Contribution from the Department of Chemistry,
North Dakota State University, Fargo, North Dakota 58105

Electronic Excitation Spectroscopy and an Angular-Overlap-Model Analysis of *fac*-Tris(glycinato)chromium(III)

WILLIAM M. WALLACE and PATRICK E. HOGGARD*

Measurement of the five components of the ^2E_g and $^2T_{1g}$ (O_h) states, with low-temperature excitation spectroscopy, yields, with the quartets, a data base sufficient to perform ligand field calculations. Such a calculation, with use of angular-overlap-model parameterization, has been performed on *fac*-Cr(gly)$_3$. The effects of differential orbital expansion, 4s–3d mixing, and deviations of bond lengths and bond angles in the crystal from C_3 symmetry have been explored. Of these, only differential orbital expansion was judged important. The doublet energies depend very strongly on the molecular geometry: the deviation of the chelate bite angles from 90°, reinforced by the ligand field asymmetry, generates considerable splitting within the ^2E, $^2T_1$ manifold. The angular-overlap parameters determined, $e_{\sigma_N} = 6700$ cm^{-1}, $e_{\sigma_O} = 8800$ cm^{-1}, and $e_{\pi_O} = 2000$ cm^{-1}, point, by comparison with those for monodentate analogues, toward inductive electron donation from the amino to the carboxylate group.

Introduction

The spin-forbidden intraconfigurational transitions in d^3 complexes have received increasing attention in recent years,[1-10] in part because these sharp-line spectra pose a substantial problem to ligand field theory. On the one hand, the peak positions can be located with a precision two orders of magnitude greater than can the spin-allowed bands in the same spectrum, while on the other, the splittings involved are not easily explained, being due, at least for tetragonal and higher symmetry, entirely to configuration interaction with other states.[10-12]

There are a number of advantages to constructing a successful model for the spin-forbidden bands. As the symmetry of the complex is lowered from octahedral, the number of parameters necessary for any of the ligand field approaches quickly begins to outstrip the number of potentially observable spin-allowed bands. At the same time the experimental resolution of these bands is problematic: it is rare, for example, for a room-temperature spectrum of a chromium(III) complex to exhibit more than a total of three components from the octahedral $^4T_{1g}$ and $^4T_{2g}$ states.[13] Even then, the precision with which the peak positions of strongly overlapping bands may be located is suspect.

One approach to this problem has been to record low-temperature polarized single-crystal spectra.[1,14-17] This permits a reliable band assignment, but again the requirement of observable dichroism limits this technique to complexes of fairly high symmetry.

All alternative proposition is to rely on the sharp spin-forbidden lines. In many cases, all five components of the O_h ^2E_g

and $^2T_{1g}$ states can be observed,[3,5,9,17,18] in addition to which the three components of the higher lying $^2T_{2g}$ state may be seen.[15,16,19] Thus there is a sufficient number of bands, all of which may be accurately measured, to yield, in principle, a unique fit even in very low-symmetry molecules with several different ligands.

There are still, however, severe problems with this approach, perhaps the greatest of which is that the configuration interaction responsible for the doublet splittings cannot be represented in analytical form, although useful perturbation approximations have been derived for some symmetries.[1,12,20,21] The precision of the peak position determination (2 cm^{-1} or better) also demands more of the ligand field model than is ordinarily necessary. Although the theory cannot be expected to reproduce band positions to this precision, band *splittings* (of a few hundred wavenumbers) approaching this precision may be aspired to.

Some specific problems have been noted previously. For example, it is not, in general, possible to fit the spin-allowed and spin-forbidden bands with the same values of the interelectronic repulsion parameters.[22,23] Another problem is that the splitting between the two components of the ^2E_g (O_h) state, which because they can be seen in both absorption and luminescence have been studied most, has often been much larger than ligand field calculations predict.[2,4,6] An experimental problem lies with the difficulty, on occasion, in distinguishing pure electronic transitions from the vibronic bands that also appear in the spectrum.

Both the fitting problems mentioned above have at times been ascribed to the inadequacy in the representation of the interelectronic repulsion in complexes in terms of two spherical parameters.[3,6,24] Even in octahedral symmetry, the total number of different repulsion terms that may arise is 10.[25] Clearly one wishes to retain the simplicity of the spherical case to the extent possible. One approach has been to argue that the free-ion Racah parameters, B and C, are reduced to a greater extent in σ-bonding orbitals. The nephelauxetic ratios β_{33}, β_{55}, and β_{35} have been proposed[26] to account for the

(1) R. L. Carlin and I. M. Walker, *J. Chem. Phys.*, **46**, 3921 (1967).
(2) R. K. Lowry and J. R. Perumareddi, *J. Phys. Chem.*, **74**, 1371 (1970).
(3) C. D. Flint and A. P. Matthews, *J. Chem. Soc., Faraday Trans. 2*, **69**, 419 (1973).
(4) C. D. Flint and A. P. Mathews, *J. Chem. Soc., Faraday Trans. 2*, **70**, 1307 (1974).
(5) C. D. Flint and A. P. Matthews, *Inorg. Chem.*, **14**, 1008 (1975).
(6) C. D. Flint, A. P. Matthews, and P. J. O'Grady, *J. Chem. Soc., Faraday Trans. 2*, **73**, 655 (1977).
(7) S. Decurtins, H. U. Güdel, and K. Neuenschwander, *Inorg. Chem.*, **16**, 796 (1977).
(8) T. Schönherr and H.-H. Schmidtke, *Inorg. Chem.*, **18**, 2726 (1979).
(9) C. D. Flint and A. P. Matthews, *J. Chem. Soc., Faraday Trans. 2*, **76**, 1381 (1980).
(10) P. E. Hoggard, *Z. Naturforsch., A*, **36A**, 1276 (1981).
(11) W. Schneider, *Helv. Chim. Acta*, **46**, 1842 (1963).
(12) R. M. Macfarlane, *J. Chem. Phys.*, **47**, 2066 (1967).
(13) C. S. Garner and D. A. House, *Transition Met. Chem. (N.Y.)*, **6**, 59 (1970).
(14) L. Dubicki, M. A. Hitchman, and P. Day, *Inorg. Chem.*, **9**, 188 (1970).
(15) L. Dubicki and P. Day, *Inorg. Chem.*, **10**, 2043 (1971).
(16) T. S. Piper and R. L. Carlin, *J. Chem. Phys.*, **35**, 1809 (1961).
(17) O. S. Mortensen, *J. Chem. Phys.*, **47**, 4215 (1967).

