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Angular Overlap Investigation on Unsymmetrical Transition Metal Complexes

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A ligand field model based on an angular overlap parameterization is applied to the study of the electronic structure of unsymmetrical cobalt(II) and nickel(II) complexes. Angular overlap parameters are obtained by fitting the spectral frequencies of the compounds and their transferability between different chromophores is investigated. The effects on the spectra due to the geometrical distortions of the chromophores from idealized symmetries are examined. Applications of the model to the study of the connection existing between spin state and coordination geometry in series of complexes are reported.

Introduction

The parameterization of the ligand field based on the angular overlap (AO) model, originally formulated by Schäffer and Jørgensen [1, 2] has gained considerable success in recent years for its simplicity and for the chemical significance which is associated to the values of its parameters. Gerloch has fully exploited the potentialities of the above method, developing a parameterization procedure which is particularly suited to the investigation of the spectral and magnetic properties of unsymmetrical transition metal complexes [3]. Gerloch's approach is applied here to obtain the values of the parameters which give best fit to the spectral data of a number of complexes. Fitting has been attained in each case by performing an extensive scan through parameter space [4]. Suitable systems for the investigation were five-coordinate complexes with known structure, possessing low symmetry or no symmetry at all. Their room-temperature electronic spectra do not provide numerous and accurate experimental data. However, the paucity of data is efficiently overcome by intelligent reduction in the number of parameters, which is made possible by the assumptions of the AO approach. The low accuracy of the data, on the other hand, is not a real drawback in view of the approximations of the method.

This investigation was essentially directed to: (a) provide a further test of the assumption of transferability of parameters between complexes, which is a very useful one and as such is often made in the applications of the AO model; (b) trace the effects on the electronic spectra due to geometrical distortions of the chromophores from idealized symmetries; (c) attempt to rationalize trends in series of complexes and study the effects of perturbations applied to model systems. In particular, the connection was investigated between coordination geometry and spin multiplicity of the ground state in series of related complexes.

Calculations

The energy differences between states of the d^n configuration of the metal atom in the field of the ligands have been calculated by the procedure described by Gerloch, making use of tensor operator techniques [3]. The terms for the electrostatic repulsions between electrons, for the spin-orbit coupling and for the interaction with the ligand field were included in the Hamiltonian. The first contribution was calculated by the procedure outlined by König and Kremer, making use of fractional parentage coefficients [5]. For the other two perturbations Gerloch's expressions were used, and the values of the relevant reduced matrix elements were obtained by the expressions reported by Koster [6]. Method (A) in reference [3] was employed for the ligand-field part of the problem. As has been pointed out [3], no symmetry of the ligand field is assumed by this procedure. Results of test calculations have been checked against values available from the literature [5].

Cobalt(II) and nickel(II) five-coordinate compounds with known structure have been considered. The spectra of some of these, having relatively high effective symmetries, had been assigned by previous investigations based on single-crystal data. Informations on the nature of the compounds investigated are reported in Table I. The constraints which, according to usual AO procedures (see below) have been imposed on the ligand-field parameters of each chromophore in order to reduce their number, are indicated in the Table. Fitting to the spectral frequencies has been obtained by the procedure of extensive scans through parameter space [4] only for

TABLE I. Donor Set, Parameters and Transition Energies for the Complexes Investigated.

