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A Molecular Mechanics Model of Ligand Effects. 6. Binding of Group 16 Donor Ligands to Cr(CO)$_5$: $E_{\rm R}$ Values for Alcohols, Ethers, and Thioethers

Moon-Gun Choi,[†] David White,[‡] and Theodore L. Brown[*,‡]

Beckman Institute for Advanced Science and Technology
and School of Chemical Sciences, University of Illinois at
Urbana-Champaign, 405 North Mathews Avenue,
Urbana, Illinois 61801, and Department of Chemistry,
Yonsei University, Seoul 120-749, Korea

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Introduction

The influence of steric effects on chemical reactivity is a longstanding theme in inorganic and organometallic chemistry. The first quantitative definition of ligand size, the cone angle, θ, was proposed by Tolman in 1970.[1,2] Cone angles have been measured for phosphines, phosphites,[2] isonitriles,[3] amines,[4] cyclopentadienes,[5] and alkyl groups.[6] However, the cone angle methodology does not take into account realistic conformational preferences for a ligand in a typical chemical environment. Further, the methodology is only appropriate for ligands with a pseudoconical geometry (i.e., the ligand must contain a pseudo-C_3 axis or higher).

Several approaches have been advanced to take account of ligand conformational preferences. Ferguson and co-workers used X-ray crystal structure data, instead of CPK models, to measure vertex angles.[7] Mosbo and co-workers employed molecular mechanics to attempt to calculate conformer-averaged cone angles for group 15 donor ligands.[8] The molecular mechanics energies and cone angles for selected conformers were calculated, and the weighted mean was computed using a Boltzmann-type analysis. A cluster cone angle was defined by Mingos to calculate the size of metal–carbonyl and –cyclopentadienyl fragments using the center of the coordination polyhedron instead of the metal as the apex for the cone.[9]

Other methodologies for the estimation of relative ligand steric requirements were recently reviewed.[10] Notable among these is the computation of solid angles for a variety of ligands.[11] The solid angle is the area (in steradians) of the shadow cast when the ligand is projected onto the inside of a unit sphere.

In an approach distinct from estimates of angles, molecular mechanics has been used to define a ligand repulsive energy, $E_{\rm R}$, with the ligand in a conformational minimum *when bound to a typical organometallic fragment.*[12] The prototypical organometallic fragment used to calculate $E_{\rm R}$ values is Cr(CO)$_5$.[12] To test the sensitivity of the parameter to the particulars of the metal center, analogous computations were carried out for a group of phosphines bound to (η^5-C$_5$H$_5$)Rh(CO).[13] There is a good correlation (r = 0.93) between $E_{\rm R}$ (based on Cr(CO)$_5$) and $E'_{\rm R}$ (based on CpRh(CO)).[13]

Steric and electronic properties of oxygen- and sulfur-containing ligands in metal complexes are important in determining the reactivities and selectivities of many important chemical processes in organometallic and bioinorganic chemistry. The group 16 donor ligands, in contrast with the group 15 donor analogs, contain only two pendant groups and one nonbonding pair of electrons when the ligand is bound to the metal. In the case of the O-donor ligands, the lone pair is sterically active. On the other hand, for S-donor ligands the likely high s-orbital character in the nonbonding orbital would suggest that the steric influence of the lone pair can be ignored.[14]

There are no reports in the literature which list steric values for group 16 donor ligands.[10] One of the reasons for this is that the cone angle methodology cannot accurately express the steric requirements of such ligands since the ligands do not contain a pseudo-C_3 axis (or higher).[2] However, the ligand repulsive energy methodology is not restricted by such a criterion and is, therefore, well-suited for the quantification of the steric requirement of this class of ligands.[12,13] In this contribution, $E_{\rm R}$ values are presented for a series of alcohols, ethers, and thioethers. The correlations between $E_{\rm R}$ and cone[2] and solid angles[11] are also discussed.