(18) C. D. Flint and A. P. Matthews, *J. Chem. Soc., Faraday Trans. 2*, **71**, 379 (1975).
(19) W. Low, *J. Chem. Phys.*, **33**, 1162 (1960).
(20) R. M. Macfarlane, *Phys. Rev. B: Solid State*, **1**, 989 (1970).
(21) L. G. Boxall, K. W. Fung, and K. E. Johnson, *J. Inorg. Nucl. Chem.*, **35**, 3523 (1973).
(22) C. K. Jørgensen, *Struct. Bonding (Berlin)*, **1**, 3 (1966).
(23) L. S. Forster *Transition Met. Chem. (N.Y.)*, **5**, 1 (1969).
(24) C. K. Jørgensen, *Prog. Inorg. Chem.*, **4**, 73 (1962).
(25) J. S. Griffith, "Theory of Transition-Metal Ions", Cambridge University Press, Cambridge, England, 1961, Chapter 8.
(26) S. Koide and M. H. L. Pryce, *Philos. Mag.*, **3**, 607 (1958).

electrostatic interaction within the e_g and t_{2g} subshells and between the two subshells, respectively. The β terms represent the ratio of B (and usually C as well) in the complex to the value in the free ion. We have adopted a basically similar approach in this paper.

The basic problem in appending corrections to the conventional ligand field treatment such as a Trees correction[27] or 4s–3d mixing[28] (also included in our treatment) lies in the overparameterization of the system. Even when a unique solution, based on a least-squares or minimax fitting process, is attained, the significance of the parameters is called into question. Lever has emphasized repeatedly that a good fit cannot be taken as evidence of a correct assignment.[29] In tetragonal complexes, for example, it has been shown that very large variations in the splitting pattern of the eight lowest ^2G-derived components result from adjustment of the σ and π asymmetry between the ligands.[10] Thus many inappropriate parameter values may be masked or "swallowed" by the ligand field asymmetry. In the angular-overlap-model treatment of the ligand potential, attaining realistic parameter values is critical, since the angular-overlap parameters should be, to a large extent, transferable from one complex to another with the same ligand.

The test case we employ here is fac-$Cr(gly)_3 \cdot H_2O$, gly = glycine, which may be prepared in a very pure state, monitoring the luminescence spectrum for isomeric or other impurities.[30] The room-temperature crystal structure is known,[31] which is important in the application of a reasonable ligand field potential. The luminescence may also be monitored to obtain an excitation spectrum in which there are five conspicuous peaks in the red part of the spectrum, which we assign to the lowest five components of the ^2G term.

Experimentally, then, $Cr(gly)_3$ is an advantageous test case. In addition it is a nearly octahedral molecule, in the sense that, if all angles around the metal were 90°, the axes would be equivalent and the holohedrized symmetry would be O_h.[32] Chelate complexes are frequently assumed to be approximately orthoaxial for the purpose of ligand field calculations,[4,9,14,15,29,33] a practice that the present paper shows to be inappropriate when considering the doublet bands.

With a complex approaching effective octahedral symmetry, the difference between the ligands assumes less importance, which allows us to concentrate on the geometric effects just mentioned as well as to evaluate some of the features that may be necessary to add to the usual ligand field treatment in order to satisfactorily model the doublet splittings.

The use of the angular-overlap model is an important part of the present analysis because it provides a convenient way to express the ligand field potential for any actual ligand geometry.[34–36] The parameters of the model, e_σ and e_π, to the extent they can be shown to take on consistent values in different complexes, can be used effectively to correlate and predict dynamic properties such as photochemical quantum yields and pathways.[37–39]
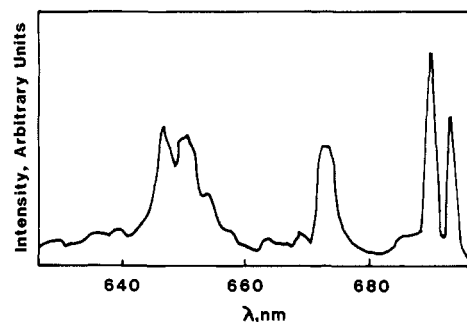

Figure 1. Excitation spectrum of fac-$Cr(gly)_3$ at 10 K.

Experimental Section

fac-$Cr(gly)_3 \cdot H_2O$. Preparation of the pure complex presents some problems because its near insolubility precludes recrystallization. The method of Gillard et al.[40] was used, except that commercial chromium(III) chloride (hydrated) and glycine were reacted in a 1:9 ratio. The red crystals collected were subjected to successive flotations in ethanol to remove remaining impurities. The luminescence spectrum at 10 K was measured, and any alteration of relative peak intensities with exciting wavelength was cause for discarding the sample.

