Table IV

Complex	M–S, Å	S–C, Å	S···S, Å (intraligand)	S···S, Å (interligand)	Dihedral angles MS_2–S_2C_6 (deg)
$Mo(S_2C_6H_4)_3$	2.367 (2)	1.726 (6)	3.110 (2)	3.091 (3)	13, 21, 30
$Nb(S_2C_6H_4)_3^-$	2.441 (2)	1.743 (8)	3.150 (3)	3.232 (3)	22, 23, 23
$Zr(S_2C_6H_4)_3^{2-}$	2.544 (2)	1.762 (10)	3.264 (5)	3.586 (5)	4, 0.5

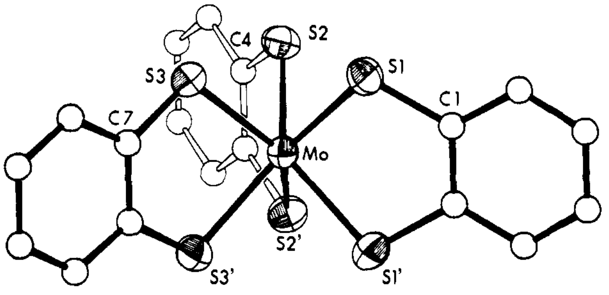

Figure 1. A perspective view of $Mo(S_2C_6H_4)_3$.

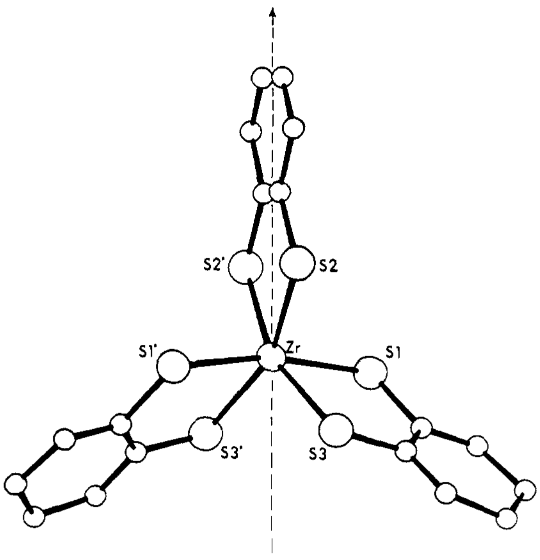

Figure 2. A perspective view of the dianion $Zr(S_2C_6H_4)_3^{2-}$.

tacts for the trigonal prismatic structure and a marked difference between the inter- and intraligand distances.

The structure of tris(benzenedithiolato)zirconium dianion was determined for the tetramethylammonium salt which crystallizes in the orthorhombic space group $P2_12_12$, unit cell dimensions a = 9.931 (2), b = 14.368 (2), c = 11.098 (2) Å, and two formula units per unit cell (ρ_{obsd} = 1.38, ρ_{calcd} = 1.381 g ml^{-1}). A preliminary set of significant reflections was used and the model was refined to 0.050. The anions are situated on the crystallographic twofold and exhibit a geometry intermediate between the trigonal prism and antiprismatic limits (Figure 2), although it is closer to the latter. Additional data are being collected for the zirconium complex to improve the precision of the structure. Fractional coordinates for all three structures are given[8] in Tables I, II, and III.

The three structures demonstrate smooth increases in M–S and S–C distances (Table IV) in going from molybdenum to zirconium. The increase in S–C distances indicates an increase in the importance of the dithiolato formulation for the ligand. The central MS_6 units have approximate symmetry D_{3h} (Mo and Nb) and D_3 (Zr), and any deviations from these idealized symmetries arise probably due to intermolecular forces rather than intramolecular effects. The change in structure of this MS_6 unit in going from niobium to zirconium appears drastic, yet even the zirconium structure is closer to the trigonal prismatic structure than simple interligand repulsions arguments[9] would predict. However, the ZrL_3^{2-} structure is closer to the expected antiprismatic structure than MoL_3^{2-} even though the 3a₁′ antibonding level should be populated in the latter complex. This difference seems to reflect the higher energy of the zirconium d orbitals compared with the molybdenum d orbitals. However, a certain amount of caution should be exercised in this comparison since different ligands are involved. One would expect the 4e′ level to increase its ligand character as the d orbital energies increase, which is consistent with the trends observed in the ligand geometries for this series of complexes. However, as the d orbital energies increase so do their M–S distances increase; thus the S_6 coordination sphere expands and there is a reduction in the interligand bonding. Clearly the system involves several subtle and correlated effects.

