

at the same time, their individual contributions to  $e_{\pi\parallel}$ —through eq 3 of part 1—will be both positive (because we consider positive denominators throughout this discussion) and hence additive, numerically as well as algebraically. We believe that the comparable values of  $e_{\pi\sigma\parallel}(\text{O})$  and  $e_{\pi\parallel}(\text{O})$  in the quinoline complex do not merely indicate experimental error or model tolerances but that they actually support the notion of both modes of misdirected valence within the planes of these chelate groups. Whether the same circumstances prevail in the cobalt complexes described in part 1<sup>6</sup> is not clear, partly through the much more difficult analyses there being based primarily upon  $g$  tensors and partly in view of the differing relative contributions to those expected from bent bonding and lone pairs in the more strongly bound systems.

In passing, we may conjecture on the reason why the acetylacetonate chelates tilt in the quinoline adduct. One cannot rule out steric forces, which we suppose play their part in the four-coordinate species. However, by tilting in the sense observed, the chelates may be maximizing overlap with metal orbitals lying in the  $xy$  plane, for that is where the repulsive effect of the electrons in the half-filled  $d_{xy}$  orbital is least. A similar proposal<sup>22</sup> has been made recently within an analysis of the formally tetrahedral  $\text{CuCl}_4^{2-}$  ion in  $\text{Cs}_2\text{CuCl}_4$ .

In summary: the present CLF analyses provide a coherent account of the valence electron distributions in a series of related complexes that lies well with mainstream chemical concepts. At the same time, confusion over the interpretation of the resultant ligand-field properties is hopefully dispelled. Throughout this<sup>6,23</sup> and the previous<sup>5,20,24</sup> series of studies we have proffered the view<sup>2,3,4,17</sup> that all ligand-field phenomena are to be seen as sequential on the underlying bonding, that, in Werner complexes at least, the role of the transition-metal  $d$  orbitals is mainly to react to the electron distribution in the bonding and other higher lying orbitals rather than to be significantly involved in the primary bonding process itself. We see the  $d$  electrons as interacting with the underlying framework of bonds "already" formed. We need not refer *explicitly* to overlap integrals within this formalism—

which, we emphasize, is merely a consequence of nature's endorsement of the basic ligand-field structure—but where such language is deemed useful we must always recognize that the overlap is not that between metal  $d$  orbitals and simple ligand functions. That view neglects the all-important electron redistribution that takes place on molecule formation. Accordingly, guesses about the relative magnitudes of such overlap integrals are wholly unreliable. Our view always has been that ligand-field parameters should be allowed free rein. The contrary view that incorporates interpretation into the approach from the beginning only serves to mix together incompatible model structures.

Inter alia, the features of electron density that seem well attested by the present analyses are (1) that acetylacetonate groups act as  $\sigma$  donors towards the copper and as  $\pi$  donors using the delocalized  $\pi$  orbitals normal to the acac plane, (2) that copper-acac bonding within or close to the acac plane is "nonideal" in the sense that geometrical constraints imposed by the chelate—and possibly crystal packing—cause misalignment of ligand orbitals and metal-oxygen vectors, (3) that such misdirected valence involves bent bonds within the chelate planes and, to a variable extent, normal to those planes, (4) that within the planes, the ligand-field analyses support the idea of a smaller bite angle defined by the bonding electron density than by the chelate donor atoms, (5) that the nonbonding lone pairs on the oxygen donors have a noticeable effect upon the  $d-d$  spectra, and (6) that the ligand-field contributions from the coordination voids throughout the series are important and similar to those established for many other similar coordinationally sparse species.

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## Ligand Fields from Misdirected Valency. 3. Ligand Hybridization in Tetragonal-Octahedral Nickel(II) Thiocyanates<sup>†</sup>

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Ligand-field analyses of the  $d-d$  spectra of seven hexacoordinate nickel(II) complexes, parameterized within the cellular ligand-field model, are presented. Several of these provide a bench mark to help substantiate the primary object of the present study: namely, to show how inclusion of a locally nondiagonal, ligand-field parameter,  $e_{\pi\sigma}$ , obviates the need to consider the thiocyanate ligand as a  $\pi$  donor in  $\text{trans-Ni}(\text{NH}_3)_4(\text{NCS})_2$  but as a  $\pi$  acceptor in  $\text{Ni}(\text{en})_2(\text{NCS})_2$  ( $\text{en} \equiv$  ethylenediamine). It is argued that the nonzero value of  $e_{\pi\sigma}$  in the latter system monitors the ligand-field effect of the nominal  $sp^2$  nonbonding lone-pair electrons established by bending of the Ni-N-CS angle.