Spectroscopic Instrumentation. Luminescence and excitation spectra were recorded on an apparatus consisting of a 150-W xenon lamp source (Photochemical Research Associates), light from which was passed through a Spex Model 1672 0.25-m double monochromator. Emitted radiation was analyzed with a Spex 1400-II 0.75-m double monochromator and a PAR Model 1140A quantum photometer. The sample was mounted in microcrystalline form with conductive grease to a sample holder attached to the cold head of an Air Products Model CSA-202 closed-cycle helium cryostat. The sample holder reached a temperature of 10 K.

Visible absorption spectra were recorded on a Cary 14 spectrophotometer.

Results

The 10 K luminescence spectrum of fac-$Cr(gly)_3$ was typical of the sharp-line phosphorescence spectra of d^3 complexes. The electronic origins (from the ^2E_g (O_h) state) were observed at 14 478 and 14 551 cm^{-1}, the latter being broader and very weak. The 73-cm^{-1} splitting was larger than that observed by Ranade et al.,[41] and excitation data indicate it is larger still. The spectrum did not vary with exciting wavelength within the spin-allowed bands. Excitation in the spin-forbidden bands produced a luminescence spectrum in which the vibronic intensities were enhanced relative to the electronic origins, with no apparent frequency shifts. There was evidence for some kind of phase transition at 12 K, producing a slight alteration of the luminescence spectrum. No further alteration was observed between 12 and 150 K.

The 10 K excitation spectrum in the ^2E_g, $^2T_{1g}$ region was recorded by monitoring a vibronic peak in the luminescence spectrum and is shown in Figure 1. The spectrum obtained was independent of the vibronic peak used. The five dominant peaks in the spectrum we assign to the electronic transitions. An alternative assignment would consider the high-energy doublet to be a triplet and assign the strong middle band to a vibronic transition to one of the ^2E_g (O_h) states. However, there is no close correspondence to a band in the low-temperature far-IR spectrum,[42] and in any case it is difficult to see why one particular vibronic transition should have such a high intensity. A room-temperature mull absorption spec-

(27) R. E. Trees, *Phys. Rev.*, **83**, 756 (1951).
(28) L. Falvello and M. Gerloch, *Inorg. Chem.*, **19**, 472 (1980).
(29) M. Keeton, B. F. Chou, and A. B. P. Lever, *Can. J. Chem.*, **49**, 192 (1971).
(30) W. M. Wallace and P. E. Hoggard, *Inorg. Chim. Acta*, **65**, L3 (1982).
(31) R. F. Bryan, P. T. Greene, P. F. Stokely, and E. W. Wilson, Jr., *Inorg. Chem.*, **10**, 1468 (1971).
(32) C. K. Jørgensen, "Modern Aspects of Ligand Field Theory", North-Holland, Amsterdam, 1971.
(33) W. W. Fee and J. N. M. Harrowfield, *Aust. J. Chem.*, **23**, 1049 (1969).
(34) C. E. Schäffer, *Struct. Bonding (Berlin)*, **5**, 68 (1968).
(35) C. E. Schäffer, *Proc. R. Soc. London, Ser. A*, **297**, 96 (1967).
(36) C. E. Schäffer and C. K. Jørgensen, *Mol. Phys.*, **9**, 401 (1965).
(37) L. G. Vanquickenborne and A. Ceulemans, *J. Am. Chem. Soc.*, **99**, 2208 (1977).
(38) L. G. Vanquickenborne and A. Ceulemans, *Inorg. Chem.*, **17**, 2730 (1978).

(39) L. G. Vanquickenborne and A. Ceulemans, *J. Am. Chem. Soc.*, **100**, 475 (1978).
(40) R. D. Gillard, S. H. Laurie, D. C. Price, D. A. Phipps, and C. F. Weick, *J. Chem. Soc., Dalton Trans.*, 1385 (1974).
(41) A. Ranade, E. Koglin, and W. Krasser, *Fresenius Z. Anal. Chem.*, **273**, 463 (1975).
(42) W. M. Wallace, Ph.D. Dissertation, Polytechnic Institute of New York, Brooklyn, NY, 1982.

Table I. Optimized Cartesian Coordinates for Ligating Atoms in *fac*-Cr(gly)₃ (in Å)

atom	x	y	z
N₁	0.049	0.172	2.066
N₂	−2.053	0.052	−0.186
N₃	0.164	−2.063	−0.029
O₁	−0.017	1.957	0.123
O₂	−0.096	0.029	−1.964
O₃	1.960	−0.132	−0.049

trum has been published that shows three bands in the spin-forbidden region, in the positions expected after consolidation of the two doublets in Figure 1.[31]

The room-temperature visible absorption spectrum has been measured in the solid state by diffuse reflectance[41,43] and mull absorption,[31] in dilute aqueous solution,[44,45] and in varying concentrations of perchloric acid.[40,43,46] To these we may add our own measurements in dimethylformamide, in which Cr-(gly)₃ is somewhat more soluble than in water, with peaks found at 528 and 393 nm.

The overall variation in reported peak positions is quite large, especially for the first band (539 nm in 70% HClO₄[40] to 501 nm in solid diffuse reflectance);[41] however the results are consistent for each medium. We have used the mineral oil mull absorption data of Bryan et al.[31] in preference to our solution data, for a better match with our solid-state excitation data.