The natural extension of the structural work is the determination of the geometry of the anions TiL_3^{2-} and TaL_3^- where spectroscopic and X-ray powder diffraction data indicate marked differences from the structures of ZrL_3^{2-} and NbL_3^-, respectively.

Acknowledgment. We thank the Research Corporation, the National Research Council of Canada, and the University of Alberta for financial support of this research.

Supplementary Material Available. Tables I–III, atom coordinates for $Mo(S_2C_6H_4)_3$, $[(C_6H_5)_4As][Nb(S_2C_6H_4)_3]$, and $[(CH_3)_4N]_2[Zn(S_2C_6H_4)_3]$, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-73-7504.

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[8] See paragraph at end of paper regarding supplementary material.

[9] D. L. Kepert, *Inorg. Chem.*, 11, 1561 (1972).

Relativistic Changes Accompanying Molecular Formation

Sir:

Since virtually all quantum mechanical calculations of molecular dissociation energies utilize the nonrela-

Table I. Relativistic Components of Total Energies[a] of Alkali Halide Molecules and Constituent Atoms

Molecule	E_M Atoms	E_M Mol	ΔM	E_D Atoms	E_D Mol	ΔD	E_F Atoms	E_F Mol	ΔF	E_S[b] Atoms	ΔS
LiF	−8,053.9	−8,033.9	−20.0	6,309.1	6,394.1	15.0	193.2	193.2		23.0	−23.0
NaF	−25,306.4	−26,269.1	−35.3	20,470.6	20,445.6	25.0	556.0	555.6	−0.4	23.0	−23.0
LiCl	−112,446.4	−112,404.0	−42.4	85,198.1	85,299.1	31.0	1,571.9	1,571.5	−0.4	50.2	−50.2
KF	−186,314.9	−186,259.9	−55.0	140,606.7	140,571.1	35.6	2,454.4	2,453.7	−0.7	23.0	−23.0
NaCl	−130,699.7	−130,684.8	−50.9	99,423.3	99,385.5	37.8	1,934.6	1,934.0	−0.6	50.2	−50.2
KCl	−289,764.2	−289,694.6	−69.6	219,121.3	219,072.7	48.6	3,832.6	3,831.8	−0.5	50.2	−50.2
LiBr	−2,209,827.0	−2,209,753.0	−74.0	1,617,180.0	1,617,128.0	52.0	16,634.8	16,634.0	−0.8	210.1	−210.1

[a] All values are in units of α^2e^2/a_0 where α is the fine structure constant. [b] Data in this column from C. E. Moore, "Atomic Energy Levels," National Bureau of Standards Circular 467, 1949.

tivistic Schroedinger equation, it is of interest to determine quantitatively the limitations of this approach. Consequently, we have undertaken a systematic study of changes accompanying molecular formation in relativistic related components of the total energy. Our approach has been to use first-order perturbation theory treating the relativistic Breit–Pauli[1] operators as perturbations and LCAO-SCF-MO solutions to Hartree–Fock equations[2] as zero-order wave functions. Our results are summarized in Table I. Heading the first four columns respectively are the mass velocity correction E_M represented by the operator

$$\mathcal{H}_M = -\frac{1}{8}\sum_i p_i^4 \quad (1)$$

where p_i represents the linear momentum of electron i; E_D, a term characteristic of the Dirac equation with corresponding operator

$$\mathcal{H}_D = \frac{1}{4}i\sum_i \mathbf{p}_i\cdot\nabla_i\left[\sum_\alpha\frac{Z_\alpha}{r_{\alpha i}} - \sum_{j\neq i}\frac{1}{r_{ij}}\right] \quad (2)$$