### 1. Introduction

The utility of ligand-field analysis as a chemical discipline surely requires that its conclusions consistently match those from more widely based techniques. It is disquieting to note, therefore, a (repeated<sup>1</sup>) observation<sup>2</sup> that angular overlap model (AOM) parameters appear to define a  $\pi$ -donor role for isothiocyanate ligands in some nickel(II) complexes but  $\pi$ -acidic behavior in others that are closely related. Thus, for  $\text{Ni}(\text{NH}_3)_4(\text{NCS})_2$  in which the  $\text{trans Ni-NCS}$  angles<sup>3</sup> are approximately  $180^\circ$ ,  $e_{\sigma}(\text{NCS})$  and  $e_{\pi}(\text{NCS})$  values have been reported<sup>2</sup> as  $3843$  and  $125 \text{ cm}^{-1}$ , respectively, while values of  $2123$  and  $-409 \text{ cm}^{-1}$  are claimed<sup>2</sup>

for  $\text{Ni}(\text{en})_2(\text{NCS})_2$  in which<sup>4</sup> Ni-N-C is  $140^\circ$ . These observations were made in two studies<sup>1,2</sup> that otherwise sought to establish a simple relationship between bond length and  $e_{\sigma}$  values for Ni-N bonds. The association of the smaller  $e_{\sigma}$  value in the second complex with a longer Ni-NCS bond ( $2.15$  vs.  $2.07 \text{ \AA}$ ) has obvious qualitative appeal, but no ready explanation of the reversed  $\pi$ -bonding role seems to be at hand. Moreover, on purely phenomenological grounds, it has been proposed<sup>1</sup> that the Ni-NCS bond

- (1) Lever, A. B. P.; Walker, I. M.; McCarthy, P. J.; Mertes, K. B.; Jircitano, A.; Sheldon, R. *Inorg. Chem.* **1983**, *22*, 2252.
- (2) Bertini, I.; Gatteschi, D.; Scozzofava, A. *Inorg. Chem.* **1976**, *15*, 203.
- (3) Porai-Koshits, M. A.; Dikareva, M. L. *Kristallografiya* **1959**, *4*, 650.
- (4) Brown, B. W.; Lingafelter, E. C. *Acta. Crystallogr.* **1963**, *16*, 753.

<sup>†</sup> No reprints available from this laboratory.

**Table I.** Geometrical and Ligand-Field Parameter Values for Hexacoordinate Nickel(II) Species

complex	formula	Ni-amine, Å	Ni-NCS, Å	$\angle(\text{Ni-N-CS}),$ deg	$e_{\sigma}(\text{amine}),$ $\text{cm}^{-1}$	$e_{\sigma}(\text{NCS}),$ $\text{cm}^{-1}$	$e_{\pi}(\text{NCS}),$ $\text{cm}^{-1}$	$ e_{\pi\sigma}(\text{NCS}) ,$ $\text{cm}^{-1}$	$\sum_i^a,$ $\text{cm}^{-1}$	$B,$ $\text{cm}^{-1}$
A	$[\text{Ni}(\text{NH}_3)_6]^{2+}$	2.15			3667				22 000	890
B	$[\text{Ni}(\text{pn})_3]^{2+}$	2.14			3700				22 200	850
C	$[\text{Ni}(\text{en})_3]^{2+}$	2.12			4070				24 420	830
D	$\text{Ni}(\text{Me}_4\text{en})_2(\text{NCS})_2$	2.25	1.99	174	3100	4800	1050		26 200	850
E	$\text{Ni}(\text{Et}_2\text{en})_2(\text{NCS})_2$	2.30, 2.08	2.08	167	2800, 4500	4300	500		25 200	870
F	$\text{Ni}(\text{NH}_3)_4(\text{NCS})_2$	2.15	2.07	180	3666	4300	600		25 664	840
G	$\text{Ni}(\text{en})_2(\text{NCS})_2$	2.10	2.15	140	4140	2800	500	1000	24 160	880

$$^a \sum_i \equiv \sum_i^{\text{ligands}} (e_{\sigma} + e_{\pi_x} + e_{\pi_y})_i$$

