid d_{t2}\mu> \\ <t_2\varkappa \mid l_\lambda \mid e\mu> &= k_e <d_{t2}\varkappa \mid l_\lambda \mid d_e\mu> \\ <e\varkappa \mid l_\lambda \mid e\mu> &= 0 \end{aligned} \tag{2}$$

The latter matrix element is zero since for e-terms the orbital angular momentum vanishes. A corresponding k-factor is therefore not defined. For octahedral symmetry the orbital reduction factor k_t is due to π-electron bonding and k_e is the corresponding factor for a combined σ- and π-bonding effect. In tetrahedral symmetry k_t contains also σ-bonding effects since from symmetry reasons t_2-orbitals have 4/9 σ-bonding, 2/9 π- and the rest δ-bonding character.[46] The k values should not be confused with the metal atomic orbital coefficients introduced in molecular orbital theory by an LCAO approximation, as is occasionally implied in the literature.[3,6] LCAO-coefficients, of course, do not vanish for σ-bonding e-molecular orbitals, whereas all non diagonal elements between e- and t_2-orbitals are zero because of symmetry reasons.[47]

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(42) B. N. Figgis, *Nature*, *182*, 1568 (1958).
(43) J. S. Griffith, The Theory of Transition Metal Ions, Cambridge University Press, Cambridge 1961.
(44) K. W. H. Stevens, *Proc. Roy. Soc.*, *A219*, 542 (1953).
(45) B. Bleaney and M. C. M. O'Brien, *Proc. Phys. Soc. B 69*, 1216 (1956).
(46) H H. Schmidtke, *Z. Naturforschg.*, *19a*, 1502 (1964).
(47) J. Owen, *Discussion Farad. Soc.*, *19*, 127 (1955).

It is, however, possible to express the orbital factors k by corresponding LCAO coefficients and normalization constants. In octahedral symmetry the corresponding t_{2g} - LCAO antibonding molecular orbital (using Owen's[47] numbering of ligand orbitals) is

$$\psi^*_{xy} = N_\pi\{d_{xy} - \frac{1}{2}\eta_\pi(p_y{}^1 + p_x{}^2 - p_y{}^4 - p_x{}^5)\} \tag{3}$$

from which a π-bonding orbital factor ($k_t = k_{\pi\pi}$ for octahedral symmetry)

$$k_{\pi\pi} = 1 - \frac{1}{2}N_\pi{}^2\eta_\pi{}^2 \tag{4}$$

has been calculated already by Steven.[44] The normalization factor

$$N_\pi = (1 - 4\eta_\pi S_\pi + \eta_\pi{}^2)^{-1/2} \tag{5}$$

depends on the π-overlap integral

$$S_\pi = \langle d_{xy} \mid p_y{}^1 \rangle \tag{6}$$

and contains the coefficient η_π which represents the degree of ligand-central metal orbital intermixing if ligand-ligand overlap is neglected.

The calculation of k_e for octahedral symmetry is more complicated. Tinkham[48] has worked out a formula starting from a t_2-wavefunction Eq. (3) and an e-function like

$$\psi^*_{x^2-y^2} = N_\sigma\{d_{x^2-y^2} - \frac{1}{2}\eta_\sigma(-\sigma_x{}^1 + \sigma_y{}^2 + \sigma_x{}^4 - \sigma_y{}^5)\} \tag{7}$$

in which σ represents a hybrid made up of s- and p-functions on the ligands such that the mixing coefficients obey $\eta_\sigma{}^2 = \eta_s{}^2 + \eta_{p\sigma}{}^2$. By using Eq. (2) ($k_e = k_{\sigma\pi}$ for O_h symmetry) the following formula is obtained:

$$\begin{aligned} k_{\sigma\pi} = {} & N_\pi N_\sigma\{1 - 2(\eta_\pi S_\pi + \eta_\sigma S_\sigma) - \\ & - \frac{1}{2}\eta_\pi\eta_{p\sigma} + \frac{1}{2}\eta_\pi\eta_s d \mid \langle p_z \mid \frac{\delta}{\delta z} \mid s \rangle \mid\} \end{aligned} \tag{8}$$

The final term arises from a translation of the angular momentum operator from the central atom to the ligand over a distance of d.