Compound[a]	Chromophore[b]	Parameters[c]	B[d]	Frequencies[e]		Ref.[f]
I	$CoN'_1N'_2N_3N_4N_5$	$e_\sigma(1,2) = 4.38(1.98), e_\pi(1,2) \leqslant 0,$ $e_\sigma(4) = 0.82e_\sigma(3,5) = 3.30(2.24)$	800	a b	5.8, 13.0, 16.2[g], 19.6[h], 19.8, 20.8 5.9, 6.4, 12.8, 14.8, 19.2, 19.8, 20.5	7; 8
II[i]	$CoN_1N_2N_3N_4N'_5$	$e_\sigma(1) = 1.26e_\sigma(2) = 1.15e_\sigma(3,4) = 3.70(2.04),$ $e_\sigma(5) = 6.50(1.97), e_\pi(5) \leqslant 0$	750	a b	5.8, 14.8, 16.5, 21.0 5.1, 5.4, 14.6, 15.6, 16.7, 20.8, 21.1	9; 10
III	$CoN_1N_2N_3N_4Br$	$e_\sigma(1) = 0.87e_\sigma(2–4) = 3.20(2.15)$ $e_\sigma(5) = 5.35(2.43), e_\pi(5) = 1.20$	780	a b	5.6, 12.3, 16.2, 18.9–19.6 5.1, 12.4, 16.4, 19.8	11; 12, 13
IV[j]	$CoCl_1Cl_2N_1N_2N_3$	$e_\sigma(1) = 0.90e_\sigma(2) = 1.87(2.34),$ $e_\pi(1) = 0.83e_\pi(2) = 0.37,$ $e_\sigma(3,5) = 1.48e_\sigma(4) = 4.90(2.11)$	770	a b	4.0, 6.0[h], 8.8, 10.8[g], 15.8, 18.9 4.2, 6.7, 8.7, 10.9, 16.0, 17.8, 18.9	14; 15
V	$CoO_1O_2O_3O_4O_5$	$e_\sigma(1) = 0.91e_\sigma(2) = 0.77e_\sigma(3–5) = 2.82(2.10),$ $e_\pi(1) = 0.80e_\pi(2) = 0.60e_\pi(3–5) \geqslant 0$	830	a b	⩽5.0, 10.5, 12.5, 18–19 4.6, 5.4, 10.5, 12.6, 18.2, 18.6, 19.0	16; 16
VI	$NiN'_4N'_5N_1N_2N_3$	$e_\sigma(1,2) = 2.10(1.96), e_\pi(1,2) \leqslant 0,$ $e_\sigma(3) = 1.30e_\sigma(4.5) = 5.71(2.08)$	940	a[k] b	6.1, 11.3, 12.2, 14.7, 23.7, ~27 6.0, 6.3, 11.3, 12.2, 14.8, 14.9, 23.7, 25.9, 26.2	17; 18
VII	$NiN_1N_2N_3N_4N'_5$	$e_\sigma(1) = 1.20e_\sigma(2) = 1.10e_\sigma(3, 4) = 3.60(2.04)$ $e_\sigma(5) = 6.00(1.97), e_\pi(5) \leqslant 0$	850	a b	7.7, 11.3, 12.5, 16.2, ~21, 24.6 7.5, 7.9, 11.5, 12.4, 14.4, 21.2, 21.7, 23.9	9; 9, 12
VIII	$NiN_1N_2N_3N_4Br$	$e_\sigma(1) = 1.06e_\sigma(2–4) = 4.30(2.10),$ $e_\sigma(5) = 5.36(2.47), e_\pi(5) = 1.00$	830	a b	7.1, 10.5, 11.3[h], 14.1, 20.0, 22.7 7.0, 10.1, 11.4, 14.0, 20.4, 22.7	19; 12
IX	$NiO_1O_2P_1P_2P_3$	$e_\sigma(1,2) = 5.14(2.00), e_\pi(1,2) = 0.85,$ $e_\sigma(5) = 1.03e_\sigma(3,4) = 6.20(2.30),$ $e_\pi(5) = 1.03e_\pi(3,4) = -0.25$	650	a b	9.8, 14.2, 18.8, 26.3 9.1, 10.5, 13.3, 15.5, 18.0, 18.6, 25.2, 25.9	20; 20
X	$CoNP_1P_2P_3Br$	$e_\sigma(1) = 0.81(2.73), e_\sigma(2–4) = 3.50(2.37),$ $e_\pi(2–4) = -0.60, e_\sigma(5) = 6.00(2.36), e_\pi(5) = 2.00$	550	a b	5.7, ~9, 10.0, 13.3, 17.5 5.8, 8.7, 9.8, 13.1, 17.4	21; 13, 22
XI[l]	$CoN_1N_2P_1P_2I$	$e_\sigma(1) = 0.59e_\sigma(2) = 1.80, e_\sigma(3,4) = 3.29,$ $e_\pi(3,4) = -0.51, e_\sigma(5) = 5.78, e_\pi(5) = 1.73$	627	a b	6.0, 11.1, 13.8, 18.8[g] 6.0, 10.3, 10.6, 13.5, 17.7, 17.8	23; 18
XII[l]	$CoN_1N_2N_3PCl$	$e_\sigma(1) = 0.74e_\sigma(2,3) = 2.32, e_\sigma(4) = 3.31,$ $e_\pi(4) = -0.52, e_\sigma(5) = 5.57, e_\pi(5) = 1.47$	703	a b	5.7, 11.7, 14.8, 19.1–19.9 5.4, 10.3, 11.6, 14.6, 18.3, 18.8	24; 18
XIII	$CoN_1N_2N_2'N_2''Br$	$e_\sigma(1) = 0.77e_\sigma(2–4) = 2.94, e_\sigma(5) = 3.16,$ $e_\pi(5) \geqslant 0$	800	a[m] b	6.3, 12.5, 18.1, 20.1 4.7, 12.2, 18.4, 18.5	25; 26
XIV	$CoCl_1Cl_2N_1N_2N_3$	$e_\sigma(1) = 1.07e_\sigma(2) = 1.96, e_\pi(1) = 1.14e_\pi(2) = 0.40$ $e_\sigma(4) = 1.09e_\sigma(3,5) = 4.42$	770	a[n] b	10.5, 15.2, 18.5–19.3 5.4, 9.8, 11.4, 16.9, 17.5, 18.8	27; 28
XV–XIX[o]						

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[a] Formulae of the compounds and list of abbreviations: (I) $Co(n_3s)(NCS)_2$, n_3s = N,N-bis(2-diethylaminoethyl)-2′-methylthioethylamine; (II) $[Co(Me_6tren)NCS]NCS$, Me_6tren = tris(2-dimethylaminoethyl)amine; (III) $[Co(Me_6tren)Br]Br$; (IV) $Co(Me_5dien)Cl_2$, Me_5dien = bis(2-dimethylaminoethyl)methylamine; (V) $Co(picox)_5(ClO_4)_2$, picox = 2-picoline