**Table II.** Calculated and Observed d-d Transition Energies for Nickel(II) Complexes, Calculated Energies Corresponding to the Parameter Sets Given in Table I

complex		transition energies, $\text{cm}^{-1}$			
obsd	B	11300	18000	28600	
calcd		11252, 11374, 11588	17659, 18040, 18292	28464, 28635, 28853	
obsd	C	10900	17800	28200	
calcd		10850, 11009, 11275	17229, 17703, 17936	28183, 28306, 28550	
obsd	D	9500	14600 16400	26300	
calcd		9122, 9443, 9614	14832, 15468, 16455	25748, 26099, 26960	
obsd	E	9140, 10420, 12120	15770 18350	28310	
calcd		9413, 10381, 12176	15876, 17990, 18168	27367, 28409, 28938	
obsd	F	10750	17400	28000	
calcd		10635, 10721, 11108	16767, 17145, 17915	27836, 27912, 28110	
obsd	G	9600	12000, 16000 17900	27700, 28300	
calcd		9566, 10100	11971, 15789 17094, 18694	26861, 27716, 29411	

angle is markedly bent in the complex  $\text{Ni}(\text{TMen})_2(\text{NCS})_2$  also ( $\text{TMen} \equiv N,N,N',N'$ -tetramethylethylenediamine), for this has been assigned a negative AOM  $e_{\pi}$  parameter as well.

An expectation that the gross nature of the isothiocyanate ligand as a pseudohalogen should not vary much between these and similar complexes does not, however, leave one oblivious of the change in hybridization that must surely accompany the change in Ni-N-C angle. If something like sp donor hybrids are appropriate in the linear systems, an approach toward sp<sup>2</sup> orbitals must be presumed in the bent ones. There arises, then, the possibility that the lone pair of electrons housed in the third sp<sup>2</sup> hybrid might make a contribution to the ligand-field energies of the metal d electrons, as in the preceding<sup>18</sup> cobalt and copper complexes involving formally sp<sup>2</sup>-hybridized oxygen donors. It is possible that misdirected valence arises here also, simply by misalignment of the NCS  $\sigma$ -donor orbitals as apparently suggested by Bertini et al.<sup>2</sup> In this paper, therefore, we investigate whether inclusion of the local, off-diagonal cellular ligand-field (CLF) parameter,  $e_{\pi\sigma}$ , into the spectral analysis resolves the anomalous  $\pi$ -bonding role suggested for the thiocyanate group.

It is, as ever, unfortunate that we must consider a fairly large number of ligand-field parameters in these near- $D_{4h}$  systems. We therefore include in the present study a number of related complexes that require a lesser degree of parametrization. Comparisons between systems are made, however, not on the basis of bond lengths, nor individual  $e_{\lambda}$  parameters, for we have argued many times that neither linear relationships between bond lengths and  $e_{\lambda}$  parameters nor the transferability of those parameters can be expected or relied upon; rather, we have extended a recently established<sup>5,6</sup> "sum rule" to provide a sounder basis for comparison in this series of nickel(II) amine complexes.

## 2. Analyses

The cellular ligand-field (CLF)<sup>25</sup> analyses seek to reproduce reported "d-d" transition energies, determined either by diffuse reflectance or by single-crystal polarization studies as detailed below. All calculations have been performed by using the CAMMAG

package<sup>11</sup> within the complete, free-ion, spin-triplet basis, <sup>3</sup>F + <sup>3</sup>P, and by employing actual molecular geometries as determined by X-ray diffraction, except where specifically stated. The spin-orbit coupling parameter  $\zeta$  has been held fixed at 450  $\text{cm}^{-1}$  throughout. Observed transition energies are compared with those computed using the "best-fit" parameters in Table II.