The complexity of this formula makes an evaluation of the range for $k_{\sigma\pi}$ impossible. An equivalent expression is valid for any further intermixing of higher ligand orbitals belonging to the same symmetry type. For instance, the inclusion of π* ligand orbitals in complexes with molecular ligands containing a π-electron system (CN^-, SCN^- etc.) would lead to a corresponding formula for $k_{\pi\pi}$. The consideration of higher orbitals therefore complicates the formulae for k such that the expressions become very soon intractable. However, the formula Eq. (8) is simplified if π-bonding effects are absent, *i.e.* $\eta_\pi = S_\pi = 0$, $N_\pi = 1$. In this case $k_{\sigma\pi}$ contains only σ-bonding parts

$$k_{\sigma 0} = N_\sigma(1 - 2\eta_\sigma S_\sigma) \tag{9}$$

The normalization factor can be formulated in correspondence to Eq. (5) as

$$k_{\sigma 0} = \frac{1 - 2\eta_\sigma S_\sigma}{\sqrt{1 - 4\eta_\sigma S_\sigma + \eta_\sigma{}^2}} \tag{10}$$

One can easily see from the squared expression

$$k_{\sigma 0}{}^2 = \frac{1 - 4\eta_\sigma S_\sigma + 4\eta_\sigma{}^2 S_\sigma{}^2}{1 - 4\eta_\sigma S_\sigma + \eta_\sigma{}^2} \tag{11}$$

that $k_{\sigma 0}{}^2$ assumes values $k \lesseqgtr 1$ independent of η if $S_\sigma \lesseqgtr 1/2$, respectively. This relation is also valid for $k_{\sigma 0}$. Of course, overlap integrals which are of the order of one half are very large for ligand-central metal interactions, *e.g.* in relevant MO-calculations[49,50] on fluoride complexes they are about 0.1; however, large values $S \lesseqgtr 1/2$ are physically in an accessible range and a possible existence should be considered. However, for large ligand-ligand interactions also overlap integrals between ligands become important so that the structure of the mixing coefficient η in Eq. (3) and (7) is changed, which in turn decreases the net ligand-metal overlap effect. Moreover, any reasonable antibonding wavefunction should be orthogonal to its corresponding bond function, *i.e.* if such a pair of functions is given by

$$\begin{aligned} \psi &= N(\chi + \gamma\varphi) \\ \psi^* &= N^*(\varphi - \eta\chi), \end{aligned} \tag{12}$$

then the two mixing parameters are not independent variables, they are connected by the orthogonality condition

$$\eta = \frac{\gamma + S}{1 + \gamma S} \tag{13}$$

where S is a group overlap integral.[48-50] It was shown[49,51] that in the antibonding linear combination η is substituted by γ+S. For octahedral symmetry the η_i-factors of Eq. (3) and (7) are

$$\eta_i = \gamma_i + 2S_i \qquad i = \sigma, \pi. \tag{14}$$

However, this substitution does not affect the discussion on the range of the $k_{\sigma 0}$-factor.

A more detailed calculation of k-factors and the corresponding gyromagnetic factors g was performed by Misetich and Watson[52] and for lower symmetry by McGarvey.[53] Since they consider all possible interactions by including all off-diagonal elements of the L-operator their formulae are too complicated to be used in a semiempirical theory. Their expressions contain many parameters which cannot be determined experimentally. An evaluation of k-factors and delocalization parameters γ_i, N_i from the experiment by neglecting various terms in these expressions is, however, doubtful.

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(48) M. Tinkham. *Proc. Roy. Soc.*, *A236*, 535, 549 (1956).
(49) S. Sugano, R. G. Shulman, *Phys. Rev.*, *130*, 517 (1963).
(50) R. F. Fenske, K. G. Caulton, D. D. Radtke, C. S. Sweeney. *Inorg. Chem.*, *5*, 951, 960 (1966).
(51) S. Sugano, Y. Tanabe, *J. phys, Soc. Japan*, *20*, 1155 (1965).
(52) A. A. Misetich, R. E. Watson, *Phys. Rev.*, *143*, 335 (1966).
(53) B. R. McGarvey, Transition Metal Chemistry, 3, 90 (1966).

In conclusion it may be said that theoretical k-values larger than one may be conceivable; they are, however, unlikely to occur for σ- and/or π-bonding effects due to an intermixing with one ligand orbital only. The situation is more complicated if the central metal orbitals interact with several ligand orbitals at one center. The calculation of k-values from simplified formulae, like *e.g.* Eq. (1), using experimental data yields only effective k-factors which generally result from various molecular orbital k-factors of different origin.