Discussion

We have adapted the positional parameters from the X-ray crystal structure determination of Bryan et al.[31] in such a way as to optimize the alignment of the glycine nitrogen and oxygen atoms with Cartesian axes centered on the chromium. The resulting coordinates are listed in Table I. It might be noted that the off-axis angles average 4.2° (i.e., the bite angle is ca. 82°) and the twist angles (out of the Cartesian planes) are all about 1.5°.

The spectrum in Figure 1 reveals splittings that are extraordinary, considering the nearly octahedral symmetry, in several respects. The ²Eg (O_h) splitting of about 90 cm⁻¹ approaches those of tetragonal complexes,[3,6,9,47] although it should be pointed out that 50-cm⁻¹ splittings are not uncommon among nominally octahedral Cr(III) complexes.[48,49] Quite uncommon, on the other hand, is the total ²E, ²T₁ splitting —ca. 950 cm⁻¹. Octahedral complexes, whether or not there is distortion in the crystal lattice, and CrL₃ complexes with symmetric bidentate ligands exhibit total splittings below 800 cm⁻¹,[49–51] and more generally near 600 cm⁻¹, which corresponds well to our calculated values for O_h symmetry (vide infra).

Still less expected is the 600-cm⁻¹ splitting of the ²T₁g state. Overall ²T₁g splittings of 80–200 cm⁻¹ have been observed for CrL₆ and Cr(L–L)₃ complexes.[48,51]

Since Cr(L–L)₃ complexes exhibit spectra not markedly different from CrL₆ spectra, the suspicion is raised that the unusual splittings in Cr(gly)₃ are in fact ascribable to ligand field asymmetry.

Energy Level Calculations.

The conventional ligand field Hamiltonian, if the central field portion is neglected, is

$$\mathcal{H} = V_{LF} + \sum_{i>j} \frac{e^2}{r_{ij}} + \xi \sum_i l_i \cdot s_i \qquad (1)$$

These terms represent the ligand field potential, interelectronic repulsion, and spin–orbit coupling.

A strong-field basis set was employed. A C_3-adapted (but not spin-adapted) set was projected from a complete set of O_h wave functions[52] for the d³ configuration. This set was primarily used to label energy levels with the C_3 eigenfunctions to which they approximated.

Computationally, it was found to be much more efficient to use an unadapted basis set consisting of functions of the type (d_a, d_b, d_c), where each d_i is a real d orbital with spin. Thus the secular determinant was 120 × 120, which could be reduced to 60 × 60 if spin–orbit coupling was neglected.

The two-electron interelectronic repulsion integrals[25] and one-electron spin–orbit coupling integrals[53] for strong-field d wave functions have been tabulated in terms of the Racah parameters B and C and the spin–orbit parameter ζ. In the standard treatment, these integrals are carried over from the spherical ion to the complex, and matrix elements are evaluated accordingly.

We have used the angular-overlap-model ligand field potential, in which the ligand contributions to the d-orbital energies, parameterized by e_σ and e_π, are additive. Schäffer has developed several methods by which the geometric positions are used to factor in the σ and π contributions of each ligand, generating a 5 × 5 matrix, $\langle d_i | V_{LF} | d_j \rangle$, representing the ligand field potential in the usual real d-orbital basis.[34–36] We have used the scheme based on the polar-coordinate representation of the ligand positions.[34,36] π bonding by the carboxylate group was included through two orthogonal contributions, while the amino group was assumed to σ bond only. e_π for –NH₂ was set to zero (some reference point is needed in the AOM framework).

The orthogonal e_π values for the carboxylate were set equal, which implies the assumption that carboxylate is a linear ligator,[34] which it certainly is not. However, the assumption is justifiable in that the largest expected perturbation is that from the carbonyl oxygen, which is twice as far from the Cr atom as the bonding oxygen and only 19° from the Cr–O bond axis.[31]

Diagonalization of the 60 × 60 or 120 × 120 secular matrix yielded the doublet and quartet energies with the appropriate degeneracies. The calculations were tested on octahedral parameter sets (with orthoaxial geometry) and yielded the required degeneracies. A least-squares fitting procedure was used to optimize the calculated energies with respect to the five doublet energies observed and the two quartets, which were each fit to the average of all six calculated spin–orbit components. Powell's conjugate direction search technique[54,55] was used, avoiding the need for derivatives.

The parameters required for the model as developed so far are $e_{\sigma N}$, $e_{\sigma O}$, $e_{\pi O}$, B, C, and ζ. Reasonable upper and lower limits can be applied to each of these, and within these limits the observed splittings could not be reproduced. In particular, the total ²E, ²T₁ splitting could not be made to exceed 650 cm⁻¹.

Problems in reproducing ²Eg splittings[3,6] have led to the supposition that the use of spherical interelectronic repulsion parameters is a primary contributor to poor empirical fits,