**A. Hexaamminenickel(II) Diperchlorate,  $[\text{Ni}(\text{NH}_3)_6](\text{ClO}_4)_2$ .** Schreiner and Hamm<sup>12</sup> have reported the mull spectrum of the complex at 77 K and determined optimal values for  $Dq$ ,  $B$ , and  $C$  for this near-octahedral system from calculations within the complete d<sup>8</sup> basis. We quote their  $B$  value in Table I, together with ones for  $e_{\sigma}$ , taken as  $10Dq/3$ , and for the trace  $\sum$ , taken as  $6e_{\sigma} = 20Dq$  in this case. The reported fit is essentially unique, thus providing one reference point in the present series.

**B. Tris(propylenediamine)nickel(II) Dinitrate,  $[\text{Ni}(\text{pn})_3](\text{NO}_3)_2$ .** A room-temperature diffuse reflectance spectrum by Vezzosi et al.<sup>13</sup> shows three spin-allowed bands. We have reproduced these, essentially uniquely, so obtaining more reference values for  $e_{\sigma}$ ,  $B$ , and  $\sum$  given in Table I.

**C. Tris(ethylenediamine)nickel(II) Dinitrate,  $[\text{Ni}(\text{en})_3](\text{NO}_3)_2$ .** Single-crystal, polarized spectra at 300 and 25 K have been reported by Dingle and Palmer.<sup>14</sup> Ligand-field analysis of both triplet and singlet transitions by Brown, Gerloch, and McMeeking<sup>15</sup> have established values for  $e_{\sigma}$ ,  $F_2$ , and  $F_4$  that are, once more, virtually unique; see Table I.

**D. Bis(isothiocyanato)bis( $N,N,N',N'$ -tetramethylethylenediamine)nickel(II),  $\text{Ni}(\text{Me}_4\text{en})_2(\text{NCS})_2$ .** This complex involves the symmetrically and fully substituted ethylenediamine chelate.<sup>16</sup> The trans NiN-CS angles are 174°. Lever et al.<sup>1</sup> resolve four spin-allowed bands from their single-crystal polarization study at 10 K. Their CLF analysis reports the values 3165, 2115, -910, and 848  $\text{cm}^{-1}$  for  $e_{\sigma}(\text{eq})$ ,  $e_{\sigma}(\text{NCS})$ ,  $e_{\pi}(\text{NCS})$ , and  $B$ , respectively, leading to a value for the trace  $\sum$  of 13 210  $\text{cm}^{-1}$ .

Despite the four parameters being matched by four spectral bands, best fits are not as uniquely defined as in complexes A-C. The values given in Table I reproduce the observed spectrum with

- (5) Deeth, R. J.; Gerloch, M. *J. Chem. Soc., Dalton Trans.* **1986**, 1531.
- (6) Woolley, R. G. *Chem. Phys. Lett.* **1985**, *118*, 207.
- (7) Gerloch, M.; Harding, J. H.; Woolley, R. G. *Struct. Bonding (Berlin)* **1981**, *46*, 1.
- (8) Gerloch, M. *Magnetism and Ligand-Field Analysis*; Cambridge University Press: Cambridge, U.K., 1983.
- (9) Gerloch, M.; Woolley, R. G. *Prog. Inorg. Chem.* **1983**, *31*, 371.
- (10) Woolley, R. G. *Mol. Phys.* **1981**, *42*, 703.

- (11) CAMMAG, a Fortran program by D. A. Cruse, J. E. Davies, J. H. Harding, M. Gerloch, D. J. Mackey, and R. F. McMeeking.
- (12) Schreiner, A. F.; Ham, D. J. *Inorg. Chem.* **1973**, *12*, 2037.
- (13) Vezzosi, I. M.; Benedetti, A.; Saladini, M.; Battaglia, L. P.; Corradi, A. B. *Inorg. Chim. Acta* **1985**, *97*, 195.
- (14) Dingle, R.; Palmer, R. A. *Theoret. Chim. Acta* **1966**, *6*, 249.
- (15) Brown, C. A.; Gerloch, M.; McMeeking, R. F., in preparation.
- (16) Turpeinen, U.; Ahlgren, M.; Hämäläinen, R. *Finn. Chem. Lett.* **1980**, 11.