N-oxide; (VI) $Ni(n_3as)(NCS)_2$, n_3as = N,N-bis(2-diethylaminoethyl)-2′-diphenylarsinoethylamine; (VII) $[Ni(Me_6tren)NCS]NCS$; (VIII) $[Ni(Me_6tren)Br]Br$; (IX) $Ni(p_3)SeO_4$, p_3 = 1,1,1-tris(diphenylphosphinomethyl)ethane; (X) $[Co(np_3)Br]PF_6$, np_3 = tris(2-diphenylphosphinoethyl)amine; (XI) $[Co(n_2p_2)I]I$, n_2p_2 = N,N-bis(2-diphenylphosphinoethyl)-2′-diethylaminoethylamine; (XII) $[Co(n_3p)Cl]ClO_4$, n_3p = N,N-bis(2-diethylaminoethyl)-2′-diphenylphosphinoethylamine; (XIII) $[Co(tpt)Br]Br$, tpt = tris(3-aminopropyl)amine; (XIV) $Co(Et_4dien)Cl_2$, Et_4dien = bis(2-diethylaminoethyl)amine; (XV) $[Co(np_3)I]I$; (XVI) $Co(p_3)SO_4$; (XVII) $[Co(pp_3)Br]PF_6$, pp_3 = tris(2-diphenylphosphinoethyl)phosphine; (XVIII) $[Ni(np_3)Cl]PF_6$; (XIX) $[Ni(n_2p_2)I]I$. [b] Labels of donor atoms are as in the original structural report. N′ stands for NCS nitrogen. [c] Constraints imposed on the e_λ parameters ($\lambda = \sigma$ or π) are specified by the chains of equalities. The scalar multipliers in the equalities are squared ratios of metal–ligand overlaps (see text). Symbols: $e_\lambda(n)$ refers to the n-th atom in the donor set, arranged as in the second column of the Table; $e_\lambda(n, m)$ is short for $e_\lambda(n) = e_\lambda(m)$ and $e_\lambda(n–m)$ is short for $e_\lambda(n) = e_\lambda(n+1) = .. = e_\lambda(m)$. Values of the independent parameters (one value for each set of equalities) are in 10^3 cm^{-1} units; in the case of compounds I–X they are followed by the corresponding M–L distances (A) in parentheses. [d] Units cm^{-1} used throughout. [e] Observed (a) and calculated (b) values of spectral frequencies, expressed in 10^3 cm^{-1} units. The experimental values are from reflectance or single crystal spectra, unless stated otherwise. The calculated values have been obtained with the e_λ and B values reported in this Table, setting $\zeta = 0$. [f] Reference to the paper reporting the structural data; reference(s) to the paper(s) reporting the spectral data for each compound. [g] Estimate of frequency value slightly different from that made in the original report. [h] Shoulder not reported previously. [i] Compound II assumed isostructural with compound VII, as in Ref. 10. [j] The (closely related) geometries of two crystallographically independent molecules have been averaged in the calculations. [k] Observed frequencies are from the absorption spectrum of the compound, which is essentially identical to the reflectance spectrum but shows better resolved bands. [l] Approximate values of parameters for the halogen atom obtained by interpolation (see text). [m] Frequencies are from the spectrum of the iodo-derivative (see text). [n] Nujol spectrum. [o] Low-spin complexes, investigated for ground-state properties: see text and footnote a to this Table. The chromophores, the relationships between parameters and references to the structural reports are as follows: (XV) $CoNP_1P_2P_3I$, $e_\sigma(1)$, $e_\sigma(4) = 0.96e_\sigma(2,3)$, $e_\pi(4) = 0.89e_\pi(2,3)$, $e_\sigma(5)$, $e_\pi(5)$ [29]; (XVI) $CoO_1O_2P_1P_2P_3$, $e_\sigma(1,2)$, $e_\pi(1,2)$, $e_\sigma(5) = 0.93e_\sigma(3,4)$, $e_\pi(5) = 0.80e_\pi(3,4)$ [20]; (XVII) $CoP_1P_2P_3P_4Br$, $e_\sigma(1) = 0.99e_\sigma(2,3) = 0.91e_\sigma(4)$, $e_\pi(1) = 0.97e_\pi(2,3) = 0.71e_\pi(4)$, $e_\sigma(5)$, $e_\pi(5)$ [30]; (XVIII) $NiNP_1P_2P_3Cl$, $e_\sigma(1)$, $e_\sigma(2–4)$, $e_\pi(2–4)$, $e_\sigma(5)$, $e_\pi(5)$ [31]; (XIX) $NiN_1N_2P_1P_2I$, $e_\sigma(1) = 1.77e_\sigma(2)$, $e_\sigma(3,4)$, $e_\pi(3,4)$, $e_\sigma(5)$, $e_\pi(5)$ [23].

compounds I–IX reported in Table I. For the other complexes in the Table (X–XIX), which have been considered for the specific purposes that will be described below, the values of some or all of the parameters have been transferred from those obtained by the above procedure for the former group of compounds (I–IX). The symmetry of the closest environment of the metal atom is C_{3v} in compounds III, VIII and XIII. It would be strictly C_1 in all of the other complexes, however it is close to D_{3h} in compound V, to C_{3v} in II, VII, X and XVIII, and it is close to C_s in the remaining complexes. The complexes I–XIV are high-spin and XV–XIX are low-spin.

According to the AO model in the additivity scheme [2] the antibonding effect on the energies of the 'metal d orbitals' due to the weak perturbation caused by a ligand atom (L) is expressed by means of $e_\sigma(L)$ and $e_\pi(L)$ parameters ($e_\delta(L)$ may be confidently neglected). These will be collectively referred to by the symbol $e_\lambda(L)$, where appropriate. Linear ligation along the metal–ligand bond has been assumed, making an approximation that, in the case of the present complexes, is probably less drastic than the other approximations of this AO model. The ratios between the values of the e_σ parameters, as well as those between the e_π parameters belonging to chemically equivalent donor atoms in each chromophore, have been assumed to be equal to the ratios between the squares of the corresponding metal-ligand overlaps [32] (overlap integrals have been calculated at the experimental M–L distances using Clementi's atomic functions for the neutral atoms [33]). The constraints that have been imposed in this manner, thus effectively reducing the number of independent parameters, are specified by the chains of equalities in the third column of Table I. The known values of bond angles about the metal atom have been used in all cases, taking advantage of an important feature of this model, whereas few, not very relevant, simplifying approximations on values of bond distances have been made. These are revealed by the constraints listed in Table I. In addition to the e_λ parameters, the model comprises the Racah B (or the nephelauxetic β) and C parameters and the spin–orbit coupling constant, ζ. The results of these calculations have been found to be scarcely affected by the particular values assumed for the ratio C/B, so that the value C/B = 4 has been used whenever states of different spin multiplicity were involved. In the calculations which included the spin–orbit perturbation, the free-ion values of ζ [34], reduced by a factor $\sim\beta$, were used. In the process of fitting the spectral data approximate values of the e_σ and B parameters were sought first. Subsequently those of the e_π parameters, which are smaller than the e_σ [35], were investigated. Finally, values of all parameters were refined by sampling at finer intervals the appropriate regions of parameter space. In the