Molecular Mechanics Methods

All molecular mechanics calculations were carried out on an Iris Indigo R3000 Silicon Graphics workstation using BIOGRAF (versions 3.1 and 3.2.1s) and Cerius (version 3.2), comprehensive molecular modeling packages developed by Molecular Simulation, Inc., Burlington, MA. The MMP2 force field[15] was employed with modifications listed in Table 1 and previous publications in this series.[12,13,16]

The equilibrium value for the Cr–O bond length (2.08 Å) was taken as the average of the values found for two reported crystal structures.[17] The equilibrium value of the Cr–S bond length (2.40 Å) was taken as the average of eight Cr(0)–disulfide distances reported in the literature.[18] The stretching force constant for Cr–O and Cr–S bonds was set as 1.6 mdyn Å^{-1}; it was chosen to be smaller than that for Cr–P

[†] Yonsei University.

[‡] University of Illinois.

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Table 1. Modifications to the Standard MMP2 Force Field Employed in This Study

A. Force Constants for Bond Stretching

bond type	k_s,[a] mdyn Å^{-1}	r_0, Å
Cr−O(sp^3)	1.600	2.08
Cr−S(sp^3)	1.600	2.40
Cr−C(sp) radial	2.10	1.88
Cr−C(sp) axial	2.10	1.85
C(sp)−O(sp) radial	17.04	1.12
C(sp)−O(sp) axial	17.04	1.15
O(sp)−LP[b]	4.60	0.60

B. Force Constants for Bond Angle Deformations

bond angle type	k_b,[c] mdyn Å rad^{-2}	θ, deg
C(sp^3)−O(sp^3)−C(sp^3)	0.770	111.0
H−O(sp^3)−H	4.170	107.5
C_{rad}−Cr−O(sp^3)	0.500	90
C_{ax}−Cr−O(sp^3)	0.00	180
Cr−O(sp^3)−C(sp^3)	0.17	130
Cr−O(sp^3)−H	0.17	126.25
C_{rad}−Cr−S(sp^3)	0.500	90
C_{ax}−Cr−S(sp^3)	0.00	180
Cr−S(sp^3)−C(sp^3)	0.170	94.3
Cr−O(sp^3)−LP	0.350	105.16

[a] Multiply by 143.88 to convert to kcal mol^{-1} Å^{-2}. [b] LP = lone pair. [c] Multiply by 143.88 to convert to kcal mol^{-1} rad^{-2}.

(2.0 mdyn Å^{-1} [16]), since group 16 donor ligands are bound less strongly than the phosphines and phosphites. (Several cases were tested in which the Cr−O force constant was reduced to 1.2 mdyn Å^{-1}; no change in the E_R values was noted.) Additional bending force constants are summarized in Table 1. It should be noted that each of the carbon atoms in the $Cr(CO)_5$ fragment was assigned a different identity, to avoid problems associated with differentiation between *cis* and *trans* carbonyl groups.[12,13,16] No parameters for the H−O(sp^3)−H angle bend were found in the BIOGRAF MMP2 parameter set. An equilibrium value of 104.5° for the H−O−H angle, based on the rotational spectrum,[19] was employed and the bond angle deformation constant adjusted until the calculated and observed equilibrium angles in H_2O agreed to four significant figures. The strain-free equilibrium H−O−H angle was assumed to increase by 3° upon complexation to Cr. No crystal structure data for Cr(0)−alcohol structures could be found in the Cambridge Structural Data Base; therefore, needed parameters were estimated by reasonable analogy with the ether complexes. All dihedral angle torsional barriers involving Cr were set equal to zero as described previously.[12,13,16]

Energy-minimization computations for a series of thioethers and their $Cr(CO)_5$ complexes were carried out using conjugate-gradient methods and procedures similar to those described previously.[12,13,16] For the O-donor ligands, only the $Cr(CO)_5L$ (L = alcohol, ether) complexes were energy-minimized. A Monte Carlo search method was used to find the best representation of the global minimum energy conformation with ligands containing many conformational degrees of freedom (e.g. SEt_2). Typically 400−1000 conformations were generated in BIOGRAF by random variation of any in a set of key dihedral angles, and each was partially minimized (200 steps). From the results of this initial minimization, selected lowest energy structures (typically within 0.1 kcal mol^{-1} of each other) were fully minimized, and this conformer was assumed to best represent the global energy minimum. In addition, molecular mechanics calculations were also performed on conformations which seemed to be intuitively promising for representing the global minimum and the lowest energy structure from the combined set selected. Cerius 3.2 was employed for the computation of E_R.