associated estimated errors of  $\pm 50$ ,  $\pm 600$ ,  $\pm 450$ , and  $\pm 10$   $\text{cm}^{-1}$ , respectively. Values given for  $e_\sigma(\text{eq})$  do not vary significantly throughout the table, for that value is determined uniquely by the transition  ${}^3\text{B}_{1g} \rightarrow {}^3\text{B}_{2g}(\text{D}_{4h})$ , corresponding to the band at ca. 9500  $\text{cm}^{-1}$ . The differences between values for the other parameters reported<sup>1</sup> by Lever et al. and those obtained by us derive from two causes. Lever et al. assigned the bands at ca. 14 600 (sh) and 16 400  $\text{cm}^{-1}$  as  $\rightarrow {}^3\text{A}_{2g}$  and  ${}^3\text{E}(\text{D}_{4h})$ , respectively; we have considered the reverse assignment. Second, of lesser consequence, we employed the true molecular coordination geometry<sup>16</sup> in our analysis while Lever et al. presumed that  $\text{D}_{4h}$  was an adequate description.

**E. Bis(isothiocyanato)bis(*N,N*-diethylethylenediamine)nickel(II),  $\text{Ni}(\text{Et}_2\text{en})_2(\text{NCS})_2$ .** The nickel-amine bond lengths in this asymmetrically substituted<sup>1</sup> chelate complex are markedly different, as shown in Table I. The trans Ni-NCS angles are  $167^\circ$ . These dimensions are averages over two (closely similar) molecules in the asymmetric moiety of the unit cell. CLF analyses are based upon the single-crystal polarized spectra at 10 K reported by Lever et al.<sup>1</sup>

The small differences between the parameter values quoted by Lever et al.<sup>1</sup> and ourselves (Table I) are due to our use of actual coordination geometry and his presumption of  $\text{D}_{2h}$  symmetry. With Lever et al. we have assumed essentially isotropic  $\pi$  interaction with the thiocyanate ligands in view of their approximate linearity and in recognition of the degree of parameterization. We estimate likely errors in  $e_\sigma(\text{NCS})$ ,  $e_\pi(\text{NCS})$ , and  $B$  of  $\pm 500$ ,  $\pm 300$ , and  $\pm 15$   $\text{cm}^{-1}$ , respectively.

**F. Bis(isothiocyanato)tetraamminenickel(II),  $\text{Ni}(\text{NH}_3)_4(\text{NCS})_2$ .** The trans Ni-NCS angles here are  $180^\circ$ , and the complex approximates  $\text{D}_{4h}$  symmetry very closely. The crystal spectrum of Hare and Ballhausen<sup>17</sup> shows three spin-allowed bands that reveal no significant energy splittings or polarization character. Our ligand-field analysis has presumed exact  $\text{D}_{4h}$  geometry for the complex and is characterized by a very widely correlated region of parameter space with respect to  $e_\sigma(\text{NCS})$  and  $e_\pi(\text{NCS})$  values. The CLF parameters quoted in Table I are selected from this correlated region simply by fixing the value of the ligand-field trace,  $\Sigma$ . Bertini et al.<sup>2</sup> have estimated that  $e_\pi(\text{NCS})$  cannot exceed 125  $\text{cm}^{-1}$ . Their assertion was based upon calculations with spin-orbit coupling explicitly neglected. They then argued that the resulting orbital singlet-doublet splitting computed with  $e_\pi(\text{NCS})$  values larger than 125  $\text{cm}^{-1}$  should be revealed in the experimental spectrum, and it is not. On the other hand, inclusion of spin-orbit coupling with  $\zeta = 450$   $\text{cm}^{-1}$ , as here, produces roughly equal splitting of three components, and we do not consider the lack of resolution in the reported spectrum to disbar the values quoted in Table I.