the Fermi contact energy, E_F, with operator

$$\mathcal{H}_F = -\frac{8\pi}{3}\sum_{i<j}(\mathbf{s}_i\cdot\mathbf{s}_j)\delta(\mathbf{r}_{ij}) \quad (3)$$

where $\mathbf{s}_i$ is the spin angular momentum operator of electron i; and the spin–spin and spin–orbit correction, E_S, with operators

$$\mathcal{H}_{SS} = \frac{1}{2}\sum_{i\neq j}(\mathbf{s}_i\cdot\nabla_i)(\mathbf{s}_j\cdot\nabla_j)\frac{1}{r_{12}} \quad (4)$$

and

$$\mathcal{H}_{SO} = \frac{1}{2}\sum_{i\neq j}\nabla_i\left(\frac{1}{r_{ij}}\right) \times \mathbf{p}_i\cdot(\mathbf{s}_i + 2\mathbf{s}_j) - \frac{1}{2}\sum_{i,\alpha}Z_\alpha\left[\nabla_i\left(\frac{1}{r_{i\alpha}}\right) \times \mathbf{p}_i\right]\cdot\mathbf{s}_i \quad (5)$$

The orbit–orbit correction is assumed to be negligible.

We have tabulated the energy corrections associated with a particular molecule and with its constituent atoms, as well as the difference between the two values. In the case of E_S, only an atomic contribution is given since no spin–spin or spin–orbit splitting of energy levels occurs in closed shell molecules. The contribution to the dissociation energy associated with relativistic interactions, D_e^{rel}, is given by the sum $\Delta M + \Delta D + \Delta F + \Delta S$. These sums are tabulated in Table II, along with the experimental dissociation energies and the ratio of the two quantities. The magnitude of D_e^{rel} is seen to vary from 0.94 kcal in LiF to 7.7 kcal in LiBr. These amounts are not insignificant. In fact, the latter represents 7.84% of the total dissociation energy. These results suggest that quantitative theoretical values for dissociation energies of molecules containing medium-sized atoms cannot be obtained within the framework of the nonrelativistic Schroedinger equation.

Table II. Relativistic Contributions to Dissociation Energies[a,b] of Alkali Halides

Molecule	D_e^{rel}	D_e^{exptl}	Ratio[c]
LiF	−0.94	138	0.6
NaF	−1.06	114	0.9
LiCl	−2.06	109	1.9
KF	−1.44	117	1.23
NaCl	−2.10	92	2.23
KCl	−2.38	101	2.36
LiBr	−7.77	99	7.84

[a] All values in kcal/mol. [b] Experimental values from L. Brewer and E. Brackett, *Chem. Rev.*, **61**, 425 (1961). [c] $100 \times |D_e^{rel}|/D_e^{exptl}$.

Concerning the general validity of this conclusion, three principal factors play a role. These are: (1) the reliability of the experimental dissociation energies, (2) the general reliability of the calculation, and (3) the general validity of the Breit–Pauli approximation.

Regarding the first of these, error estimates on thermodynamically determined dissociation energies are on the order of 1.5%. A variation of this magnitude would not affect our overall conclusion. Concerning the second factor, the calculation was quite difficult to perform since extreme care was required to ensure that the atomic and molecular calculations were comparable. Sophisticated numerical techniques had to be resorted to in order to ensure the retention of significant figures. However, we think we have succeeded in accomplishing our purpose since the trends in Tables I and II are far from random.

Finally, there is the question of the general validity of the Breit–Pauli approximation. The derivation of this Hamiltonian starting with the Dirac equation requires a disturbing amount of hand waving. However, the largest contribution to the relativistic energy, as can be seen in Table I, comes from the p^4 term which can be gotten directly from Einstein's special relativity equation. Furthermore, the largest contribution to the overall relativistic energy comes from the atomic spin–spin, spin–orbit correction. This value is well determined. Thus, in our estimation, our conclusions

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(2) R. L. Matcha, *J. Chem. Phys.*, 53, 485 (1970).

are valid in spite of the limitations inherent in the Breit–Pauli approximation. At any rate, no alternative way to do the calculation is presently feasible in our estimate. For example, it would be meaningless to calculate the atomic relativistic energy using a relativistic Hartree–Fock procedure since the formalism for doing a similar molecular calculation has not yet been developed and the two calculations must be performed in exactly the same manner. A more detailed analysis of these results and general validity of the various approximations and alternate methods of obtaining relativistic corrections is in preparation.