(43) H. Oki and K. Otsuka, *Bull. Chem. Soc. Jpn.*, **49**, 1841 (1976).
(44) N. Israily, *C.R. Hebd. Seances Acad. Sci., Ser. C*, **262**, 1426 (1966).
(45) M. Takahashi and S. Takamoto, *Bull. Chem. Soc. Jpn.*, **50**, 3413 (1977).
(46) H. Mizuochi, A. Uehara, E. Kyuno, and R. Tsuchiya, *Bull. Chem. Soc. Jpn.*, **44**, 1555 (1971).
(47) W. N. Shepard and L. S. Forster, *Theor. Chim. Acta*, **20**, 135 (1971).
(48) C. D. Flint and P. Greenough, *J. Chem. Soc., Faraday Trans. 2*, **70**, 815 (1974).
(49) C. D. Flint and D. J. D. Palacio, *J. Chem. Soc., Faraday Trans. 2*, **75**, 1159 (1979).
(50) C. D. Flint and D. J. D. Palacio, *J. Chem. Soc., Faraday Trans. 2*, **76**, 82 (1980).
(51) C. D. Flint and A. P. Matthews, *J. Chem. Soc., Faraday Trans. 2*, **72**, 579 (1976).
(52) J. R. Perumareddi, *Coord. Chem. Rev.* **4**, 73 (1969).
(53) C. J. Ballhausen, "Introduction to Ligand Field Theory", McGraw-Hill, New York, 1962, Chapter 6.
(54) M. J. D. Powell, *Comput. J.*, **7**, 155 (1964).
(55) J. L. Kuester and J. H. Mize, "Optimization Techniques with Fortran", McGraw-Hill, New York, 1973.

Table II. Interelectronic Repulsion Parameters in Amine and Carboxylate Complexes of Cr(III)

complex	β_{35}	β_{55}	B, cm^{-1}	ϵ	ref
Cr(ox)$_3$$^{3-}$	0.68	0.88	808	0.88	a
Cr(NH$_3$)$_6$$^{3+}$	0.71	0.90	827	0.89	a
Cr(en)$_3$$^{3+}$	0.67	0.88	808	0.87	a
fac-Cr(gly)$_3$			805	0.878	this work

a Reference 22.

although Ferguson and Wood[56] have argued that allowing the repulsion parameters to vary independently, rather than requiring them to assume a fixed ratio to the free-ion values (as is often done), may be sufficient, a position supported by Witzke.[57]

We have attempted to account for the presumed "differential orbital expansion" through the introduction of one additional parameter, ϵ, defined such that a two-electron electrostatic repulsion integral is assigned a value according to

$$(d_a d_b|V|d_c d_d) = \epsilon^n (d_a d_b|V|d_c d_d)_0 \qquad (2)$$

The subscript 0 refers to the value (in terms of B and C) the integral would have in spherical symmetry, n is the number of wave functions in the integral representing e_g orbitals, and B and C must now be specified as applying to repulsion within the t_{2g} orbitals (i.e., B_{55} and C_{55}).

A further refinement to the calculation was the incorporation of 4s–3d mixing, which has proved fruitful for square-planar complexes.[28] This was done by means of a parameter, δ, representing the lowering of the energy of the d_{z^2} orbital through one-electron interactions with the 4s orbital. In near-C_3 symmetry there is no reason to suppose the d_{z^2} interaction to be greater than that with $d_{x^2-y^2}$, so δ was allowed to be negative. In any case the effect can be expected to be small.[58]

Either of the two additional parameters (δ or ϵ) by itself could be adjusted so as to increase the total $^2E_1$, $^2T_1$ splitting to 950 cm^{-1} as required. Neither of the values necessary to do this appeared reasonable, and therefore both were retained in the fitting process, leaving eight parameters to fit seven observed peaks. It thus becomes very important to examine the constraints on the solution, in order to be able to restrict the area of search as much as is feasible. Some values have been reported for the octahedral splitting parameter, Δ or $10Dq = 3e_\sigma - 4e_\pi$.[36] In Cr(III) histidine complexes,[59] $\Delta_N = 22700$ cm^{-1} and $\Delta_O = 17100$ cm^{-1} were obtained. Δ_N and Δ_O may then be constrained to a range about these values. The sum, $\Delta_N + \Delta_O$, is essentially self-constrained, since the energy of the first spin-allowed band is, in the orthoaxial approximation,[60] $^1/_2(\Delta_N + \Delta_O)$. Similarly the energies of the ^2E, $^2T_1$ levels in the first (free-ion) approximation are $9B + 3C$, and this sum is effectively self-constrained.

The 4s–3d mixing parameter, δ, cannot be so high as to produce any visible splitting of the quartets. We have constrained it to a maximum of 2500 cm^{-1} (which leads to a $^4T_{2g}$ (O_h) splitting of about 2000 cm^{-1}). From values for other O- and F-containing, π-donating ligands, $e_{\pi O}$ is expected to be in the range 1000–2000 cm^{-1}.[29]

Finally, some values for β_{35} and β_{55} have been tabulated by Jørgensen,[22] from which our parameters B (=B_{55}) and ϵ may be derived. Table II shows these for amine and carboxylate

Table III. Optimum Doublet and Quartet Energies in *fac*-Cr(gly)$_3$

		ΔE(calcd), cm^{-1}	
state	ΔE(exptl), cm^{-1}	normal geom	altered geom^a
$^2E_a(^2E_g)$	14 485	14 471	14 478
$^2E_b(^2E_g)$	14 579	14 569	14 573
$^2A(^2T_{1g})$	14 842	15 031	14 959
$^2E_b(^2T_{1g})$	15 350	15 229	15 233
$^2E_a(^2T_{1g})$	15 442	15 400	15 458
$^4T_{2g}$(av)	19 880	19 695	19 752
$^4T_{1g}$(av)	26 040	26 195	26 067

final parameters^c	normal geom	altered geom^a
$e_{\sigma O}$, cm^{-1}	8832 ± 331	8826 ± 93
$e_{\pi O}$, cm^{-1}	2000 ± 547^b	1995 ± 189
$e_{\sigma N}$, cm^{-1}	6843 ± 346	6709 ± 274
B, cm^{-1}	805 ± 16	738 ± 18
C, cm^{-1}	2833 ± 50	3017 ± 56
ζ, cm^{-1}	266 ± 349	115 ± 633
ϵ	0.878 ± 0.005	0.909 ± 0.007
δ, cm^{-1}	2393 ± 34	6 ± 1508

a Ligand atoms assumed to lie 50% further from Cartesian axes in same direction (see text). b Boundary value. c Error margins represent only errors propagated from uncertainties in peak positions.[62]

ligands. It should be mentioned that Jørgensen kept C/B fixed to the free-ion ratio in this calculation. Ferguson and Wood's approach would involve adjusting B and C independently[61] instead. Our fitting procedure used both methods, thus the values for B and ϵ in Table II, though quite consistent, were adopted only as upper bounds.