**G. Bis(isothiocyanato)bis(ethylenediamine)nickel(II),  $\text{Ni}(\text{en})_2(\text{NCS})_2$ .** The trans Ni-NCS bonds in this symmetrically chelated complex are markedly bent,<sup>4</sup> being  $140^\circ$ . Bertini et al.<sup>2</sup> have reported single-crystal polarized spectra at liquid-helium, liquid-nitrogen, and room temperatures. They have reproduced the observed transition energies, essentially perfectly, with the CLF values  $e_\sigma(\text{en}) = 4010$ ,  $e_\sigma(\text{NCS}) = 2123$ ,  $e_\pi(\text{NCS}) = -409$ ,  $\Sigma = 18650$ , and  $B = 883$   $\text{cm}^{-1}$  but assumed  $\text{D}_{4h}$  molecular symmetry. Using the actual geometry, which is much closer to  $\text{D}_{2h}$ , and the same parameter values yields a markedly poorer fit; however, the negative value for  $e_\pi(\text{NCS})$  prompted the present study, of course. Our own ligand-field analysis began with the parameter set  $e_\sigma(\text{en})$ ,  $e_\sigma(\text{NCS})$ ,  $e_\pi(\text{NCS})$ , and  $B$  together with the actual molecular geometry. Good reproduction of the observed spectrum is possible but again only with retention of a negative value for  $e_\pi(\text{NCS})$ . Furthermore, use of this parameter set optimized to either  $\text{D}_{4h}$  or  $\text{D}_{2h}$  molecular geometry yields a trace,  $\Sigma$ , of only about 19 000  $\text{cm}^{-1}$ .

Both failings are removed by inclusion of a nonzero  $e_{\pi\sigma}$  parameter value in recognition of a locally nondiagonal ligand field; the trace is now comparable with those found for other members of the present series, and the thiocyanate group continues to be

seen as a  $\pi$ -donor ligand. The sign of  $e_{\pi\sigma}(\text{NCS})$  cannot be established in this system because nothing physical defines the sense of the locally chosen  $x$  axis, the direction of ligand bending or misdirected valence is communicated to the computation only by the sign of the parameter itself. A similar loss of information was noted for  $e_{\pi\sigma\perp}(\text{O})$  in the preceding study<sup>18</sup> of the four-coordinate copper acetylacetonates. A representative "best-fit" parameter set is included in Table I; corresponding calculated transition energies are given in Table II.

The retention of an isotropic  $e_\pi(\text{NCS})$  in the circumstances of the bent Ni-N-C-S bond is, of course, illogical. In the limit of pure  $\text{sp}^2$  hybridization for that angle being  $120^\circ$ ,  $e_{\pi\parallel} = 0$  arises only through the misdirected valence of the lone pair. Unfortunately, the present analysis is unable to resolve any difference between  $e_{\pi\parallel}$  and  $e_{\pi\perp}$  values for the Ni-NCS interaction, mostly for reasons of underdeterminacy but also, no doubt, because these values might well not differ too much despite their ultimate origins.

### 3. Discussion

Both Bertini<sup>2</sup> and Lever<sup>1</sup> have established an essentially linear relationship between  $e_\sigma(\text{amine})$  values and bond lengths in several of these nickel(II) complexes, and we concur. On the other hand, the previously published values of  $e_\sigma(\text{NCS})$  gave roughly the opposite trend with respect to bond length while those in Table I now fit well with the general scheme. This encourages further the criterion<sup>19,20,5,6</sup> of the transferability of the ligand-field trace,  $\Sigma$ . In turn, credence is lent to the CLF analysis of G with the inclusion of the  $e_{\pi\sigma}$  parameter, notwithstanding our inability to determine its sign. The strength of an argument for a recognition of some form of misdirected valence in this molecule finally rests with the positive value of  $e_\pi(\text{NCS})$  so that chemical intuition about the qualitative constancy of the  $\pi$ -donor role of the thiocyanate group throughout the series may be upheld.

A central feature of any ligand-field model should be to provide a rationalization of ligand-field properties of complexes in terms of electron distributions. The effective ligand-field potential that acts upon the central metal d(f) electrons arises from the spatially most significant part of the electron density; orbitals, molecular or otherwise, are not directly the sources of the ligand-field potential, and their relative phases are not in themselves of direct concern to ligand-field models. In a recent series of papers<sup>19-21</sup> we have shown how confidence in the superpositional approach to ligand field theory, known previously as one form of the AOM but hereafter as the cellular ligand-field model,<sup>22</sup> may now be placed to the extent of requiring modern interpretations of various transition-metal complex properties to reflect *all* aspects of the ligation, at least to some extent. No longer does it suffice to consider merely coordination number and gross molecular symmetry, nor even the detailed arrangement of ligand donor atoms. Features of the electron distribution further out from the central metal do affect ligand-field properties directly, and the present paper provides a *demonstrable* example—though one with generality—of that proposition. No longer need we be content with the coarse-grained view of ligand-field electronic properties that has characterized this area for decades; parametric though all ligand-field models are, we can now expect to monitor and interpret electron distribution together with their attendant chemical implications using the full vocabulary of mainstream chemical theory.