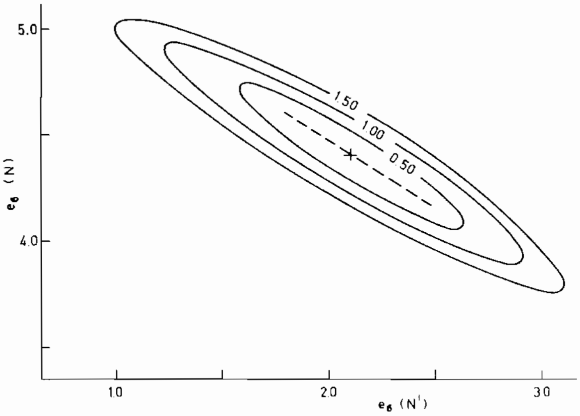

Fig. 1. Lowest contours of the S function in the two-dimensional space of the nonzero e_λ parameters (see text; units 10^3 cm^{-1}) for the compound $Ni(n_3as)(NCS)_2$ (VI). Best fit attains along the dashed line, with S values lower than 0.30. The position of the minimum value of S is marked by a cross.

region(s) of good fit, the position of the minimum of the function $S = \Sigma_i\delta_i^2$ ($\delta_i = \nu_i^{calcd} - \nu_i^{obsd}$ for the i-th transition (the summation being over the observed transitions) was determined with the aid of contours traced in multiparameter space [4].

Result and Discussion

Quality of Fitting

The values of the ligand field parameters of low-symmetry chromophores generally cannot be defined accurately by fitting to the spectral data. This is due to the unfavorable ratio of the number of observables *versus* that of the parameters required and to the existence of correlations between specific groups of parameters. The extent of such correlations may be appreciated by inspection of Fig. 1 showing contours of the S function defined above, on the plane of the two independent e_σ parameters defined for compound VI. Although this is a special case, it is quite illustrative of the general situation. Good fit to the spectral data is attained over an extended region in the proximity of the dashed line in the Figure. The sum of the e_σ values of all donor atoms in the complex is practically constant over the region of good fit, a result that is reminiscent of the rule of average environment. In view of the paucity of experimental data and of the problem posed by the correlations, the number of parameters has been maintained as low as possible in the calculations. Two e_σ parameters were allowed to vary independently for each of the complexes I–IX, that have been thoroughly investigated. One e_π parameter was required in addition for the complexes I–VIII and two were required for complex IX. Values of $e_\pi(N')$ (N' = NCS nitrogen atom) turned out to be quite small (possibly negative) in all cases and were set equal to zero, without prejudice for the quality of fitting. The same approximation was made for the value of $e_\pi(O)$ for complex V. On the other hand, there were definite indications that the e_π values of the halogen atoms should be substantially greater than zero for the compounds III, IV and VIII. In the case of complex IX, due to the correlations between the four e_λ parameters, satisfactory fittings were obtained even with sets of physically unacceptable e_λ values (*e.g.* $e_\pi(O) < 0$ and $e_\pi(P) > 0$). Imposing the condition $e_\pi(O) > 0$, then only values $e_\pi(P) < 0$ were found to give good fit. Since the uncertainty on such e_π values was still large, a conservative approach was adopted: the lowest $|e_\pi|$ values which gave good fit were chosen.

The set of independent e_λ values at the point of minimum of the S function is reported in the third column of Table I for each of the compounds I–IX. Such values are defined unambiguously, since a unique minimum of S was found in all cases (subject to constraints, as specified above, in the case of compound IX) in the region of the physically significant values of the parameters. However such optimal sets of values are not sharply defined, since the minimum of S was very flat in all cases [36]. The e_λ values that have been used for compounds X–XIV in the calculations to be described below are also listed in Table I. They have been transferred from compounds I–IX, except for some of the parameters of X, that have been obtained by the procedure described above for compounds I–IX. The energy differences between states, calculated with such sets of parameters, are compared with the spectral frequencies in the fifth column of the Table. The quality of fitting is generally good, although not exceptionally so. This could have been expected, in view of the small number of parameters used. Indeed, inspection of the third column in Table I reveals that the number of parameters involved in the present calculations on compounds I–IX is generally lower than that required by other ligand field models, in their applications to systems with low effective symmetries.

A useful property of this AO model is that the principal features of the spectrum (ordering of the energies of states and ratios between energy differences) are reproduced with sufficient accuracy even if approximate values of the parameters are used. This may be due in part to the fact that the eigenvalues are not particularly sensitive to concerted variations of the parameters, but it should mainly result from the fact that the geometry of the chromophore is taken into detailed account by this parameterization procedure. Such property of the model is illustrated by the results obtained for the cobalt compounds with geometry close to the trigonal bipyramidal (TBP). The spread of energies of the ‘essentially P’ states (*i.e.* the three highest quadruplet states in C_1 symmetry) of the metal atom in such chromophores varies considerably from case to case: it is small for compounds I, V and XIII (Table I), large for compounds II, X, XI and XII, and intermediate in the case of III [37]. Such differences between the spectra of the compounds are correctly brought about by the calculations, even using e_λ values considerably different from the optimal sets, reported in Table I. This indicates that the above differences between the spectra of such compounds are primarily due to geometric factors whose operation (definitely not obvious at the outset) is properly accounted for by this calculational procedure. A further advantage of this type of parameterization is that it produces a faster convergence to the correct assignment and reduces the possibilities of making wrong assignments. For instance, in the case of compound III the correct sequence of energy eigenvalues [13, 38] attains over an extended region of physically significant values of the parameters so that the path toward the region of good fit may be easily found by trial variations of the parameters. Indeed, the alternative assignment of the spectrum of this compound [39], which raised a considerable dispute [38], is definitely excluded.

The frequencies of few transitions in the spectra of compounds I–IX could not be fitted accurately by these calculations (*e.g.* those at *ca.* 16200 cm^{-1} in the spectra of compounds I and VII; the latter was badly reproduced also by previous ligand field calculations [9]). It is not clear to what deficiencies of the model these failures should be primarily attributed.