The results of the optimization are shown in Table III. The doublet energies were assigned weights of 10 with respect to the average quartet energies. The approximate C_3 symmetry labels have been used to identify the doublet levels. The overall splitting of the ^2E, $^2T_1$ levels could be fairly well approximated within the present model, as could the ^2E_g (O_h) splitting, while the $^2T_{1g}$ splittings were poorly fit.

The parameter set used to generate the "best-fit" energies is also listed in Table III. The error margins reported are based only on the propagation of the uncertainties in the experimental values,[62] 2 and 20 cm^{-1}, respectively, for the doublet and quartet states. Other sources of error are discussed below. A large standard deviation in Table III corresponds to a small influence on the calculated energies; thus the error margins serve to assess the relative significance of each of the parameters.

Spin–orbit coupling, in particular, is seen to be relatively unimportant. Indeed, adjusting the spin–orbit parameter, ζ, from 0 to 275 cm^{-1}, the approximate value in the free ion,[63] alters the doublet splittings by at most 6 cm^{-1}. Similarly small effects are seen in the $^4T_{2g}$ and $^4T_{1g}$ (O_h) states, while the ground-state splitting was calculated to be 1.0 cm^{-1} at $\zeta = 275$ cm^{-1}. These results are not surprising for nearly trigonal symmetry.[12]

One problem characteristic of ligand field fitting processes is the possibly high degree of interdependence of the parameters. The correlation matrix generated in the least-squares fit with use of the parameter set of Table III is shown in Table IV. The cross correlation among all the variables is quite marked. Reparameterization to {Δ, Δ_O, $e_{\pi O}$, B, $3B + C$, ϵ, δ,

(56) J. Ferguson and D. L. Wood, *Aust. J. Chem.*, **23**, 861 (1970).
(57) H. Witzke, *Theor. Chim. Acta*, **20**, 171 (1971).
(58) M. Gerloch, J. H. Harding, and G. Wooley, *Struct. Bonding (Berlin)*, **46**, 1 (1981).
(59) P. E. Hoggard, *Inorg. Chem.*, **20**, 415 (1981).
(60) C. E. Schäffer and C. K. Jørgensen, *Mat.-Fys. Medd—K. Dan. Vidensk. Selsk.*, **34**, 13 (1965).

(61) Ferguson and Wood's method actually consists of varying the free-ion term energies parametrically and then fitting these term energies with Racah or Slater–Condon parameters.[56] In end effect, even if not conceptually, this is equivalent to adjusting B and C independently.[57]
(62) A. A. Clifford, "Multivariate Error Analysis", Wiley-Halsted Press, New York, 1973.
(63) D. S. McClure, *Solid State Phys.* **9**, 428 (1959).

Table IV. Matrix of Correlation Coefficients for the Parameter Set of Table III[a]

	$e_{\sigma N}$	$e_{\sigma O}$	$e_{\pi O}$	B	C	δ	ϵ	ζ
$e_{\sigma N}$	1.000	0.889	0.972	0.936	-0.943	0.477	0.688	-0.974
$e_{\sigma O}$		1.000	0.969	0.912	-0.915	0.470	0.667	-0.945
$e_{\pi O}$			1.000	0.963	-0.967	0.482	0.728	-0.991
B				1.000	-1.000	0.510	0.848	-0.981
C					1.000	-0.511	-0.841	0.984
δ						1.000	0.468	-0.497
ϵ							1.000	-0.749
ζ								1.000

[a] The correlation coefficients depend on the weights assigned to the observables. Doublet peaks were weighted 10 times more heavily than quartet peaks.

ζ tends to decouple these to some extent (especially Δ). Such interdependence tends to make minimum search methods inefficient, although conjugate direction methods offer advantages in overcoming this.[64]

Effects of Geometry. Since *fac*-Cr(gly)$_3$ in the solid state at room temperature has only approximate C_3 symmetry, it is of interest to ask whether these deviations from C_3 might be responsible for the apparently anomalous splitting of the $^2T_{1g}$ (O_h) state. The "best-fit" parameter set was used to recalculate energies in an idealized molecule, in which the ligand coordinate positions were averaged to yield C_3 symmetry of the CrN$_3$O$_3$ chromophore. This resulted in alterations of the transition energies by only 5 cm^{-1} or less.

The Cr–N and Cr–O bond lengths are also not identical, and we attempted to take this asymmetry into account by allowing the AOM parameters to vary as functions of the bond length, r:

$$e_{\lambda_i} = (e_{\lambda_i})_0 (r_{i_0}/r_i)^n \qquad i = N \text{ or } O; \ \lambda = \sigma \text{ or } \pi \qquad (3)$$

One of each type of ligand serves as a reference with $r = r_O$, $e_\sigma = e_{\sigma_O}$, etc. The value of n would be 5 or 6 according to classical crystal field theory,[65] with the ligands regarded as point charges or dipoles. However, the effect of changes in ligand distance on metal d-orbital energies probably corresponds more closely to Born repulsion, pointing to an n of 6–12. Even with $n = 12$, however, the transition energies were altered by amounts less than 1.0 cm^{-1}.