While we long suspected<sup>23,24</sup> that forms of misdirected valency affect ligand-field properties, there remained the exigency to demonstrate the idea unequivocally. The legacy of the present

- (18) Deeth, R. J.; Duer, M. J.; Gerloch, M. *Inorg. Chem.*, preceding papers in this issue.  
 (19) Deeth, R. J.; Gerloch, M. *Inorg. Chem.* **1984**, *23*, 3846.  
 (20) Deeth, R. J.; Gerloch, M. *Inorg. Chem.* **1985**, *24*, 1754.  
 (21) Deeth, R. J.; Gerloch, M. *Inorg. Chem.* **1985**, *23*, 3853.  
 (22) Deeth, R. J.; Gerloch, M.; Woolley, R. G., in preparation.  
 (23) Cruse, D. A.; Gerloch, M. *J. Chem. Soc., Dalton Trans.* **1977**, 152.  
 (24) Cruse, D. A.; Gerloch, M. *J. Chem. Soc., Dalton Trans.* **1977**, 1613.  
 (25) The CLF model corresponds exactly to the ligand-field version of the AOM that has always been employed by us.<sup>7-10</sup>

studies is that we may justifiably include such effects in future ligand-field analyses when the chemistry demands, even though such inclusion may not be analytically supportable by the given data and circumstances. After all, the neglect of the  $e_{\sigma\sigma}$  parameter in the presence of nearby lone pairs or of bent bonds constitutes an assumption in itself. Far better, surely, to guess—though not refine, perhaps—a nonzero value for it by informed extrapolation from the present studies and so improve estimates of the remaining

CLF parameters that are optimized. Of course, we do not expect to find CLF values for misdirected valence to be any more transferable between systems than are diagonal  $e_{\lambda}$  values.

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## Clusters of Ionic Molecules: Octahedral vs. Planar Ring Structures of LiF, LiOH, and LiNH<sub>2</sub> Hexamers

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Accurate ab initio calculations have been performed to study the structures and energies of the hexamers of LiF, LiOH, and LiNH<sub>2</sub>. Large basis sets including diffuse and polarization functions have been used in these calculations. Distorted octahedral structures are found to be significantly more stable than planar hexagonal-type structures for all three hexamers. The results are compared to those from previous studies on the tetramers of these molecules. The energies of hexamerization are calculated to be  $\approx 310$  kcal/mol for LiF and LiOH and  $\approx 270$  kcal/mol for LiNH<sub>2</sub>.

### Introduction

Lithium compounds are known to associate in solvents, in the crystal, and even in the gas phase.<sup>1-5</sup> Colligative measurements, NMR investigations, mass spectrometric observations, and X-ray crystal structure determinations have shown that aggregation is typical in these compounds. The earliest and the most well known examples are the X-ray structures of ethyllithium<sup>6</sup> and methyl-lithium,<sup>7</sup> which show the existence of tetramers having an essentially tetrahedral arrangement of lithium atoms with the alkyl groups being attached to the faces of the tetrahedron. Numerous other examples involving dimers, trimers, tetramers, and hexamers have now been observed.<sup>1-5</sup>

The smaller oligomers, viz. dimers, trimers, and tetramers, have formed the object of a large number of theoretical studies.<sup>8-15</sup> However, with the exception of a study on (LiH)<sub>6</sub><sup>16</sup> and a small basis set calculation on (CH<sub>3</sub>Li)<sub>6</sub>,<sup>9</sup> hexamers have been described only experimentally.<sup>17-25</sup> On the basis of early experiments involving colligative, infrared, and NMR data, Brown et al.<sup>17-19</sup> proposed a symmetrically bridged octahedral structure for alkyllithium hexamers. This basic structure has since been confirmed by X-ray structural investigations on cyclohexyllithium<sup>22</sup> and (trimethylsilyl)lithium.<sup>23</sup> Molecular weight determinations by Fraenkel et al.<sup>24</sup> established that the state of aggregation of (2-methylbutyl)lithium in hydrocarbon solvents is six. On the basis of NMR line-shape analysis, they have also suggested an octahedral structure for this compound. More recently, Barr et al.<sup>25</sup> have determined the structures of the hexamers of several iminolithium compounds and have seen similar octahedral geometries.

