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A crystal field model for the spectral assignment of pseudotetrahedral halocomplexes of nickel (II) with substituted thioureas

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Chimica. — *A crystal field model for the spectral assignment of pseudotetrahedral halocomplexes of nickel* (II) *with substituted thioureas.*

Nota di Giovanni Ciullo, Turiddu Tarantelli e Claudio Furlani (*), presentata (**) dal Corrisp. G. Sartori.

Riassunto. — Complessi misti di alogenuri di Ni(II) con tiouree N, N'-disostituite mostrano in solventi moderatamente dissocianti quale l'acetone, uno spettro di campo dei leganti attribuibile al cromoforo pseudotetraedrico $[NiS_2X_2]$. Viene presentata una dettagliata analisi di campo dei leganti, inclusiva delle componenti di simmetria rombica e degli effetti di accoppiamento spin-orbita, che consente l'assegnamento in linea di massima di tutte le componenti orbitali degli stati spettroscopici eccitati di campo dei leganti, tanto spin-permessi quanto spin-proibiti. Viene messo in evidenza l'effetto dell'intorno cristallino nel provocare sensibili variazioni di forma dello spettro di campo dei leganti e dello spettro di trasferimento di carica.

N, N'disubstituted thioureas (L) are known to give several types of coordination compounds with nickel(II) halides (1, 2), including pseudotetrahedral NiL_2X_2 (X=Cl, Br, I), tetragonal NiL_4X_2 and octahedral NiL_6X_2. We have reported previously preparation, characterisation and preliminary spectral interpretation of such kinds of complexes, and in the present work we report the use of a crystal field model in order to attempt a more detailed assignment of the system of energy levels of the pseudotetrahedral NiL_2X_2 species.

$[NiS_2X_2]$ chromophores of approximate symmetry T_d, molecular point group C_{2v}, are present either in solid NiL_2X_2 complexes as can be obtained only with thioureas containing bulky aromatic substituents, or in solutions of any NiL_nX_2 compounds ($n = 2, 4, 6$) in moderately dissociating solvents such as acetone. Thus, experimental data on the electronic structure of $[NiL_2X_2]$ chromophores can be obtained either from solid state (reflectance or single crystal) spectra of dihalobis(naphthylthiourea)nickel(II) or dihalobis(N, N'-diphenylthiourea)nickel(II), or from solution spectra of any NiL_nX_2 complex in acetone solution ($n = 2, 4, 6$ and L = any N, N'-disubstituted thiourea) where, according to [1] and [2] quantitative dissociation $NiL_nX_2 \rightleftarrows NiL_2X_2 + (n-2)L$ takes place. The spectra correspond grossly to the expectations for pseudotetrahedral Ni (II) chromophores, with bands of complex contour in the regions 9–10 kK corresponding to the tetrahedral transition $a\,^3T_1 \rightarrow {}^3A_2$, and 13-16 kK corresponding to tetrahedral

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(**) Nella seduta del 13 giugno 1970.

$a\,^3T_1 \rightarrow b\,^3T_1$. There is a distinct but small hypsochromic shift in the series of X ligands $I < Br < Cl$, whereas no detectable changes in band frequencies appear to occur depending on the nature of the coordinated substituted thiourea; some smaller but detectable changes occur between different solid and solution spectra, as will be discussed below. Apart from such solid state effects, this leaves us with the task of assigning only three kinds of spectra.

TABLE I.

Ligand-field absorption spectra of $[NiL_2X_2]$ *chromophores.*

X = Cl, Br, I; L = N,N′-disubstituted thiourea; experimental position of maxima and shoulders (in parenthesis) in kK, and molar absorbances (for crystal spectra, only relative absorbances are given).

	parent T_d transition	X = Cl	X = Br	X = I
Solution spectra (*)	$a^3T_1 \rightarrow {}^3A_2$	9.6_0 (49) 10.2_5 (38) 10.7_5 (37)	9.3_5 (59) 9.9 (52) 10.3 (57)	(8.7) ((62)) 9.7_2 (94)
	$a^3T_1 \rightarrow b^3T_1$	15.3_5 (200) 16.1_5 (208)	(14.7) ((286)) 15.3_6 (305)	13.9 (520)
Single crystal spectra (**)	$a^3T_1 \rightarrow b^3T_1$	—	13.7–14.0 (*p*) 14.39 (*d*)	12.9 (*p*)
		—	15.56 (*p*) 15.42 (*d*)	13.48 (*p*)
		—	16.9_5 (*p*) ~16.7 (*d*) 18.2*w*(*p*)	~15.5 *w* (*p*) 16.35*w* (*p*)

(*) Taken from acetone solutions of NiL_4X_2 at room temperature (L = N,N′–di–*n*–butylthiourea), dissolving as $[NiL_2X_2]$ species; with other L thiourea ligands, absorption frequencies are unchanged, and only molar extinction values vary slightly, e.g. $[NiL'_2Br_2]$ (L′ = N,N′–diphenylthiourea) absorbs at 9.3_0 (46), 9.9 (42), 10.3 (46) and (14.4) ((220)), 15.45 (260).