The primary effect, then, appears to involve the contraction of the chelate ligand from 90° bond angles. This is well illustrated by Figure 2, in which the variation of the doublet energies with bite angle is calculated, stepping by equiangular amounts from orthoaxial coordination through the actual angles and extrapolating to a 33% greater contraction in the same direction. The variation in quartet energies is larger, but not so great as to induce splittings that might be visible or to alter substantially the average energy. The curves in Figure 2 do not converge to two levels in the limit of orthoaxiality because of the quasi-tetragonal symmetry caused by inclusion of s–d orbital mixing in the calculation.

The substantial dependence of the doublet energies on angular geometry is also tied up with the ligand field asymmetry. When the two coordinating groups are equivalent, the angular effects are reduced. This is particularly striking for the ^2E_g (O_h) state, for which the splitting is reduced by a factor of 6, compared with that in Figure 2, when the angular-overlap parameters of N and O are averaged.

Comparison of Figure 2 with the experimental data in Table II suggests that a further angular distortion might effectively account for the observed splittings. This approach is not entirely unreasonable since one of the major compromises in this study involved merging data acquired at different tem-
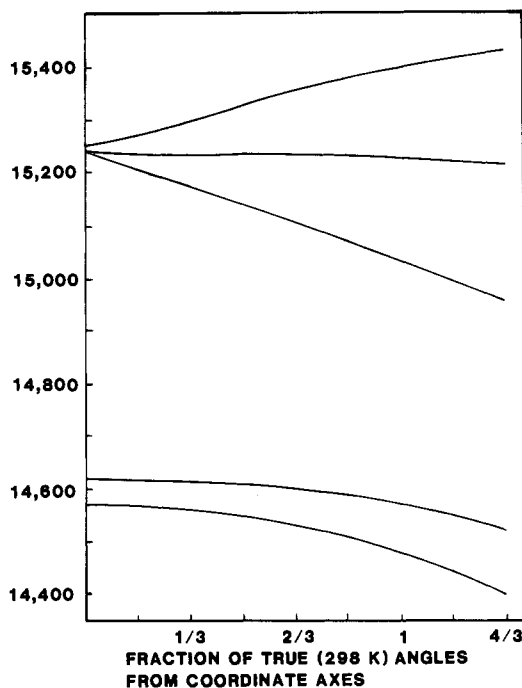

Figure 2. Calculated ^2E_g and $^2T_{1g}$ transition energies as a function of bond angles. The abscissa represents a linear variation of all ligand angles from a set of Cartesian axes through the actual bond angles, extending 33% beyond the actual angles in the same direction. Parameters used (in cm^{-1}, except for ϵ): $e_{\sigma_O} = 8832$, $e_{\pi_O} = 2000$, $e_{\sigma_N} = 6843$, $B = 805$, $C = 2833$, $\zeta = 266$, $\delta = 2392$, $\epsilon = 0.878$.

peratures: the crystal structure determination and visible absorption spectrum at room temperature and the excitation spectrum at 10 K.

The nearly symmetric distortion (past the room-temperature bond angles) used in Figure 2 represents only one of many possible distortions, symmetric and unsymmetric, that may have quite different effects on the doublet energies. To evaluate the possible effects on the whole parameter set, however, we have tested a geometry in which the ligand angular positions are 50% further from the Cartesian axes than in the room-temperature molecule. We have ignored bond length changes, which might also be significant.

The least-squares best-fit parameter set is included in Table III, as are the calculated energy levels. As expected from Figure 2, the results are considerably better, though the $^2T_{1g}$ splittings are still not well reproduced. An important point is that the interelectron repulsion parameters B and ϵ moved away from the imposed boundary constraints. The s–d mixing, represented by δ, essentially vanished. On the other hand, the ligand field parameters were not much changed.

Conclusions. Because of the number of observable bands, it is in principle possible, for a d^3 complex, to determine the AOM parameters e_σ and e_π for each ligand, as well as the other parameters in a ligand field analysis, by including the five

(64) P. R. Adby and M. A. H. Dempster, "Introduction to Optimization Methods", Chapman and Hall, London, 1974.
(65) R. Finkelstein and J. H. Van Vleck, *J. Chem. Phys.*, **8**, 790 (1940).

components of the ^2E, $^2T_1$ states. These are most easily measured through excitation spectroscopy, which, however, generally requires low temperatures.

The question still remains whether the doublets can be fit within a ligand field theoretical framework to the accuracy required and whether the parameters so obtained have any meaning. The *fac*-Cr(gly)$_3$ molecule is a good test case. Unlike the situation for tetragonal symmetry,[10] the doublet (and quartet) energies are not strongly dependent on the ligand field asymmetry, so that it is not as easy to cover defects in the model by adjusting the parameters.

What can be said is that the doublet energies and splittings depend quite strongly on the angular geometry, operating synergistically with the ligand field asymmetry. The 10 K doublet energies could not be reproduced with use of the room-temperature geometry, whereas certain more or less arbitrary distortions led to a much better fit. The "best-fit" values for the AOM parameters themselves were not much affected by the distortions, although the statistical errors were large and e_{π_O} was at or near the boundary we imposed (2000 cm^{-1}).