The procedure for calculating E_R values of alcohol, ether, and thioether ligands was similar to that reported previously:[12,13,16] the global energy minimized structure was obtained and the van der Waals energy term modified from the exponential-6 form to the purely repulsive form:

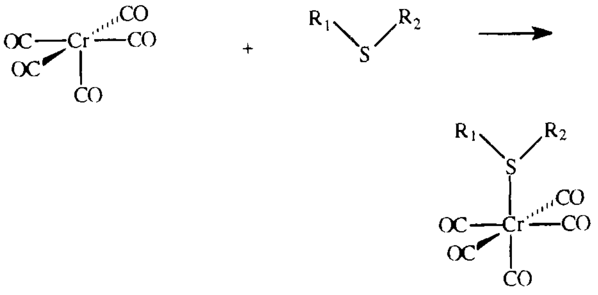
$$E_{vdW}(\text{repulsive}) = \sum D_0 \exp\left[\frac{\gamma(r_0 - r)}{r_0}\right] \quad (1)$$

where D_0 represents the potential well depth in the full exponential-6 expression, γ is typically 12.5, r is the interaction distance, and r_0 is the sum of the two scaled van der Waals radii for the interacting atoms. With all internal coordinates frozen, the Cr−L bond is allowed to vary in length about the equilibrium value, r_e, and the van der Waals repulsive energy calculated at each distance. In practice, the computed energy varies linearly with respect to the Cr−L distance over a range of approximately 0.08 Å on either side of r_e (R^2 = 0.995−0.997). The ligand repulsive energy is then calculated from[20]

$$E_R = -r_e\left[\frac{\partial E_{vdW}(\text{repulsive})}{\partial r(\text{Cr}-\text{L})}\right] \quad (2)$$

Results and Discussion

Molecular mechanics calculations were carried out for a series of disulfide ligands and $Cr(CO)_5L$ (L = alcohol, ether, and thioether) complexes. The calculated total molecular mechanics energies, E_T, of free disulfides and values for the bond stretch (E_b), bond angle bend (E_θ), torsion angle (E_ϕ), and van der Waals (E_{vdW}) energy components of the total energy, the total molecular mechanics energies and components (as above) for $Cr(CO)_5L$ (L = group 16 donor ligand), and the energy differences corresponding to complex formation (eq 3) are summarized in the supplementary material. The molecular mechanics energy change (eq 4) in this process is obtained by computing the energy-minimized structures for $Cr(CO)_5$, the free disulfide ligand, SR_2, and the complex $Cr(CO)_5(SR_2)$, where E_{Cr-S}, E_S, and E_{Cr} correspond to the molecular mechanics energies of $Cr(CO)_5(SR_2)$, SR_2, and $Cr(CO)_5$, respectively.



(3)

$$\Delta E = E_{Cr-S} - E_S - E_{Cr} \quad (4)$$

Inspection of the data reveals the major contribution to the change in total energy occurs in the van der Waals term. Small changes are evident in the bond stretch and angle deformation terms, and slightly larger changes, in the torsional strain term. Table 2 lists comparisons of the computed and experimentally derived key bond distances and angles for $Cr(CO)_5(THF)$ and $Cr(CO)_5[S(Et)(CH_2Ph)]$.

The E_R values and r_e distances for the $Cr(CO)_5L$ (L = group 16 donor ligand) complexes are presented in Table 3. (The E_R values listed here differ in many cases from the more preliminary values published in recent reviews.[10]) The equilibrium Cr−O bond length varies from 2.09 to 2.15 Å across the series. The much larger value observed for the OMe(*t*-Bu) complex is an artifact of the form of the stretching potential function employed and is indicative that a stable metal−ligand bond is not formed.[16]

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(20) The minus sign in this equation was omitted in previous publications in this series.[12,13,16] The slope of the plot between van der Waals repulsive energy and distance is negative, since the repulsive energy (eq 1), which is positive, decreases with Cr−L distance. For convenience, to make E_R a positive value, the negative of the slope is used.