(**) NiL_2X_2 (X = Br, I; L = N,N′–diphenylthiourea) either pure (*p*) or isomorphically diluted (*d*) into ZnL_2X_2; spectra are taken either // or ⊥ to the extinction directions of the most developed crystal face.

Table I and fig. 1 report a summary of experimental data valid for each of the three $[NiS_2X_2]$ chromophores, irrespective of the nature of substituent groups in L; in the following treatment, we shall refer normally to solution spectra, but the bottom part of Table I, and fig. 4 show smaller differences between solution and crystal spectra in different environments; fig. 2 shows more details of the reference spectrum and an attempt to a Gaussian analysis of the actual complete ligand-field spectra of the investigated $[NiS_2X_2]$ chromophores.

In the violet limit a strong absorption due to charge transfer transitions sets in; we can easily identify the principal maximum of the charge transfer $S \rightarrow Ni$ at 28 kK, besides the $I \rightarrow Ni$ transition at some 23 kK in the iodo-complexes. Such frequencies are in rough agreement with the known optical

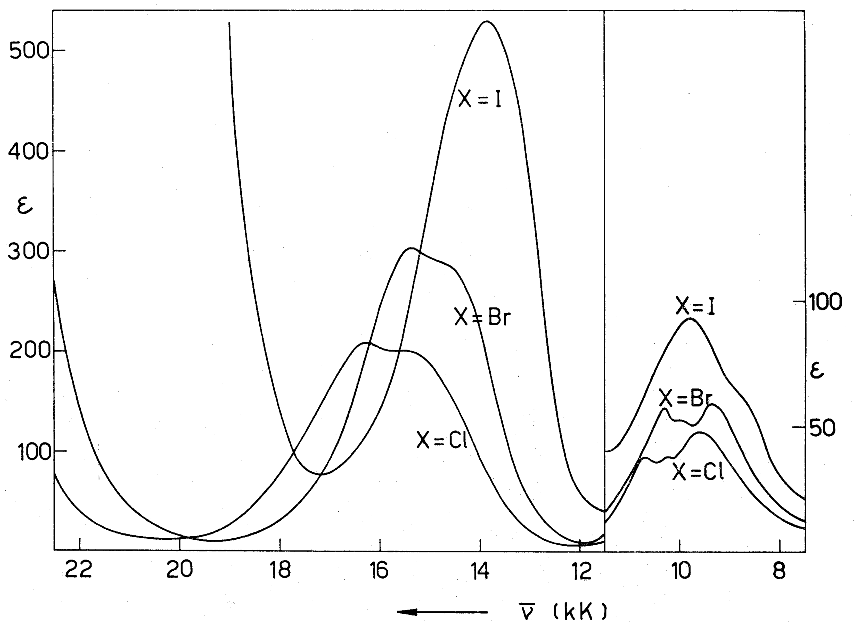

Fig. 1. – Molar absorption spectra of pseudotetrahedral $[NiS_2X_2]$ chromophores contained in $[NiL_2X_2]$ species (X = Cl, Br, I ; L = N,N′-diphenylthiourea) as present in acetone solutions prepared from solid NiL_4X_2.

electronegativity values of Ni (II), of sulphur and of the halogens, and we would not comment further on them, since we are not particularly concerned in the present work with the rationalization of charge transfer transitions, were it not for the fact that the $S \rightarrow Ni$ c.t. band has some structure, and shows clearly a shoulder around 24.5 kK or so. Now, this might even cast doubt on the existence of tetrahedral coordination in the investigated complexes: it is namely well known that two most intense transitions of tetrahedral Ni (II), $a\,^3T_1 \rightarrow {}^3A_2$ and $a\,^3T_1 \rightarrow b\,^3T_1$ fall close to two octahedral transitions, ${}^3A_{2g} \rightarrow {}^3T_{2g}$, respectively ${}^3A_{2g} \rightarrow a^3T_{1g}$. In order to distinguish between octahedral and tetrahedral chromophores, we have to consider whether an infrared absorption (tetrahedral $a^3T_1 \rightarrow {}^3T_2$) occurs in the region 3–6 kK, and in our case we have indications of such an absorption, but this is recognised as a rather unfavorable range for spectral measurements; absence of any absorption in the region 22–30 kK (typical of $^3A_{2g} \rightarrow b\,^2T_{1g}$ absorptions) would be definite evidence for tetrahedral structure, but no such evidence can be claimed where, as in the present case, absorptions, even if possibly of different origin, are present in such range. Since all other evidence for the tetrahedral nature of our NiL_2X_2 complexes was until now only indirect (high molar absorptions of the *d–d* bands, m.w. measurements showing molecular complexity NiL_2X_2 in acetone solutions, etc.), we looked for more direct evidence, and we found it from a preliminary investigation of solid (reflectance and single crystal) spectra of the involved species.