Effective Symmetry

The assignments of the electronic spectra are generally performed with reference to idealized effective symmetries, higher than those actually possessed by the chromophores. In order to obtain an estimate of the approximations involved by such procedure, the results obtained for some of the present compounds using the structural data and the ligand field parameters reported in Table I, have been compared with those obtained by calculations in which higher, idealized symmetries, appropriate to the specific cases, were assumed.

For the complexes with approximate TBP coordination geometry, the idealized C_{3v} symmetry has been assumed, by suitably averaging angles and parameter values. It has been thus verified that the assumption of C_{3v} symmetry is quite appropriate for the case of compound XI (maximum shift of *ca.* 100 cm^{-1} between the eigenvalues from the calculations performed for the 'experimental' and for the idealized model) and it would be probably reasonable in other cases (300 cm^{-1} max. shift for compound VII, 600 cm^{-1} for II and 700 cm^{-1} for XII). The differences between the results for the two models were larger for the compounds V and I (max. shifts 1300 cm^{-1} and 1600 cm^{-1}, respectively). An approximate connection between the magnitudes of the above shifts and the extent of the distortions from C_{3v} symmetry seems to exist, as the average deviation from the mean of the equatorial angles for the above cobalt compounds is: 1.1° (XI), 5.1° (II), 3.7° (XII), 7.8° (V), and 8.8° (I). It appears that the assumption of C_{3v} effective symmetry is untenable for these TBP systems if the amount of distortion is as large as that existing in compound V: indeed the spectrum of that compound has been assigned in C_{2v} symmetry [16]. In agreement with this fact, the calculations indicate that the eigenvectors of the excited states are considerably affected by distortions of such amount.

In the case of the nickel compound VI having square pyramidal (SP) geometry, the fitting has been found to be virtually as good in the idealized C_{4v} symmetry as in the C_1 ($\sim C_s$) experimental one. Moreover, the eigenvectors were little affected by the change in symmetry. Indeed, the spectrum of VI is quite similar to that of another square-pyramidal nickel(II) compound that has been assigned in C_{4v} symmetry [32]. Probably, such a high effective symmetry is related to the property of 'holohedrized symmetry' of the metal environment, which is incorporated in the AO description of the states of d^n configurations [2]. The effects of this may be more conspicuous for the SP rather than the TBP chromophores, because there is a larger number of ligands placed approximately *trans* to each other in the former geometry than in the latter. The spectrum of the cobalt compound IV with geometry intermediate between the SP and the TBP, exhibits maximum shifts in the frequencies of 2200 and 2700 cm^{-1} from the values calculated for the C_{4v} and C_{3v} symmetries, respectively.

Fundamental State

The spin multiplicity of the ground state is calculated correctly for all high-spin compounds listed in Table I, using the values of the parameters reported in that Table. The lowest doublet state of the cobalt complexes lies at 9000 (I), 5600 (II), 9700 (III), 10200 (IV), 10200 (V), 9000 (X), 8200 (XI), 8300 (XII), 9700 (XIII), 8900 cm^{-1} (XIV) above the lowest quadruplet state and in the case of the nickel complexes the singlet–triplet separation is: 11700 (VI), 8900 (VII), 8100 (VIII), and 8800 cm^{-1} (IX). The ground state of the low-spin complexes XV–XIX is also correctly calculated using values of the e_λ parameters derived from compounds I–IX and reasonable values of B [40] with fixed C/B = 4 ratio. These results suggest that it is feasible to apply the present AO model to the study of trends in the relative energies of the lowest states of the different spin multiplicities, as is done in a later section.

TABLE II. Normalized Values of Parameters.[a]

M = Co					*M = Ni*
		$e_\sigma(N)$	(M–N = 2.10 A)		
I	4.44			VI	5.44
II	3.29			VII	3.20
III	3.54			VIII	4.30
IV	4.99				
		$e_\sigma(N')$	(M–N = 2.00 A)		
I	4.15			VI	1.92
II	6.26			VII	5.69
		$e_\sigma(Br)$	(M–Br = 2.45 A)		
III	5.17			VIII	5.55

[a] Columns list serial numbers of the compounds and values of parameters (10^3 cm^{-1}) separately for cobalt and nickel complexes. The $e_\sigma(L)$ values in Table I have been referred to the same M–L distance, as indicated, through multiplication by the ratio of squared overlaps.

The ground state picture obtained for the TBP nickel(II) complexes, that would possess an orbitally degenerate ground state in the idealized C_{3v} symmetry if the spin–orbit perturbation was negligible, is worthy of note. The ^3E ground state of the NiN_4Br chromophore (VIII), having C_{3v} local symmetry, is split by the spin–orbit interaction into three almost equally spaced pairs of levels, the overall separation being *ca.* 760 cm^{-1} (ζ = 400 cm^{-1}). Such splittings should produce detectable effects on the value of the magnetic susceptibility at low temperatures and allow the rationalization of the low value of the magnetic moment of the compound [9, 12]. The ground state of the NiN_4N' chromophore (VII) is split into a fundamental triplet and a second triplet of levels lying as high as 1400 cm^{-1}. This rationalizes the fact that the magnetic moment of this compound is as low as that of the square-pyramidal nickel complexes [9]. Since the eigenvectors are considerably modified from the case of D_{3h} symmetry, it is not clear how such high effective symmetry may be operative for the assignment of the polarized spectrum of the compound [9].

Transferability of Parameters

In order to facilitate the comparisons, values of the $e_\sigma(N)$ parameters and, separately, those of the $e_\sigma(N')$ and $e_\sigma(Br)$ parameters, that have been obtained for different compounds by the extended scan procedure, have been referred to a single value of the M–L distance. The values so 'normalized' are reported in Table II. Those pertaining to pairs of chromophores with identical donor set but different metal atoms appear on the same line in the Table. Compounds II and III are isostructural with VII and VIII, respectively, whereas I and VI have different geometries. The values of a specific parameter are found to vary considerably from compound to compound, even allowing for the fact that such values are affected by large uncertainties. In particular, the differences between the $e_\sigma(N')$ value of VI and those derived for the other isothiocyanates is exceptionally high. The situation is similar for the $e_\lambda(O)$ values of V and IX and for the $e_\lambda(P)$ of IX and X, which are not reported in Table II, but may be obtained from Table I. The extension of the region of good fit (Fig. 1) allows the choice of values of a specific parameter for different compounds in much closer agreement with each other, than those listed in Table II. However, the agreement between *all* parameters of different chromophores cannot be simultaneously improved by such procedure.