Table 2. Comparison between the Key Bond Distances (Å) and Angles (deg) for the X-ray Crystal Structures of $Cr(CO)_5(THF)$ and $Cr(CO)_5[S(Et)(Bz)]$ and Their Structures Computed Using MMP2

	$Cr(CO)_5(THF)$		$Cr(CO)_5[S(Et)(Bz)]$	
bond dist or angle[a]	X-ray[b]	calcd	X-ray[c]	calcd
Cr−D	2.123	2.129	2.458	2.433
D-C6	1.431	1.420	1.872	1.822
D-C8	1.425	1.416	1.810	1.822
C6−D−C8	109.8	108.2	106.0	98.2
Cr−D−C6	124.2	122.1	112.0	109.5
Cr−D−C8	125.0	122.8	106.0	110.0
D−Cr−C1			88.9	89.1
D−Cr−C2			92.7	93.0
D−Cr−C3			90.9	89.6
D−Cr−C4			93.9	93.6
D−Cr−C5			179.6	177.3

[a] D refers to the donor atom (O or S). Numbering schemes as for refs 18a and 17. [b] Reference 18a. [c] Reference 17.

The equilibrium Cr−S bond distance remains approximately 2.4 Å for all complexes studied, except $Cr(CO)_5[S(t\text{-}Bu)_2]$, which shows the largest positive value for ΔE (15.181 kcal mol^{-1}). In this case as well, the larger value of the Cr−S bond is indicative that a stable Cr−ligand complex is precluded by the steric repulsive interaction. Not surprisingly, this ligand also has the highest ligand repulsive energy (E_R = 79 kcal mol^{-1}).

Since no steric data for group 16 donor ligands have, to our knowledge, appeared in the literature, there is no basis for comparison of the repulsive energy values. The trends that are to be expected intuitively are obeyed, i.e., H_2O < MeOH < EtOH < (*n*-Pr)OH and $O(S)Me_2 < O(S)Et_2 < O(S)(n\text{-}Pr)_2 < S(t\text{-}Bu)_2$ (Table 3). One trend appears anomalous: the E_R value for $S(s\text{-}Bu)_2$ ligand is smaller than that for the $S(i\text{-}Pr)_2$ ligand (61 kcal mol^{-1} vs 71 kcal mol^{-1}). Since there are more atoms in the $S(s\text{-}Bu)_2$ ligand than in the $S(i\text{-}Pr)_2$ ligand, it is reasonable to expect a greater repulsive interaction in the former. Indeed, if one of the β-H atoms in the $S(i\text{-}Pr)_2$ complex is replaced with a methyl group and energy-minimized, the resulting E_R value is 79 kcal mol^{-1}. However, after the conformational space of $Cr(CO)_5[S(s\text{-}Bu)_2]$ is searched, a low-energy conformer with E_R = 61 kcal mol^{-1} is found. In this unusual case, the changes in ligand conformation that lead to the lowest energy structure in $Cr(CO)_5[S(s\text{-}Bu)_2]$ also result in a lower total repulsive force between ligand and metal complex.

Ligand repulsive energy values for the isobutyl ligands are all consistently larger than those for the *sec*-butyl analogs. This result relates to the conformational preferences of the S−C bonds; the $S(i\text{-}Bu)_2$ ligand contains two methyl groups in sterically unfavorable positions, whereas the $S(s\text{-}Bu)_2$ ligand contains only one such methyl group.

For simple mixed sulfide systems, such as SMeEt, the ligand repulsive energy for the ligand is the arithmetic mean of the E_R values of the symmetrical ligands SMe_2 and SEt_2. This is one of the assumptions made by Tolman[1,2] in estimating θ values for unsymmetrical phosphines. It applies only if the alkyl groups do not undergo conformational changes in the different ligands (i.e., the ethyl group in SMeEt is in a conformation similar to that in SEt_2). It is of interest that only the large aromatic ligands show a change of conformation between the symmetrical and asymmetrical cases (e.g., E_R for S(*n*-Bu)Bz is 64 kcal mol^{-1} whereas the arithmetic mean of the E_R values for $S(n\text{-}Bu)_2$ and SBz_2 is 56 kcal mol^{-1}).