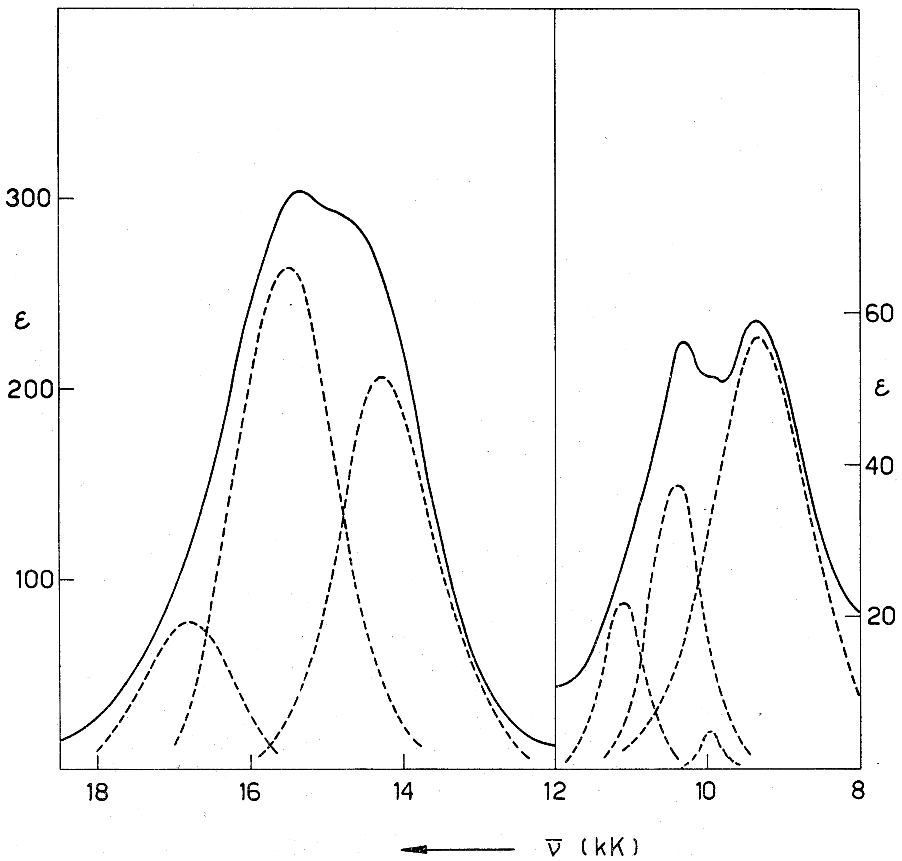

Fig. 2. – Gaussian analysis (in wavenumbers) of the spin-allowed $a^3T_1 \rightarrow {}^3A_2$ and $a^3T_1 \rightarrow b^3T_1$ (T_d) bands of the $[NiS_2Br_2]$ pseudotetrahedral chromophore, measured as in fig. 1. For numerical data on the experimental unresolved spectrum and on the gaussian components, see Table I and II, respectively.

Single crystal spectra of Ni(diphenylthiourea)$_2$Br$_2$ show grossly similar absorption patterns to the corresponding solution spectra, but with some non-negligible differences in band shapes and peak positions; the ~ 24 kK absorption is even more marked than in solution spectra. However, for want of data on the crystal structure, we do not know what the exact geometry of coordination is in the solid state (X-ray powder spectra of Ni(diphenylthiourea)$_2$Br$_2$ and of the corresponding tetrahedral CoL$_2$Br$_2$ are similar but not equal; the two substances are not isomorphous). On the other hand, we could prepare the analogous zinc (II) compound ZnL$_2$ Br$_2$, which contains certainly a tetrahedral chromophore, as is proved by the spectrum of solid solutions with the isomorphous Co complex being equal to the crystal spectrum of the pure cobalt (II) compound, as well as to its solution spectrum, which are recognised as typical of tetrahedral Co (II). Now, NiL$_2$ Br$_2$ can be dissolved isomorphically to a small extent into solid ZnL$_2$ Br$_2$, and its spectrum in such solid solutions, where the chromophore is certainly tetrahedral, is now completely similar to its solution spectrum in acetone (figs. 3 and 4).