The AOM parameters derived appear reasonable. e_{σ_N} for the amino group is somewhat lower than for NH$_3$ or ethylenediamine,[66] while e_{σ_O} for the carboxylate group is in the top range of values reported for π-donor ligands such as OH$^-$ and F$^-$.[29,33] Inductive electron donation from amine to carboxylate may well account for this.

Similarly, e_π values have been reported from OH$^-$ and F$^-$ from 1400 to above 2000 cm^{-1},[29,33,67] so again 2000 cm^{-1} is

a reasonable value for the glycine carboxylate, even though it was a boundary value in the calculation.

Some specific conclusions apply to future work in which spin-forbidden peaks form most of the data base for ligand field calculations.

1. s–d mixing, as predicted,[58] should be ignored for six-coordinate complexes.

2. Inclusion of differential orbital expansion has proven very useful. Arguments against this approach[56,57] have been based largely on data from octahedral complexes. For lower symmetry complexes it does not appear possible to fit at least the spin-forbidden bands without invoking differential orbital expansion in some form.

3. The strong angular dependence of the doublet energies suggests incorporation of one or more geometric parameters in the fitting process. Lever and Hollebone[68] have attempted this using one azimuthal angle (formally equivalent to a bite angle), representing trigonal distortion. Although they could not check the angles so calculated (the Cr(III) was present as impurity ions), they suggest in any case that the azimuthal angle may properly be regarded as a phenomenological parameter in the fitting process, without necessarily requiring agreement with crystallographic data. The idea behind this is presumably to consider the angle as a generator of the low-symmetry ligand field.

(66) J. Glerup, O. Mønsted, and C. E. Schäffer, *Inorg. Chem.*, **15**, 1399 (1976).
(67) H. L. Schläfer, M. Martin, and H.-H. Schmidtke, *Ber. Bunsenges. Phys. Chem.*, **75**, 787 (1971).
(68) A. B. P. Lever and B. R. Hollebone, *J. Am. Chem. Soc.*, **94**, 1816 (1972).

Contribution from the Institut für Organische Chemie der Friedrich-Alexander-Universität Erlangen-Nürnberg, D-8520 Erlangen, Federal Republic of Germany, the School of Chemistry, University of Hyderabad, Hyderabad 500134, India, and the Department of Chemistry, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15235

Lithiated Ammonia, Amide Anions, and Ammonium Ions. An ab Initio Study of Structures, Bonding, and Energetic Relationships

ERNST-ULRICH WÜRTHWEIN,[1a] K. D. SEN,[1b] JOHN A. POPLE,[1c] and PAUL VON RAGUÉ SCHLEYER*[1a]

Monomeric lithiated nitrogen species, in anionic (NLi$_{2-n}$H$_n^-$), neutral (NLi$_{3-n}$H$_n$), and cationic (NLi$_{4-n}$H$_n^+$) forms, were studied by ab initio molecular orbital theory. Geometries were calculated at the 3-21G//3-21G and 4-31+G//4-31+G basis set levels (the latter being particularly appropriate for the description of the anions). The lithiated ammonias, LiNH$_2$, Li$_2$NH, and Li$_3$N, are planar, LiNH$^-$ is linear, and Li$_2$N$^-$ is bent. Angles involving Li tend to be wider than those with H. Lithiation increases the proton and lithium cation affinities markedly. Nevertheless, the presence of a larger number of lithiums is unfavorable, and disproportionation reactions (in which the lithium substituents are distributed to different molecules) are exothermic. The corresponding carbon compounds, Li$_3$CH and Li$_4$C, behave differently in this respect. While lithium substitution in Li$_2$NH$_2^+$ and Li$_4$N$^+$ reduces the preference for tetrahedral over planar geometries markedly, the effect is smaller than in the analogous carbon compounds. Heats of formation are estimated, e.g., $\Delta H_f^\circ{}_0$(LiNH$_2$) = 13.8 ± 1.2 kcal/mol. The Li–N bond energy D_0(Li–NH$_2$) = 65 ± 4 kcal/mol, is about 20 kcal/mol larger than the Li–C bond energy in Li–CH$_3$. The estimated heat of formation, $\Delta H_f^\circ{}_0$(Li$_3$N) = 84 ± 8 kcal/mol, is indicated to be over 130 kcal/mol more positive for the gas phase than the experimental value for the solid state. This underscores the importance of aggregation of lithium compounds. The nature of nitrogen–lithium bonding is complex. The ionic component (σ donation from lithium to nitrogen) may predominate, but considerable π back-bonding from nitrogen to lithium can take place, and these species have some covalent character. Polylithiated species, e.g., NLi$_3$, are not indicated to be more ionic than those with fewer lithiums. Although it is customary to write a formal positive charge on nitrogen in ammonium ions, Mulliken populations indicate these nitrogens to be negatively charged; the positive charge resides on the more electropositive substituents.

Introduction

Owing to its superionic conductivity in the solid state, lithium nitride, Li$_3$N, has been the subject of extensive ex-

perimental studies.[2] The other lithiated ammonias, LiNH$_2$ and Li$_2$NH, also are well-known.[3,4] Lithium reacts with

(1) (a) Friedrich-Alexander-Universität Erlangen-Nürnberg. (b) University of Hyderabad. (c) Carnegie-Mellon University.

(2) Review: *Nachr. Chem., Techn. Lab.* **1978**, *26*, 310.
(3) Lappert, M. F.; Dower, P. P.; Sanger, A. R.; Srivastava, R. C. "Metal and Metalloid Amides"; Wiley: New York, 1980.