Table 3. Ligand Repulsive Energies, E_R (kcal mol^{-1}), r_e (Å), and Cone (deg) and Solid Angle Values for Group 16 Donor Ligands

L	E_R	r_e	$\theta(PHR_2)$[a]	Ω_S[b]	Ω° [c]
H_2O	4.2	2.085	87	0.0918	70.6
MeOH	21	2.094	97	0.138	87.2
EtOH	27	2.098	102	0.167	96.5
n-PrOH	28	2.097	102	0.185	102
Me_2O	24	2.141	118	0.208	108
MeOEt	63	2.150	112	0.234	116
MeO(*n*-Pr)	65	2.148	112	0.247	119
Et_2O	67	2.158	132	0.256	122
EtO(*n*-Pr)	69	2.155	112	0.288	130
$(n\text{-}Pr)_2O$	71	2.152	132	0.300	133
$(n\text{-}Bu)_2O$	71	2.152	132	0.320	138
MeO(*t*-Bu)	75	2.463	129	0.239	117
THF	51	2.129		0.213	110
SMe_2	42	2.424	108	0.190	103
SEt_2	59	2.434	117	0.258	122
$S(n\text{-}Pr)_2$	64	2.435	117	0.299	133
$S(i\text{-}Pr)_2$	71	2.438	136	0.286	129
$S(n\text{-}Bu)_2$	63	2.433	117	0.325	139
$S(i\text{-}Bu)_2$	68	2.430	124	0.358	147
$S(s\text{-}Bu)_2$	61	2.432	136	0.305	134
$S(t\text{-}Bu)_2$	79	2.765	150	0.303	134
SBz_2[d]	49	2.424	139	0.224	113
SMeEt	51	2.428	112	0.227	114
SMe(*n*-Pr)	51	2.427	112	0.247	119
SMe(*i*-Pr)	54	2.431	121	0.242	118
SMe(*n*-Bu)	52	2.428	112	0.251	120
SMe(*i*-Bu)	54	2.427	116	0.284	129
SMe(*s*-Bu)	46	2.420	121	0.254	121
SMe(*t*-Bu)	57	2.430	129	0.249	120
SMeBz	56	2.426	123	0.264	124
SEt(*n*-Pr)	62	2.434	117	0.280	128
SEt(*i*-Pr)	58	2.427	126	0.258	122
SEt(*n*-Bu)	62	2.435	117	0.284	129
SEt(*i*-Bu)	63	2.433	121	0.315	137
SEt(*s*-Bu)	53	2.422	126	0.273	126
SEt(*t*-Bu)	68	2.438	134	0.285	129
SEtBz	63	2.433	128	0.289	130
S(*n*-Pr)(*i*-Pr)	53	2.424	126	0.275	127
S(*n*-Pr)(*n*-Bu)	65	2.434	117	0.305	134
S(*n*-Pr)(*i*-Bu)	65	2.431	121	0.322	138
S(*n*-Pr)(*s*-Bu)	55	2.423	126	0.293	131
S(*n*-Pr)(*t*-Bu)	69	2.440	134	0.304	134
S(*n*-Pr)Bz	64	2.431	128	0.305	134
S(*n*-Bu)(*i*-Bu)	68	2.433	121	0.340	143
S(*n*-Bu)(*s*-Bu)	56	2.422	126	0.315	137
S(*n*-Bu)(*t*-Bu)	72	2.435	134	0.326	139
S(*n*-Bu)Bz	64	2.430	128	0.315	137
S(*i*-Bu)(*s*-Bu)	55	2.419	130	0.330	140
S(*i*-Bu)(*t*-Bu)	72	2.436	137	0.341	143
S(*s*-Bu)(*t*-Bu)	61	2.425	143	0.317	137
S(*i*-Bu)Bz	64	2.429	132	0.336	142
S(*s*-Bu)Bz	64	2.425	137	0.302	133
S(*t*-Bu)Bz	73	2.438	145	0.310	135
S(*i*-Pr)Bz	61	2.425	137	0.289	130

[a] Calculated as follows: $\theta(PHR_2) = {}^1/_3(\theta(PH_3)) + {}^2/_3(\theta(PR_3)$,[1,2] with a M−P distance of 2.28 Å. [b] Calculated according to the methodology in ref 12 with a Cr−O(S) distance of r_e. Ω_S is the solid angle divided by 4π. [c] Calculated from the methodology in ref 12. Ω° is the solid cone angle in degrees. [d] Bz = benzyl, CH_2Ph.