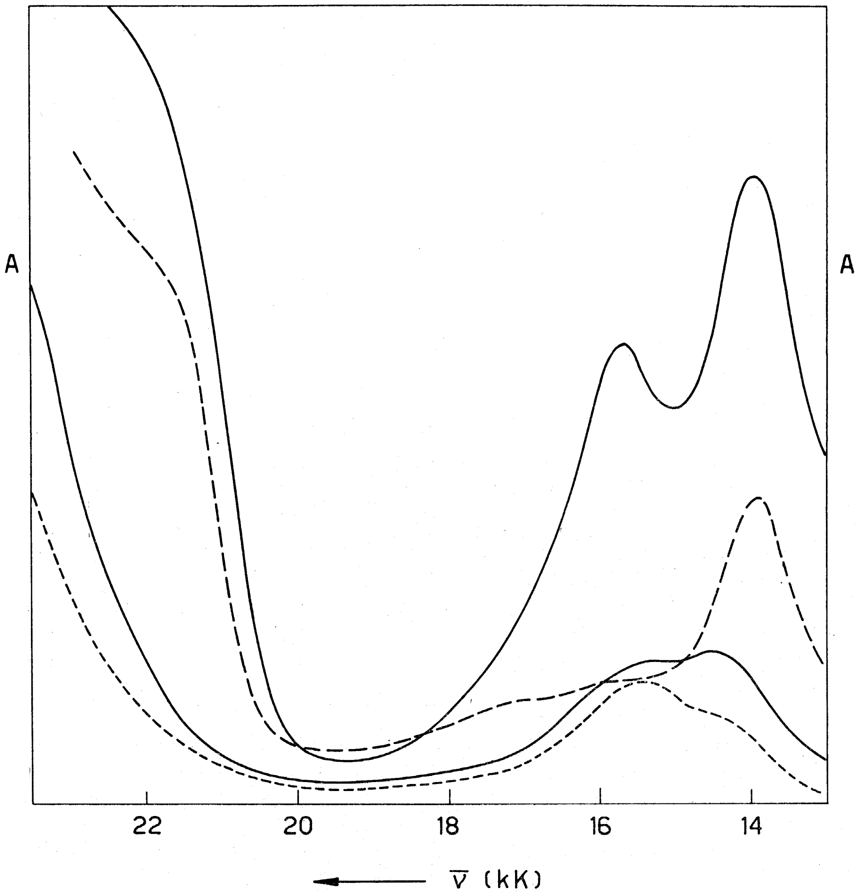

Fig. 3. – Single crystal absorption spectra of Ni(N,N'-diphenylthiourea)$_2$Br$_2$ pure (upper curves) and diluted isomorphically in the corresponding Zn^{II} compound (lower curves). Full and dashed lines are spectra polarised // and ⊥ to the extinction directions along the most well-developed crystal face. Ordinate is absorbance in arbitrary scale.

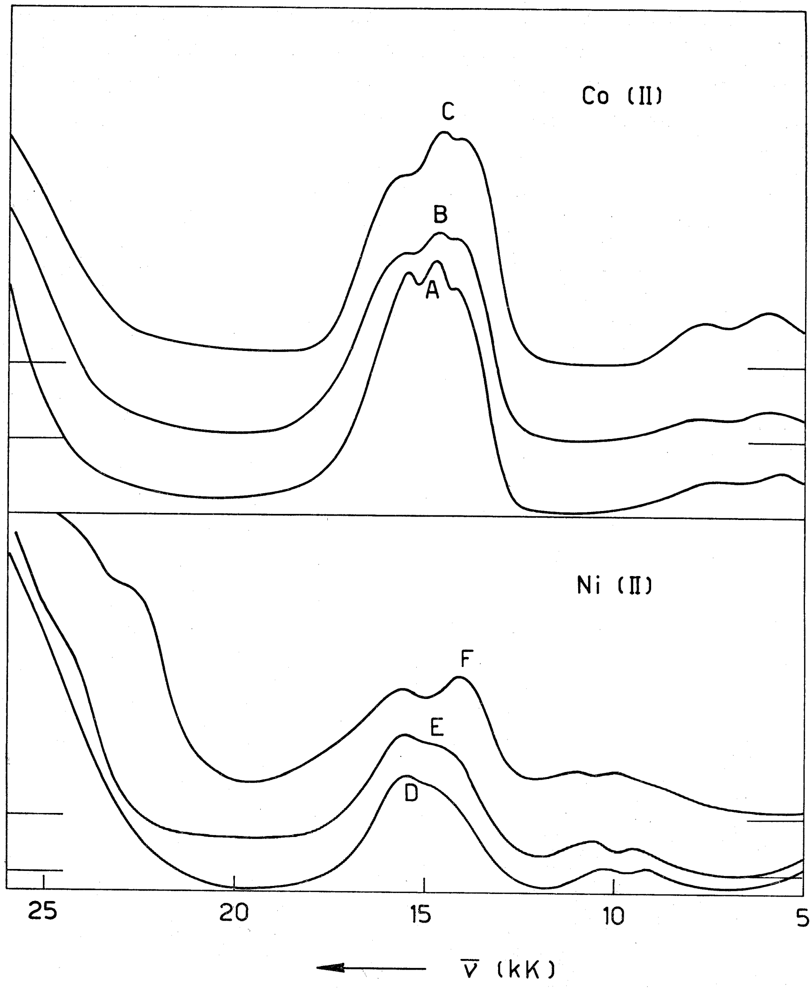

Fig. 4. – Electronic reflection or absorption spectra of pseudotetrahedral M^{II}(N,N'-diphenylthiourea)$_2$Br$_2$ species in different environments.