A_2- and E-ground terms. We now introduce the k-values of Eq. (2) into the approximate formulae for the paramagnetic susceptibility of coordination compounds derived by Lewis and Figgis.[1,2] In cubic symmetry A_2- and E-ground terms gain orbital angular momentum by combination with the excited T_2-term by spin-orbit coupling. The susceptibility by the first order Zeeman effect is given by[2,43]

$$\chi = \frac{N\beta^2}{3kT} g^2[J(J+1)] \tag{15}$$

in which the gyromagnetic splitting factor by first order perturbation theory (for the z-direction) is

$$g = \frac{1}{M_J} < \psi_i' \mid L_z + 2S_z \mid \psi_i' > \tag{16}$$

The wavefunction ψ_i' refers to a second order function for the ground state i, which contains T_2-components by combination through the spin-orbit coupling operator $\lambda(L_z \,.\, S_z)$. For A_2-ground terms

$$\psi_i'(A_2) = (1+c^2)^{-1/2}[\psi_i(A_2) - c\psi_j(T_2)] \tag{17}$$

$$c = \frac{M_S}{\mid 10Dq \mid} < \psi_i(A_2) \mid \lambda L_z \mid \psi_j(T_2) > \tag{18}$$

the g-factor becomes

$$g = 2 - \frac{2\lambda}{\mid 10Dq \mid} < \psi_i(A_2) \mid L_z \mid \psi_j(T_2) >^2 \tag{19}$$

The symmetry functions for A_2 and T_2 resulting from F-terms are given by[43]

$$\text{F:} \quad \psi(A_2) = \sqrt{\frac{1}{2}}[\mid 32 > - \mid 3{-}2 >]$$

$$\psi(T_2) = \sqrt{\frac{1}{2}}[\mid 32 > + \mid 3{-}2 >]$$

those for E and T_2 arising from D-terms are

$$\text{D:} \quad \psi(E) = \sqrt{\frac{1}{2}}[\mid 22 > + \mid 2{-}2 >]$$

$$\psi(T_2) = \sqrt{\frac{1}{2}}[\mid 22 > - \mid 2{-}2 >] \tag{20}$$

The functions $\mid L\, M_L >$ are not necessarily atomic wavefunctions, they also may contain molecular orbital wavefunctions of the type given in Eq. (3) and (7). In the latter case L, M_L labels a wavefunction of certain symmetry and orientation in the space that is equivalent to the corresponding atomic function. In each case A_2- or E-terms combine with T_2-terms by the matrix element

$$\begin{aligned} < \psi(E[D]) \mid L_z \mid \psi(T_2[D]) > &= < \psi(A_2[F]) \mid L_z \mid \psi(T_2[F]) > \\ &= \frac{1}{2}[< L2 \mid L_z \mid L2 > - < L{-}2 \mid L_z \mid L{-}2 >] \end{aligned} \tag{21}$$

Using Griffith's nomenclature[43] for real wavefunctions

$$\begin{aligned} &< L \pm 2 \mid L_z \mid L \pm 2 > = \\ &= \pm < E\varepsilon \mid L_z \mid T_2 0 > + \frac{1}{2} < T_2 0 \mid L_z \mid T_2 0 > \end{aligned} \tag{22}$$

the matrix element of Eq. (19) becomes

$$\begin{aligned} &< \psi(A_2) \mid L_z \mid \psi(T_2) > = \\ &< E\varepsilon \mid L_z \mid T_2 0 > = k_c < D_E \mid L_z \mid D_{T2} > \end{aligned} \tag{23}$$

where the symmetry adapted orbital factor k_c defined by Eq. (2) reduces the matrix element of molecular functions into that of atomic functions. Evaluating the matrix elements of D-states in Eq. (23) the g-factor for A_2-ground terms becomes

$$g = 2 - \frac{8\lambda k_c^2}{\mid 10Dq \mid} \qquad (A_2) \tag{24}$$

The correction term to the spin only value for g due to spin-orbit coupling depends on a reduction factor k, which describes a combined σ- and π-bonding effect. Earlier[1-5] this k-factor was interpreted as being entirely due to π-bonding effects of t_2 electrons. The interpretation of the k-factor in terms of σ- and π-bonding effects as discussed in the preceding section is an important result. Since π-electron bonding in general is less pronounced or even negligible compared to σ-bonding effects it is $k_{\sigma 0}$, Eq. (9), that has to be applied (for octahedral symmetry) rather than $k_{\pi\pi}$, Eq. (4), when considering covalent bonding by the orbital reduction technique.