The range of E_R values for SR_2 ligands is much smaller than that computed for the corresponding PR_3 ligands; in part, this arises because three rather than two R groups are varied in the series. However, an additional, and important, contributing factor is that the sulfide ligands are free to tilt to relieve steric repulsive interactions as the R groups grow larger. The restoring force resulting from tilting, reflected in the Cr−S−C bending force constants, is much smaller than experienced in the PR_3 complexes, in which the same tilting would merely push one of the three R groups against the basal CO groups of $Cr(CO)_5$. We compared E_R values for $O(SO)R_2$ ligands with θ values for PHR_2 ligands, generated by the Tolman methodology.[1,2] A correlation might be expected because the H atom in the P-donor ligand represents a constant contribution to the cone angle values. The correlation between E_R and θ (PHR_2) was poor for the S-donor ligands ($r = 0.57$; 41 data points). The correlation between E_R (SR_2) and θ (PR_3) values is also poor ($r = 0.56$; 9 data points), for the same series. These results can be explained in terms of the tilting action available to the sulfide ligands but not to PR_3. The correlation between E_R(OR_2) and θ(PHR_2) ($r = 0.82$; 12 data points) is somewhat better. The OR_2 ligands are better analogs for the PHR_2 series because the active lone pair on O is analogous to the constant H ligand in PHR_2.

It would be useful to compare the E_R values for the group 16 donor ligands with a different steric measure of the same ligands. Solid angles for the S- and O-donor ligands, calculated using the methodology of White *et al.*,[11] are presented in Table 3. There is an excellent correlation between E_R and solid angle Ω_S ($r = 0.91$; all data) for the O-donor lignads and a less satisfactory correlation for the S-donor ligands ($r = 0.77$; all data). Similar correlations were observed between E_R and solid cone angle $\Omega°$ ($r = 0.91$ for O-donors and 0.76 for S-donors). The regression equations allow us to calculate an *absolute steric threshold*, provided the uncertainty in the intercept is not too large. The absolute steric threshold is the point at which significant repulsive metal−ligand interactions occur; i.e., it is the value of $\Omega°$ at which E_R approaches zero. For the O-donors, the absolute steric threshold ($\Omega° = 70°$) is comparable to the values for P- ($\theta = 76, 82°$) and N-donor ($\theta = 76°$) ligands.[12,13] The uncertainty in the absolute steric threshold for the S-donor ligands is very large because the correlation between E_R and $\Omega°$ is poor.

If the coordinated ligand is in a conformation that minimizes its steric effect, then the sizes of ethyl-, *n*-propyl- and *n*-butyl-substituted ligands should be closely similar; PEt_3, $P(n\text{-}Pr)_3$, and $P(n\text{-}Bu)_3$ are assigned the same cone angle on the basis of this assumption.[1,2] This kind of behavior is not observed in the trend of ligand repulsive energies. Although the E_R values for $S(n\text{-}Pr)_2$ and $S(n\text{-}Bu)_2$ are almost identical (64 and 63 kcal mol^{-1}, respectively), they are significantly larger than the E_R value for SEt_2 (59 kcal mol^{-1}). The repulsive interaction between adjacent alkyl groups bound to sulfur results in the *n*-propyl- and *n*-butyl-substituted ligands opening from the minimum cone angle conformation. The effect is also seen for the O-donor analogs.

Intuitively, the S-donor ligands might be expected to possess larger E_R values than the O-donors. This is true for Me_2O and SMe_2 but not for the other ligands studied. The O-donor ligands exhibit a larger steric requirement than the corresponding S-donors because the Cr−O bond length is ≈0.3 Å shorter than the Cr−S bond length. The shorter the Cr−L bond length, the greater the repulsive energy between the groups bonded to the central coordinating atom (S or O) and the CO groups of the $Cr(CO)_5$ fragment, hence the larger the E_R value. The E_R value for Me_2O is smaller than that for SMe_2 because in this case the purely repulsive terms are quite small.

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Supplementary Material Available: Calculated molecular mechanics global minimum energies for free disulfide ligands (Table S1) and for $Cr(CO)_5L$ complexes with S- and O-donor ligands (Table S2) and the changes in molecular mechanics energies upon complexation of the sulfides (Table S3) (7 pages). Ordering information is given on any current masthead page.