A) $M^{II} = Co^{II}$ in acetone solution (+ excess ligand); B) reflectance of mixed crystals (polycrystalline) of Co^{II} dissolved in Zn^{II}; C) reflectance of the pure solid Co^{II} compound (undiluted); D) $M^{II} = Ni^{II}$ in acetone solution; E) reflectance of mixed crystals (polycrystalline) of Ni^{II} dissolved in Zn^{II}; F) reflectance of the pure solid Ni^{II} compound (undiluted). Ordinate scale (absorbance or remission function) is arbitrary.

So we take this for a proof that, although crystal effects may be of importance in determining minor details of the spectrum, the chromophores investigated here are essentially tetrahedral and that a tetrahedral or nearly tetrahedral model is a reasonable approach to its interpretation, the $\sim$ 24 kK absorption being regarded rather as a charge-transfer satellite than as a *d–d* transition.

Although the main features of the visible spectra can be grossly accounted for by a ligand field model of symmetry T_d, a more accurate treatment in a field of lower symmetry seems appropriate for several reasons. Indeed the relatively large spectrochemical difference between neutral sulphur and halide ligands suggests that distortion of the ligand potential from T_d symmetry should be conspicuous, and this is confirmed by the relatively low magnetic moment (3.2–3.4 B.M.) consistent with effective removal of the orbital degeneracy via lower symmetry, by the relatively wide spread of components under the envelope of the $\rightarrow b\,{}^3T_1$ band, and by the low frequency ratio $\bar{\nu}_3/\bar{\nu}_2 \sim 1.5$–$1.6$, which is much lower than in other tetrahedral Ni (II) complexes (e.g. 2.0 in $[NiCl_4]^{2-}$ [3, 4]), and could be reconciled with the model of an average tetrahedral field only by assuming unrealistically high values of $|\Delta|$, e.g. $\Delta_{tetr.} = -5.2$ kK for NiL_2Br_2. Generally speaking, pseudotetrahedral Ni (II) complexes need (more strongly than e.g. Co (II) pseudotetrahedral complexes) consideration of their actual lower symmetric structure, since predictions based upon the method of average environment would be grossy in error owing to the orbital splitting of the ground state, which makes transitions start from the actual lowest split term and not from the center of gravity of $a\,{}^3T_1$, thereby changing substantially the ratios of transition frequencies from the predicted tetrahedral values. Furthermore, minor details of the experimental spectrum, such as the occurrence of several well defined smaller absorbtions presumably due to spin-forbidden transitions, clearly require a more realistic and detailed assignment procedure. Therefore, the availability of complete reckoning schemes for pseudotetrahedral Ni (II) complexes including spin-orbit and C_{2v} ligand field components [5] prompted us to attempt a detailed ligand field assignment of the spectra of the three chromophores $[NiS_2Cl_2]$, $[NiS_2Br_2]$, and $[NiS_2I_2]$.

We performed calculations according to different coupling schemes, using $\Delta_{tetr.}$ values for halides taken from the literature assignment of $[NiX_4]^{2-}$ species (3, 4, 5, 6), and several tentative values for $|\Delta_{tetr.}(S)|$ in the range 4.5–5.5 kK, which seems a reasonable guess in view of the general position of thioureas in the spectrochemical series, and of the spectrochemical ratio between thioureas and halides in the analogous CoL_2X_2 complexes [7, 8]. The ratios of the crystal field parameters $G(2)_{L,X}/G(4)_{L,X}$ were calculated theoretically [9] so as to reproduce the $|\Delta_{tetr.}|_X = 20/27\, G_{4X}$ values given in Table II with $f = 1.70$–1.92, $R = 4.00$ at. u. Besides, we considered also small distortions from tetrahedral geometry when looking for the best fit between calculated and experimental transition frequencies. The numerical results were fully independent of the adopted coupling scheme; the results reported in Table II are taken from calculations in the strong-field scheme $A\,(\gamma_i m_{\gamma_i} m_{s_i}) \rightarrow \psi\,(\Gamma_{C_{2v}} M_\Gamma M_S) \rightarrow \psi\,(\bar{\Gamma}_{C_{2v}} M_{\bar{\Gamma}} M_J)$ [5] which allows easier genealogical characterisation of the actual energy levels in terms of strong-field configurations.

Acceptable agreement between calculated and experimental transition frequencies can be obtained with relatively large variations in the values of adopted parameter sets (see Table II). As a general trend, assumption of tetrahedral angles led to worse results (in particular, too low calculated frequencies for $\rightarrow {}^3A_2(T_d)$), while better results could be obtained when allowing for a slight flattening of the coordination tetrahedron, e.g. assuming

TABLE II.