The second order Zeeman-effect leads to an expression containing a matrix element which is identical to that of Eq. (19). Consequently the temperature independent part of Eq. (1)

$$\chi_A = \frac{8Nk_c^2\beta^2}{\mid 10Dq \mid} \qquad (\text{for } A_2) \tag{25}$$

also depends on the combined σ-π-parameter k_c.

T_1-ground terms. In a calculation of the magnetic susceptibility of $T_1[F]$-ground terms the intermixing with the $T_1[P]$-term by crystal field effects has to be considered: Following Figgis *et al.*[4] the second order wavefunction

$$\psi'(T_1) = (1+c^2)^{-1/2}[\psi(T_1[F]) + c\psi(T_1[P])] \tag{26}$$

leads to a matrix element for L_z

$$< \psi'(T_1) \mid L_z \mid \psi'(T_1) > = m_{T1} \,.\, A \tag{27}$$

which is for isotropic k-factors ($k_t = k_e = k$)

$$A = \frac{\frac{3}{2} - c^2}{1 + c^2} k \tag{28}$$

Here $m_{T1} = 0, \pm 1$ labels the three T_1-orbital components. The factor 3/2 arises from the equivalence of T_1- and P-states with respect to the operations L_x, L_y, L_z as shown by Abragam and Pryce.[54] The parameter c varies between zero and $-1/2$ for the weak field and strong field limit, respectively.

The matrix element Eq. (27) for symmetry adapted k-factors is calculated in the same way as shown for A_2- and E-ground terms. The corresponding expression obtained for T_1-ground terms is

$$A = \frac{4/5 k_e (1 - c^2) + 1/5 k_t (7/2 - c^2)}{1 + c^2} \tag{29}$$

The magnetic susceptibility χ_A is calculated from A in the usual way.[2,4] Since A depends on k_e essentially, σ-bonding effects also play an important role in the magnetic properties of T_1-terms that has not been realized before.[4]

T_2-ground terms. Because of the direct correspondence of t_2- and p-functions[43] with respect to the operations L_x, L_y, L_z, the matrix elements

$$< T_2 \varkappa \mid L_\lambda \mid T_2 \mu > \; = \; - < P \varkappa \mid L_\lambda \mid P \mu > \tag{30}$$

can be directly calculated from atomic functions $\mid LM_L \rangle = \mid 1 \pm 1 \rangle$. The matrix element of L_z is directly reduced to atomic terms by

$$\begin{aligned} < T_2 \pm 1 \mid L_z \mid T_2 \pm 1 > \; &= \\ k_t < D_{T2} \pm 1 \mid L_z \mid D_{T2} \pm 1 > \; &= \; \mp k_t \end{aligned} \tag{31}$$

For octahedral T_{2g}-ground terms the orbital reduction factor therefore contains only π-electron delocalization effects. However, it can be shown that expectation values for the other L-components also depend on the $k_{\sigma\pi}$-parameter. Tetrahedral T_2 terms contain both, σ- and π-bonding components, as discussed in the introduction to this chapter. Since an exact differentiation of σ- and π-bonding effects can be made for any orbital from symmetry considerations[46] it is always possible to discuss σ- and π-bonding parts separately, also for tetrahedral symmetry.

The correlation of orbital reduction factors with the nephelauxetic effect. If orbital reduction factors describe electron delocalization of d-orbitals (charge transfer from the central ion into the ligand system) these factors should be related in some way to the electron repulsion (Racah-) parameters. A decrease of these parameters compared to their free ion values is known as the nephelauxetic effect.[6] An attempt to find such a relation was made earlier[39] assuming pure π-delocalization of t_{2g}-electrons in octahedral symmetry. As a result of this theory the delocalization factor $k_{\pi\pi}$ and the nephelauxetic quotient $\beta = B/B^0$ (Racah parameters: B for the compound, B^0 for the free ion) both should decrease continuously with increasing ligand-central metal intermixing coefficients η_π as defined in Eq. (3). Such a behaviour would furnish corresponding results from magnetic and optical data: electron delocalization is manifested by a uniform decrease of the parameters k and β. However, the experimental results in general do not agree with this prediction: experimental k-parameters do not vary[1-5] in the same way as β in a series of complexes of a certain central metal ion with different ligands (such a series of ligands ordered according to decreased values of β is called the nephelauxetic series[55]). This disagreement between theory and experiment is found when comparing th k-values determined by Lewis and Figgis from susceptibility measurements for numerous coordination compounds with the nephelauxetic series[6,55] which is obtained from optical data. For instance, aquo-complexes which usually show small nephelauxetic effects, yield strongly decreased $k_{\pi\pi}$-parameters.[5] For bromide and cyanide complexes the k-factor is not much different from the value for localized d-orbitals[4,39] although these ligands are known to have a large nephelauxetic effect. It is noticed that also the quotient of spin-orbit parameters λ/λ_o varies differently from corresponding k-factors in a series of ligands.[4] The present experimental results lead to similar conclusions. An inspection of Table II shows that for tetrahedral Co^{II} complexes the variation of k with different ligands is very small that no comparison with optical parameters can be made. For octahedral Ni^{II} compounds a uniform variation of k and $\beta = B/B_0$ can be observed. However, for octahedral Cr^{III} and tetrahedral Fe^{II} complexes where k-values larger than one have been determined the order of ligands is reversed. The nephelauxetic series is only followed if instead of k its absolute deviation from one (the value for localized d-orbitals) is considered:

$$\begin{array}{lll} Cr^{III}A_6 & \mid 1-k \mid : & H_2O \sim NH_3 < en < NCS^- < N_3^- < CN^- \\ Fe^{II}A_4 & \mid 1-k \mid : & Cl^- < NCSe^- < NCS^- < Br^- \end{array} \tag{32}$$

Unfortunately no more experimental data on k-factors are available in the literature. The question if such a connection between the nephelauxetic series and the deviation of k from the localized orbital value really exists cannot be answered.

In any case it is doubtful whether decreased k-factors in general represent d-electron delocalization. Such a delocalization is usually understood as a penetration of d-electrons into the ligand system due to an expansion of the free ion orbitals. This corresponds in terms of wavemechanics to an increase of the integral $\langle \psi \mid r \mid \psi \rangle$ when the atomic d-orbitals is substituted by a molecular orbital function. The radius vector r is originated on the central metal. An expansion of orbitals in the electron repulsion integral B can only decrease the value of this integral. Indeed, all the B-parameters determined from experiment are smaller than the corresponding free ion value. Moreover, it is possible to distinguish between different β-quotients from optical data.[56] The β-parameters can

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(54) A. Abragam, M. H. L. Pryce, *Proc. Roy. Soc.*, *A205*, 135 (1951), *A206*, 173 (1951).

(55) C. E. Schaffer, C. K. Jørgensen, *J. Inorg. Nucl. Chem.*, *8*, 143 (1958).

(56) C. K. Jørgensen, Structure and Bonding *1*, 3 (1966).

be correlated to the k_e-, k_t-factors in Eq. (2). For octahedral symmetry three β-parameters are defined depending on the orbitals, e_g and/or t_{2g}, in the electron repulsion integral B. Using Jørgensen's nomenclature[56] the corresponding β- and k-factors are correlated

$$\begin{aligned} \beta_{55} &\rightarrow k_{\pi\pi} \\ \beta_{35} &\rightarrow k_{\sigma\pi} \\ \beta_{33} &\rightarrow \text{not defined} \end{aligned} \tag{33}$$

For octahedral d^3- and d^8-systems two of these β-parameters can be determined experimentally. Their magnetic counterparts k may be calculated from paramagnetic resonance measurements by an accurate determination of the gyromagnetic factors. A calculation has been carried out until now for compounds with small ligand-central metal overlap (*e.g.* fluoride complexes).[48,49,52] For compounds with large overlap effects, however, also k-values larger than one have to be envisaged which are theoretically and experimentally conceivable. In this range an interpretation of k-factors in terms of electron delocalization is more difficult. Let us consider compounds with pure σ-bond interactions. In this case ligand-central metal π-bonding overlap S_π and the mixing coefficient η_π vanish. The resulting Eq. (10) for octahedral symmetry is discussed more conveniently in its quadratic form, Eq. (11), which is reformulated by

$$k_{\sigma 0}^2 = 1+\eta^2\frac{4S^2-1}{1-4\eta S+\eta^2} \tag{34}$$

An inspection of this equation leads to the following conclusions:

(1) for overlap integrals $S = 0.5$ the formula for $k_{\sigma 0}$ assumes the free ion value unity, and it is independent from the mixing coefficient η,

(2) for $S > 0.5$ and not much different from 0.5, the factor $k_{\sigma 0}$ is > 1 and varies only slightly with small η- parameters. $k_{\sigma 0}$ increases with increasing η,

(3) for $S < 0.5$, the factor $k_{\sigma 0}$ is < 1, it decrases with increasing η.