In this study, we have undertaken a detailed investigation of the structures and energies of the hexamers of LiF, LiOH, and LiNH<sub>2</sub>. The basic structures considered are the distorted octahedral form ( $D_{3d}$ ) and the hexagonal planar arrangement ( $D_{6h}$ ) in order to establish the relative energies of the octahedral vs. planar arrangements. In a previous study on the tetramers of these compounds,<sup>14</sup> we found that (LiF)<sub>4</sub> and (LiOH)<sub>4</sub> prefer tetrahedral structures, whereas (LiNH<sub>2</sub>)<sub>4</sub> is more stable as a planar  $D_{4h}$  framework. The calculated square-planar arrangement of (LiN-

Table I. Optimized Geometries (Å and deg) of the Hexamers

struct	param	distorted octahedral ( $D_{3d}$ )		hexagonal planar ( $D_{6h}$ )	
		HF/STO-3G	HF/3-21G	HF/STO-3G	HF/3-21G
(LiF) <sub>6</sub>	Li-F	1.646, <sup>a</sup> 1.691 <sup>b</sup>	1.745, <sup>a</sup> 1.829 <sup>b</sup>	1.537	1.629
	Li-Li	2.286, 2.834	2.419, 2.963	3.007	3.108
	F-F	2.431, 2.857	2.631, 3.065	2.924	3.178
	Li-F-Li			156.0	145.2
	F-Li-F			144.0	154.8
(LiOH) <sub>6</sub>	Li-O	1.758, <sup>a</sup> 1.781 <sup>b</sup>	1.836, <sup>a</sup> 1.896 <sup>b</sup>	1.659	1.735
	Li-Li	2.290, 2.869	2.375, 2.957	2.986	3.054
	O-O	2.681, 3.162	2.857, 3.320	3.310	3.469
	O-H	0.976	0.964	0.977	0.966
	Li-O-Li			128.2	123.3
	O-Li-O			171.8	176.7
(LiNH <sub>2</sub> ) <sub>6</sub>	Li-N	1.903, <sup>a</sup> 2.024 <sup>b</sup>	1.989, <sup>a</sup> 2.055 <sup>b</sup>	1.844	1.909
	Li-Li	2.272, 3.026	2.323, 3.116	3.185	3.223
	N-N	3.198, 3.255	3.295, 3.452	3.689	3.814
	N-H	1.031, 1.033	1.018, 1.020	1.032	1.020
	H-N-H	100.6	104.9	101.4	105.7
	Li-N-Li			119.4	115.2
	N-Li-N			180.6	184.8

<sup>a</sup> For each Li, there are two equivalent bonds with this length. <sup>b</sup> For each Li, there is only one bond with this length.

(H<sub>2</sub>)<sub>4</sub> was in good agreement with the experimental results of Lappert et al.<sup>26</sup> on a larger analogue, [Li(NCMe<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CMe<sub>2</sub>)<sub>4</sub>

- Wakefield, B. J. *The Chemistry of Organolithium Compounds*; Pergamon: Oxford, England, 1974.
- Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. *Metal and Metalloid Amides*; Wiley: New York, 1980.
- Schleyer, P. v. R. *Pure Appl. Chem.* **1983**, *55*, 355; **1984**, *56*, 151 and references cited therein.
- Brown, T. L. *Pure Appl. Chem.* **1970**, *23*, 447.
- Setzer, W.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 353.
- Dietrich, H. *Acta Crystallogr.* **1963**, *16*, 681.
- Weiss, E.; Lucken, E. A. J. *Organomet. Chem.* **1964**, *2*, 197.
- Rupp, M.; Ahlrichs, R. *Theor. Chim. Acta* **1977**, *46*, 117.
- Graham, G.; Richtsmeier, S.; Dixon, D. A. *J. Am. Chem. Soc.* **1980**, *102*, 5759.

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