Parameter values, and predicted ("best fit") and observed (*) *values of energy of spectroscopic levels of* $[NiS_2X_2]$ *chromophores.*

Parameter values (in kK)	X = Cl	X = Br	X = I
$\Delta_{tetr.}$ (S)	—5.20	—5.20	—5.20
$\Delta_{tetr.}$ (X)	—3.70	—3.55	—3.34
B	0.75	0.70	0.65
β	0.72	0.67	0.623
λ	—0.24	—0.22	—0.19
$\widehat{XNiX}$ (assumed)	116°	116°	116°

One-electron energy levels (in kK)	X = Cl	X = Br	X = I
$1a_1 (\sim z^2)$	—3.11	—3.06	—2.99
$a_2 (xy)$	—2.19	—2.16	—2.10
$b_1 (yz)$	+0.24	+0.10	—0.10
$2a_1 (\sim x^2 - y^2)$	+2.56	+2.51	+2.44
$b_2 (xz)$	+2.51	+2.61	+2.76

Choice of axes and symmetry elements.

Orientation of the chromophore

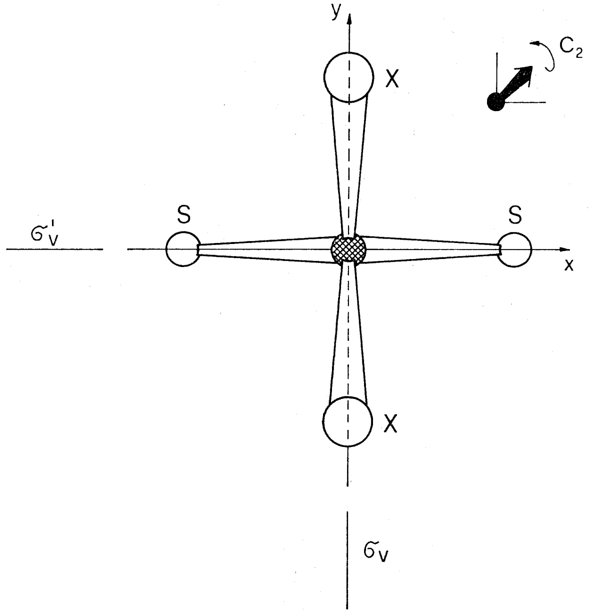

TABLE II (*Continued*).

Electronic energy levels in (kK)		X = Cl		X = Br		X = I		Approximate eigenvectors calculated for the eigenvalues of column 5 (X = Br), in terms of % of relevant contributions from orbital *d*-holes of the predominant spin-multiplicity; T = % of total triplet admixture in states having predominant singlet character.
Parent T_d term	Orbital C_{2v} term	Pred. (**)	Obs. (*)	Pred. (**)	Obs. (*)	Pred. (**)	Obs. (*)	
a^3T_1	$^3B_2$	.00	ground-state	.00	ground-state	.00	ground-state	86% $(xz\cdot x^2-y^2)$ + 7% $(xz\cdot z^2)$
	$^3A_2$	1.95		1.98		2.02		70% $(xz\cdot yz)$ + 15% $(yz\cdot x^2-y^2)$ + 8% $(xy\cdot x^2-y^2)$
	$^3B_1$	2.30		2.41		2.53		68% $(yz\cdot x^2-y^2)$ + 11% $(xz\cdot xy)$ + 13% $(xz\cdot yz)$
$^3T_2$	$^3B_1$	4.80	—	4.73	—	4.60	—	65% $(xz\cdot xy)$ + 21% $(yz\cdot x^2-y^2)$
	$^3A_1$	5.02	—	5.00	—	5.01	—	83% $(z^2\cdot x^2-y^2)$ + 9% $(xz\cdot xy)$
	$^3B_2$	6.02	—	6.01	—	6.05	—	68% $(yz\cdot xy)$ + 29% $(xz\cdot z^2)$
$^3A_2$	$^3A_2$	9.86	9.4_8 (44)	9.73	9.3_0(54)	9.46	8.9 (62)	95% $(xy\cdot z^2)$
$^1E+^1T_2$ (^1D)	$^1B_2$	11.62	10.2 (7)	10.78	9.9 (7)	10.00	9.7 (9)	82% $(xz\cdot x^2-y^2)$ + 8% T
	$^1A_1$	11.72	10.75 (26)	10.89	10.4 (38)	10.05	10.0 (84)	46% $(xz\cdot xz)$ + 40% $(x^2-y^2\cdot x^2-y^2)$ + 6% T
	$^1B_1$	13.10	11.6 (8)	12.55	11.1 (22)	11.99		62% $(yz\cdot x^2-y^2)$ + 22% $(xz\cdot xy)$ + 11% T
	$^1A_1$	13.61	—	13.02	—	12.42		31% $(yz\cdot yz)$ + 24% $(x^2-y^2\cdot x^2-y^2)$ + 10% T
	$^1A_2$	13.85	—	13.26	—	12.56		82% $(xz\cdot yz)$ + 10% T
b^3T_1	$^3A_2$	14.95	15.0_0 (168)	14.26	14.3_5 (290)	13.54	13.45(530) | 12.9 (***)	79% $(xy\cdot x^2-y^2)$ + 13% $(xz\cdot yz)$
	$^3B_2$	15.80	16.4_5 (170)	15.11	15.4_5 (275)	14.23	14.3 (430) | 13.4_8(***)	59% $(xz\cdot z^2)$ + 25% $(yz\cdot xy)$
	$^3B_1$	17.35	18.1_5 (44)	16.60	16.8_0 (80)	16.00	(15.5)(***)	54% $(yz\cdot z^2)$ + 28% $(yz\cdot x^2-y^2)$
$^1\Gamma$ (^1G)	$^1B_1$	18.64		18.07	18.2 (***)	17.14	16.3_5	72% $(xz\cdot xy)$ + 26% $(yz\cdot x^2-y^2)$ + 1% T
	$^1A_1$	18.89		18.34		17.44		71% $(z^2\cdot x^2-y^2)$ + 17% $(xz\cdot xz)$ + 2% T
	$^1B_2$	19.42		18.90		17.95		55% $(xz\cdot z^2)$ + 33% $(yz\cdot xy)$ + 1% T
	$^1A_2$	19.53		19.00		18.12		99% $(xy\cdot x^2-y^2)$; $\sim$ 0 T
	—	—		—		—		