Eq. (34) therefore reflects the k-variations which are found experimentally. For small overlap effects the k-parameters decrease with increasing d-electron delocalization. In this case the parameters k and β vary in a similar way. For large overlap integrals the k-factors become less sensitive relative to delocalization effects. For sufficiently large ligand-metal overlap, k increases with increasing electron delocalization, and it is the deviation from the free ion k-value which describes the extent of electron delocalization.

We are, of course, aware that results derived from simplified formulae like Eq. (34) have to be considered with care. Certainly this expression is not able to explain all experimental findings. Because of the complete neglect of π-bonding effects the results apply only for a limited number of compounds. A more rigorous treatment should include other atomic orbitals of equal symmetry type on the ligand centers as indicated by Eq. (8).

Finally the question is discussed whether an independent variation of orbital reduction factors on one hand and the electron repulsion and spin-orbit coupling parameter on the other hand can be physically explained. It is recalled that the angular momentum operator from which the k-factor arises, only affects the angular part of the wavefunction, while the electron repulsion and the spin-orbit coupling operator $\xi(r)(L.S)$ also operates on the radial part of the wavefunction. Since each operator has a different weighting function the various regions of the wavefunctions are of different importance for the expectation value of each operator. When the orbitals participate in chemical bonding which replaces the particular atomic orbital in the integrals by a molecular orbital, the change in electron density is in general different for different regions in space. We expect a relatively minor change in the k-factors on chemical bonding because the angular part of the wavefunction practically remains unchanged in the bond region . However, the expectation value for radial dependent operators is relatively more influenced if the orbital functions participate in covalent bonding. Electron repulsion parameters B and spin-orbit coupling constants ζ_{nd} (or λ) therefore are strongly affected by electron delocalization effects. In addition it is likely that for certain central metal-ligand interactions k-factors and B-parameters change in a different way for a given electron delocalization. This leads to an independent variation of k- and B- (or λ-) parameters if covalent bonding occurs. Since in the electron delocalization integral $<\psi|r|\psi>$ only radial parts of the wavefunctions are important it is the parameters B or λ, which are more significant for determining delocalization effects rather than the k-factors. The latter may be conveniently used to describe the change of orbital angular momentum on chemical bonding.

When calculating expectation values for spin-orbit coupling by molecular orbitals containing distinct electron delocalizations one may distinguish between two effects: (1) One is the change in orbital momentum compared to localized d-functions which is considered by the factor k, (2) the other effect results from a noticeable radial expansion of the d-orbitals due to the decreased net charge on the central ion which always is accompanied by chemical bonding:

$$\begin{array}{llll} (1) & \lambda_o(L.S) & \rightarrow & \lambda_o k(L.S) \\ (2) & & \rightarrow & \varkappa\lambda_o k(L.S) \end{array} \tag{35}$$

Here λ_o is the spin-orbit coupling parameter for the free ion. Since ζ_{nd}, that is a multiple of λ_o, depends very much on the atomic charge of the central ion[43] the parameter

$$\varkappa = \frac{\lambda}{\lambda_o} \tag{36}$$

where λ is the spin-orbit parameter for the radially expanded atomic function, is in general smaller than one. Using Landé's empirical rule[57] ϰ can be ap-

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(57) R. Landé, *Z. Physik.*, 25, 46 (1924).

proximated by

$$\varkappa = \left(\frac{Z_{\text{eff}}+1}{Z+1}\right)^2 \tag{37}$$

where Z represents the charge of the free ion and Z_{eff} is the effective charge on the central metal in the complex. The spin-orbit coupling parameter λ' for the compound which is determined from the experiment, is equivalent with the above factors by comparison with Eq. (35)

$$\lambda' = \varkappa k \lambda_0 \tag{38}$$

Since $\varkappa$ usually is distinctly smaller than one for strong covalent bonding it may compensate possible factors $k > 1$. If chemical bonding has a smaller effect on k- than it has on $\varkappa$-values, a net decrease of the spin-orbit coupling parameter is expected. In fact experimentally determined λ'-parameters are usually found smaller than their corresponding values λ_0 for the free ion.

Conclusions

The results obtained can be summarized as follows:

(1) The orbital reduction factor k also contains σ-bonding effects.

(2) For small ligand central metal overlap, k and $\beta = B/B_0$ or $\beta^* = \lambda'/\lambda_0$ vary uniformly with electron delocalization effects (covalent bonding).

(3) For large overlap effects the variation of k and β (or β^*) can be different. k-factors larger than one are conceivable.

(4) The unique behaviour for the k-parameter arises from the fact that it is originated from an operator which affects the angular part of the wavefunction only.

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