It appears from the limited amount of data in Table II that transfer of parameters between compounds that are not 'closely related' to each other, can provide, at most, initial guesses as to their values. However, as the comparison between the results for the pairs of isostructural compounds in Table II indicates, the situation should be more favorable for 'closely related' compounds. An additional indication is that the change in the nature of the metal atom should not affect the values of the parameters as much as changes in the structure or ligand environment.

Further tests on the transferability of parameters within sets of related chromophores have been provided by the results of calculations on the following groups of compounds: (a) III, X, XI and XII; (b) III and XIII; (c) IV and XIV.

(a) The nitrogen atoms in the equatorial positions are gradually replaced by phosphorus donors if the above TBP complexes are arranged in the order III, XII, XI, and X. Correspondingly, the tetrahedral distortion in the geometry of the chromophore increases [41]. With values of the parameters obtained as described in Ref. 42, satisfactory agreement is found between the observed and calculated spectral frequencies (Table I). The agreement is probably due in part to the favorable circumstance that the effective symmetry is close to C_{3v} for all these complexes (see above).

(b) Compounds III and XIII possess the same set of donor atoms, but they do not have identical ligand molecules. Both possess C_{3v} symmetry, but they exhibit different sorts of distortions from the idealized TBP geometry (Table I). The e_λ values of XIII have been transferred directly from III, setting $e_\pi(Br)$ = 0 for simplicity, in view of the very long Co–Br distance in XIII (2.66 Å). Accurate fitting was not expected as the values of the spectral frequencies of compound XIII were not available from the literature and those of the isospectral iodide [26] were referred to. The value of B has been adjusted in order to partially account for the above approximation. The quality of fitting for 'compound XIII' is modest. However, the most significant trend which is observed on going from III to XIII, consisting of a decrease in the separation between the transitions to the 'P states', is reproduced by the calculations, even though it is overestimated. Such feature of the spectrum of compound XIII is indicative of an effective symmetry close to D_{3h} with ratio $e_\sigma(ax)/e_\sigma(eq) < 1$ [16]. This fact was not obvious *a priori* for the case of compound XIII but it is consistent with the entries in the third column of Table I.

(c) Compounds IV and XIV possess identical donor sets, but slightly different ligand molecules and coordination geometry. Parameters have been transferred from IV to XIV, without change in B. The frequencies of transitions are calculated accurately enough, with the exception of that at 15200 cm^{-1}. It is not clear what approximation or fault of the model is most responsible for this fact.

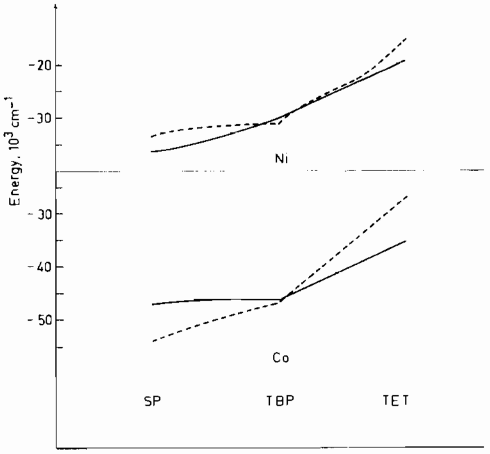

Fig. 2. Energies of the lowest high-spin (———) and low-spin (– – – –) states for the d^7 and d^8 $M(np_3)X$ models along paths connecting the three limiting geometries considered. Spin–orbit interaction neglected.

Applications

An important application of the model consists in the rationalization of trends within series of complexes. Two investigations of this type have been made.

The nickel(II) complex cations with formula $[Ni(np_3)X]^+$ (X = Cl, Br, I) are low-spin and possess the TBP geometry detected for compound XVIII [31, 41]. The analogous cobalt(II) derivatives with X = Cl or Br are high-spin and have the trigonal-bipyramidal tetrahedrally-distorted geometry (TET) of compound X [21], whereas the cobalt complex with X = I may be high-spin in the solid state, with the above TET geometry, or it may be low-spin with the SP geometry found for the compound XV [29], depending on the nature of the counterion [41]. Such connection between spin state and geometry has been investigated by performing calculations on idealized models of the TBP, TET, SP and intermediate geometries, for the configurations d^7 and d^8 [43]. Of course, the interaction between the ligand atoms and the d shell contributes only a small fraction to the total energy of the complex. However, it is reasonable to expect that the above differences between complexes of the two metals with identical ligand and donor sets should be actually determined by the differences in that small contribution to the total energy.

The effects of the distortions applied to the model systems from the TBP geometry to the SP and to the TET one have been investigated and the trends calculated for the energies of the lowest states of different spin multiplicity are shown in Fig. 2 [44]. As appears from the Figure, in the case of the d^7 configuration a considerable stabilization of the low-spin state relative to the high-spin state takes place in the course of the distortion from the TBP to the SP geometry, whereas the opposite occurs along the TBP → TET path. In the case of the d^8 configuration, on the other hand, the largest relative stabilization of the low-spin state with respect to the high-spin state attains in the TBP geometry, over a range of B values. Obviously, only trends are significant here: these are consistent with experiment. The fact that the low-spin state and the associated SP geometry are relatively more stable for the iodo complex than for the other derivatives of cobalt may be rationalized as follows. The low-spin state is stabilized in every case by a decrease in the nephelauxetic ratio (as occurs, in particular, when iodine is substituted for another halogen in the coordination shell). Since the slopes of the curves are scarcely sensitive to variation of the B or C values, it appears from Fig. 2 that in the case of the d^7 configuration the stabilization of the low-spin state is associated with preference for the SP geometry. This is probably the maximum information that may be obtained for such systems by a ligand field model. Results of EH molecular orbital calculations, performed for the TBP → TET path [21], are substantially in agreement with the present ones, although they focus on different aspects of the problem.