(*) From gaussian resolution of the experimental spectra of Table I (molar absorption coefficients in parenthesis).
(**) Calculated with the parameters whose values are listed above.
(***) Single crystal spectrum.

$\overline{X}\widehat{Ni}\overline{X} = 116^\circ$ instead of $109^\circ 28'$, and data of Table II refer to this assumed geometry. Although angular distortions are usually small in cobalt (II) complex with thioureas [10, 11], they appear more plausible in nickel (II) complexes, also in view of the stronger distortions observed in $Ni(Ph_3P)_2Cl_2$ [12, 13], where $\overline{Cl}\widehat{Ni}\overline{Cl} = 125^\circ$. We also noticed that spin-orbit splittings were generally small (usually less than a tenth of a kK), so in Table II we present, and subsequently discuss, our results in terms of the parent orbital C_{2v} terms.

In what follows we shall first illustrate the points of wide agreement between calculated and observed spectra, and shall then turn to comment on the lack of specificity of parameter choices, hence on the limitations of validity of the present treatment. Features of the experimental spectra which can be qualitatively explained by our calculations even with different choices of spectral parameters include:

1) A peculiarity of the experimental spectra is the complex contour of the $a\,{}^3T_1 \rightarrow {}^3A_2$ band, which would be expected to remain unsplit also in symmetries lower than tetrahedral, owing to the nondegeneracy of the excited state. A possible explanation offered by our calculations is the mixing with close-lying singlet terms (the lowest derivatives of ${}^1D$), where mixing becomes more efficient the closer the interacting levels approach. The nephelauxetic trend of the ligands $Cl < Br < I$ suggests stronger lowering of the singlets, hence stronger mixing in the iodocomplex, which results in higher intensity of the components and apparent spectrochemical inversion between I and Br or Cl, if only the most intensive component of the envelope is observed.

2) The tetrahedral level $b\,{}^3T_1$ is predicted to split into three orbital components in C_{2v}, spread over an interval of about 2 kK; however, the transition to one of the three components ($\rightarrow {}^3B_1\,(C_{2v})$) should be electronically forbidden (the ground-state is constantly predicted as a ${}^3B_2$ in all our calculations, and the C_{2v} selection rules ${}^3B_2 \overset{x}{\longleftrightarrow} {}^3A_1$; ${}^3B_2 \overset{y}{\longleftrightarrow} {}^3A_2$; ${}^3B_2 \leftarrow\!|\!\rightarrow {}^3B_1$; ${}^3B_2 \overset{z}{\longleftrightarrow} {}^3B_2$ allow transitions to all split components of the excited tetrahedral triplet levels, except to ${}^3B_1$ from $b\,{}^3T_1$). This prediction compares therefore favourably with the experimental situation, where only two components of $b\,{}^3T_1$ are clearly evident, and the location of the third one is not even indicated with certainty by gaussian analysis of the complex band envelope.

We feel this could be a satisfactory explanation of the complex structure of the $\rightarrow b\,{}^3T_1$ band in our pseudotetrahedral complexes, differently from the case of $[NiX_4]^{2-}$ where, on the ground of the regular tetrahedral structure of the groundstate, dynamic Jahn-Teller distortions of the excited states are to be considered as the main source of the observed splitting; such dynamic distortions cannot be excluded in our case, but are not necessary, in view of the strong static distortion already existing.

3) Several spin-forbidden transitions are predicted in the region between the two main spin-allowed bands and on the blue tail of the $\rightarrow b\,{}^3T_1$ band, which find a satisfactory correspondence with smaller observed absorptions

(in part also with regard to the trend of intensities, as estimated through the calculated percent of triplet admixture).

4) Some comment is required by the relatively high spectrochemical position of sulphur; indeed, applying the theoretical (and experimentally rather well verified) ratio of 9 : 4, the corresponding octahedral Δ value would be more than 11 kK, placing thiourea much higher than water and close to amines in the spectrochemical series of octahedral nickel (II) complexes. Although no self-evident explanation can be presented by now, we might argue that π–backbonding effects occur more easily and to a larger extent in tetrahedral than in octahedral complexes of thioureas; this is also reflected in the relatively short metal-sulphur distance in tetrahedral cobalt(II)—thiourea halide complexes (2.33 Å in $Co(tu)_2Cl_2$ [11]; compared with 2.52 Å in high-spin octahedral $Co(tu)_4Cl_2$ [14]).

Turning now to the less conclusive aspects of the present analysis, we remark that the very fact that acceptable overall agreements with experiment can be obtained within relatively large variations of the adopted parameter set, prevents any precise determination of the latter. In fact, the choice of the best parameters depends largely upon the weight put on agreement with some partial features of the experimental behaviour, and we can only note how parameter variations correlate with particular features of the experimental spectra. Thus, an increase in the assumed $|\Delta_S|$ or $|\bar{\Delta}|$ value can be counterbalanced by a decrease of B in the calculated position of the $\rightarrow b\,{}^3T_1$ transitions and leads to a better mixing between the ${}^3A_2$ triplet and the lowest singlets from ${}^1D$, but is likely to give too high calculated position of ${}^3A_2$, and care has to be exerted in avoiding unreasonably high values of $|\Delta_S|$. Widening of the $\widehat{XNiX}$ angle makes the splitting of xz and yz unsymmetrical around a_1 ($\sim x^2 - y^2$), and splits off further xy and a_1 ($\sim z^2$); this is reflected in higher calculated values for all triplet transitions (with respect to pure tetrahedral geometry), i.e. reduces the need of assuming unplausibly high $|\Delta_S|$ values.

It is also to be noted that the one-electron energy levels of Table II are difficult to reconcile with any reliable choice of the angular overlap $e_{\lambda L}$ parameters: while the four energy differences between the five one-electron energy levels are in principle sufficient to determine $e_{\sigma(Cl,S)}$ and $e_{\pi(Cl,S)}$, the $e_{\lambda L}$ values thus obtained are highly positive, e.g. $e_{\sigma S} = 10.68$, $e_{\sigma Br} = 8.60$ $e_{\pi S} = 5.12$, $e_{\pi Br} = 4.38$ kK for the one-electron energies of the Br column in Table II, and far from the range usually assumed for such ligands (e_π between zero and 1 kK, $e_\sigma \sim$ 3–6 kK); values closer to the usual range can reproduce well the one-electron energies except for z^2, xy falling much closer together (e.g. $e_{\sigma Br} = 4.05$, $e_{\sigma S} = 5.20$, $e_{\pi Br} = 1.05$, $e_{\pi S} = 0.95$ kK reproduce to ∓ 0.4 kK the highest three one-electron energies of column 2 (Br) in Table II, while placing z^2 at -2.70 and xy ar -2.50 kK). This is a consequence of $E(xy) - E(z^2)$ being given in the angular overlap model essentially as $(3/2 \sin^2 2\vartheta_X - 2 \sin^2 \vartheta_X)\, e_{\pi X}$, which requires large values of $e_{\pi X}$ (and indirectly of all other $e_{\lambda L}$'s) to account for the experimental splitting, while the electrostatic model is favored in its ability to account for large $E(xy) - E(z^2)$ by the larger flexibility of its $Y_2^0 G(2)_L$ terms.

At the present stage it is however impossible to make any serious assessment of the reliability of both reckoning schemes as to the present problem, until the actual geometry of coordination, from which the one-electron energy parameters ε_i depend so strongly, will be known experimentally in an exact way.

A more correct procedure, escaping the limitations and inherent weakness of the point ligand crystal-field model, would be to leave in the ligand-field calculations all one-electron energy levels free to variational adjustments while looking for the best fit with experiment, instead of accepting the constraint of the relative positions of the ε_i as dictated by the electrostatic model. However, such a procedure would be of little use in the present situation, due to lack of crystal data on the exact geometry of coordination, which is a twofold reason of uncertainty.

Knowledge of the crystal structure would in fact allow real identification of the symmetry of energy levels in polarized crystal spectra instead of mere confrontation of calculated with experimental sequences of levels, and would also remove to ambiguity connected with the already mentioned strong dependence of the ε_i on the bond angles in the coordination polyhedron. For the moment, we can at least state with confidence that even within the limitations of the crystal field model our calculations indicate the lines of interpretation of the ligand field spectrum of the investigated chromophores, and yield a first approximation to the values of the ligand-field strengths and other spectrochemical parameters; besides there are good indications that such calculations can be applied to assignment of finer spectral details with possible use of variational extensions to which the employed reckoning scheme is amenable, as soon as more qualified experimental data will be available. An X-ray structure investigation of $Ni(diphenylthiourea)_2Br_2$ has been started recently by M. Nardelli and coworkers [15], and we plan to refine the interpretation of the visible spectra, when the structure investigation will have yielded those stereochemical data which are needed to exploit more thoroughly the interpretive possibilities of the present reckoning scheme.

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