The second application has been to the pair of isomorphous compounds IX and XVI [20]. These have the same donor set and a very distorted geometry, possibly closer to the SP than to the TBP type. The nickel complex (IX) is high-spin and has longer metal-ligand distances than the cobalt complex (XVI), which is low-spin. The values of the parameters obtained by fitting the spectrum of the nickel compound have been used for that of cobalt, ignor-

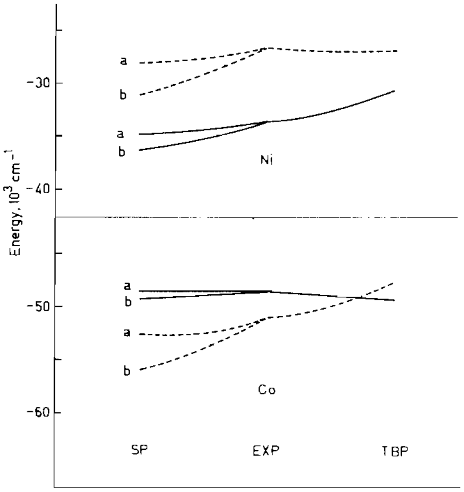

Fig. 3. Trends in the energies of the lowest high-spin (———) and low-spin (– – – –) states of idealized models of the MO_2P_3 chromophores (M = Co, Ni) with averaged metal–ligand interactions, along paths connecting the experimental geometries (EXP) of compounds IX (Ni) and XVI (Co) with the TBP geometry (right) and the SP geometry (left). The two SP models considered have: (a) α = 100° and 1.0 elongation coefficient, (b) α = 95° and 1.1 elongation coefficient.

ing the differences in the nature of the metal atoms, however applying corrections to account for the changes in metal–ligand bond distances. In this way the spin multiplicity of the ground state of the cobalt compound is correctly calculated for any reasonable value of B (C = 4B). It has been checked that the differences in the metal–ligand bond lengths between the two complexes (which are associated, as usual, with the different spin states) are not sufficient *per se* to determine the change in spin multiplicity. In fact, the nature of the ground state does not change if the environments of the two metal atoms are interchanged, *i.e.* if the e_λ values and the geometry of compound IX (XVI) are used, with suitable values of the Racah parameters, in the calculations on the d^7 (d^8) model. In order to understand whether a connection between the spin state and the unusually distorted geometry of these two complexes exists, two models have been considered, each formed with five identical donor atoms, which were assigned parameter values equal to the means of those in compound IX and, respectively, XVI. The effects of the following distortions from the experimental geometries of the two compounds have been investigated: (a) toward the (closest) model with TBP geometry; (b) toward the SP geometry, with angle α = 100° between the axial and basal ligands; (c) toward an SP model with α = 95° and decreased apical field strength, corresponding to 1.10 elongation coefficient [45]. The values of the e_λ parameters have not been modified along trends (a) and (b), whereas they have been properly changed (imposing constancy of the value of their sum) along trend (c), in order to account for the increasing apical elongation. The trends in the energies of the two lowest states of different multiplicity are shown in Fig. 3, for B values intermediate between those of high-spin and of low-spin complexes (*ca.* 600 cm^{-1}; ζ = 0). The trends towards the SP geometries are similar for the d^7 and the d^8 configurations, whereas those toward the TBP geometry are different. As a consequence of this and of the different relative location of the high-spin and low-spin states for the two models, the separation between the two states reaches a maximum in correspondence of the experimental geometry in the case of the d^8 configuration but not in the other case (Fig. 3). Therefore, the overall qualitative indication from these calculations is that different spin states are stabilized for the two metal atoms by this donor set and such tendency is maximized by the particular geometry of the chromophores. It is also interesting to notice that the fundamental doublet state of the d^7 configuration is considerably stabilized along path (c) in Fig. 3. Although such trend does not necessarily correspond to that in the total energy, it is consistent with the fact that the coordination geometry in the cobalt complex is more distorted toward the axially elongated square pyramid than that in the nickel complex.

Conclusions

The existence of correlations between the ligand field parameters required to fit the spectral frequencies of angularly distorted complexes sets a severe limit to the accuracy in the determination of their values. If the number of parameters is imposed to be low, by making reasonable approximations, then the values which are obtained for the parameters vary considerably from chromophore to chromophore. The ensuing difficulties in the choice of parameters should be greatly reduced if more experimental data, in addition to the values of frequencies from the electronic spectrum, become available. In fact, the parameterization of the ligand field that makes use of the angular overlap approximations and of detailed consideration of the coordination geometry [3] is found, in agreement with the results of previous investigations, to provide a substantially correct description of the electronic structure of unsymmetrical complexes. Useful applications of this ligand field model, for which accurate values of parameters are not required, consist in the rationalization of trends within series of complexes.

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References

1 C. E. Schäffer and C. K. Jørgensen, *J. Inorg. Nuclear Chem., 8,* 143 (1958); *Mat. Fys. Medd. Kgl. Dan. Vid Selsk., 34,* 13 (1965).

2 C. E. Schäffer, *Structure and Bonding, 5,* 68 (1968); *14,* 69 (1973).

3 M. Gerloch and R. F. Mc Meeking, *J. Chem. Soc. Dalton,* 2443 (1975).

4 M. Gerloch, R. F. Mc Meeking and A. M. White, *J. Chem. Soc. Dalton,* 2452 (1975).

5 E. König and S. Kremer, 'Ligand Field Energy Diagrams', Plenum Press, New York (1977).

6 G. F. Koster, in J. C. Slater, 'Quantum Theory of Atomic Structure', Vol. II, McGraw–Hill, New York (1960) p. 157.

7 P. Dapporto and M. Di Vaira, *J. Chem. Soc. A,* 1891 (1971).

8 L. Sacconi and R. Morassi, *J. Chem. Soc. A,* 575 (1970).

9 I. Bertini, M. Ciampolini, P. Dapporto and D. Gatteschi, *Inorg. Chem., 11,* 2254 (1972).

10 I. Bertini, M. Ciampolini and D. Gatteschi, *Inorg. Chem., 12,* 693 (1973).

11 M. Di Vaira and P. L. Orioli, *Inorg. Chem., 6,* 955 (1967).

12 M. Ciampolini and N. Nardi, *Inorg. Chem., 5,* 41 (1966).

13 I. Bertini, D. Gatteschi and A. Scozzafava, *Inorg. Chem., 14,* 812 (1975).

14 M. Di Vaira and P. L. Orioli, *Inorg. Chem., 8,* 2729 (1969).

15 M. Ciampolini and G. P. Speroni, *Inorg. Chem., 5,* 45 (1966).

16 I. Bertini, P. Dapporto, D. Gatteschi and A. Scozzafava, *Inorg. Chem., 14,* 1639 (1975).

17 M. Di Vaira, *J. Chem. Soc. A,* 148 (1971).

18 L. Sacconi and R. Morassi, *J. Chem. Soc. A,* 2904 (1969).

19 M. Di Vaira and P. L. Orioli, *Acta Crystallogr., B24,* 595 (1968).

20 C. Benelli, M. Di Vaira, G. Noccioli and L. Sacconi, *Inorg. Chem., 16,* 182 (1977).

21 M. Di Vaira, *J. Chem. Soc. Dalton,* 1575 (1975).

22 L. Sacconi and I. Bertini, *J. Am. Chem. Soc., 90,* 5443 (1968).

23 A. Bianchi, P. Dapporto, G. Fallani, C. A. Ghilardi and L. Sacconi, *J. Chem. Soc. Dalton,* 641 (1973).

24 P. Dapporto and G. Fallani, *J. Chem. Soc. Dalton,* 1498 (1972).

25 J. L. Shafer and K. N. Raymond, *Inorg. Chem., 10,* 1799 (1971).

26 L. V. Interrante and J. L. Shafer, *Inorg. Nuclear Chem. Letters, 4,* 411 (1968).

27 Z. Dori, R. Eisenberg and H. B. Gray, *Inorg. Chem., 6,* 483 (1967).

28 Z. Dori and H. B. Gray, *J. Am. Chem. Soc., 88,* 1394 (1966).

29 C. Mealli, P. L. Orioli and L. Sacconi, *J. Chem. Soc. A,* 2691 (1971).

30 M. Di Vaira, *J. Chem. Soc. Dalton,* 2360 (1975).

31 M. Di Vaira and L. Sacconi, *J. Chem. Soc. Dalton,* 493 (1975).

32 M. A. Hitchman, *Inorg. Chem., 11,* 3387 (1972).

33 E. Clementi, 'Tables of Atomic Functions', IBM Corp., San Jose, California (1965).

34 J. S. Griffith, 'The Theory of Transition Metal Ions', Cambridge, University Press (1971).

35 M. Gerloch and R. C. Slade, 'Ligand Field Parameters', Cambridge, University Press (1973).

36 The values of the e_λ parameters reported in Table I for the compounds III, V and X do not closely agree with those that have been obtained by previous investigations on the same compounds [13, 16]. This is due to differences in the effective symmetry and in the number of parameters assumed by the alternative ligand field models. In particular, in the previous investigation on compounds III and X constraints were imposed on the variations of the e_λ (Br) parameters, in order that the number of independent e_λ parameters did not exceed that of the independent d–d transitions [13]. Such constraints have been relaxed in the present study.

37 The transitions to the 'P states' are identified on the basis of assignments previously performed for the single-crystal polarized spectra of representative compounds (II, V and X; references in Table I) as well as on the basis of the results of the present calculations.

38 I. Bertini, M. Ciampolini and L. Sacconi, *J. Coord. Chem., 1,* 73 (1971).

39 J. S. Wood, *Inorg. Chem., 7,* 852 (1968).

40 Transfer of parameters from the high-spin to the low-spin systems has involved approximations (*e.g.* the specific nature of the halogen atom has not been taken into account, parameters being calculated for a hypothetical bromide ligand at 'normal' bond distance from the metal) in view of the fact that these low-spin systems have been essentially considered in order to provide a basis for idealized models (see section on 'applications') and to explore the conditions for the change of spin multiplicity of the ground state.

41 L. Sacconi, *Coord. Chem. Reviews, 8,* 351 (1972).

42 The values of e_σ(N) and e_σ(Br) for compound X have been transferred from III and those of e_π(Br), e_σ(P), e_π(P) and B have been found by fitting the spectrum, using a coarse grid in parameter space. The e_σ(N) values for XI and XII have been transferred from III and those of e_λ(P) from X. Values of parameters for the halogen atom and those of B for XI and XII have been interpolated between III and X.

43 The geometries of compounds X, XV and XVIII, slightly idealized, have provided models of the TET, SP and TBP coordination types, respectively. Parameters have been transferred from compounds III, VIII, IX and X, making simplifying approximations for the 'halogen atom', analogous to those described in Ref. 40.

44 The trends shown in Fig. 2 have been calculated using the same sets of parameters for the d^7 and d^8 configurations, as they have been found not to depend critically on the particular choices of parameter values (whereas they do depend on the geometry of the chromophores). Along the paths TBP → SP and TBP → TET values of parameters have been varied proportionately to the extent of the distortion from the initial to the final geometry.

45 As defined in Ref. 41, the elongation coefficient is the ratio of the M–L (apical) to the M–L (basal) bond length.