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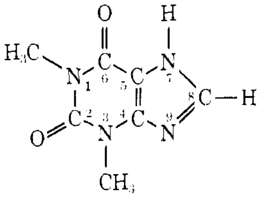
Intramolecular Hydrogen Bonding in Metal–Purine Systems. Synthesis and Structure of a Cobalt(III)–Theophylline Complex

Sir:

The role of metal ions in nucleic acid chemistry is both widespread and under considerable investigation. Several areas of metal nucleic acid chemistry under study include: (1) alteration of coding specificity in protein synthesis;[1] (2) stabilization of the manifold structure of nucleic acids;[2] (3) preparation of "heavy molecule" derivatives of yeast phenylalanine transfer RNA as aids in phasing the structure by X-ray methods;[3] (4) the use of heavy-metal-containing moieties in attempts to sequence nucleic acid biopolymers by electron microscope techniques.[4] Our interest stems primarily from this last consideration. We have been attempting to find and study inert metal complexes which will specifically react with one of the four purine or pyrimidine residues in the biopolymer—selectivity of reaction being a prerequisite for the sequencing method.

Our approach to the induction of selectivity is to utilize the different hydrogen bonding potentials of the nucleotides in the formation of hydrogen bonds to ligands of the reacting complex. The assignment of the metal binding site in biopolymers is best preceded by studies on model systems. Generally, the bases, the nucleosides, and the nucleotides have disadvantages as models. The bases may bind *via* N-9, a site blocked in the nucleic acid, and the nucleosides are generally weak ligands. On the other hand, the nucleotides often bind using the phosphate group, and this minimizes the possibility of selectivity toward nucleotides of different bases. However, we believe that the substituted purine, theophylline (1,3-dimethyl-2,6-oxopurine (I)), serves as a good model for the guanine class of nucleosides, *i.e.*, those nucleosides with a carbonyl group at position 6 of the pyrimidine ring, and possibly for the nucleotides (nucleic acid). The coordination in the complex reported here is through N-7, a site which is accessible and presumedly favorable in the biopolymer. Specific interligand hydrogen bonds (*e.g.*, with the ligand ethylenediamine) are present in the complex. These specific interactions may be sufficient to induce selective reaction of such complexes with the guanine residues in the nucleic acid biopolymer.



I

The complex was prepared in a similar fashion to the previously reported adenine complex[5] and formally contains in the coordination sphere of the cobalt(III) the monoanion of theophylline ($C_7N_4O_2H_7^-$), a chloride anion, and two ethylenediamine groups ($[Co(en)_2Cl(C_7N_4O_2H_7)]^+Cl^-$). The complex crystallizes in the triclinic system, space group $P\bar{1}$, with Friedel-reduced cell constants: $a = 10.034$ (3), $b = 10.711$ (4), and $c = 9.499$ (4) Å; $\alpha = 109.49$ (3), $\beta = 93.17$ (3), and $\gamma = 75.87$ (2)°; $V = 932.8$ (5) Å^3; and $Z = 2$. Besides the complex cation and chloride anion, there are two independent water molecules in the asymmetric unit. Intensity data were collected with Mo Kα radiation ($\lambda = 0.71069$ Å) on a Syntex $P\bar{1}$ computer-controlled diffractometer. A highly orientated graphite crystal monochromatized the incident beam of the spectrometer. A total of 4315 independent intensities (4202 above zero) were collected on a crystal which was a cut cube 0.25 mm on an edge. The θ–2θ scan method was employed (maximum 2θ of 55°) in the data collection. Atomic positions for the cobalt and its primary coordination sphere were obtained from a Patterson map. A Fourier synthesis then revealed the rest of the atoms in the structure including the two water molecules. It was noted early in the analysis that one of the ethylenediamine groups was disordered; this group has been treated isotropically in the least-squares refinement, and the 16 one-half hydrogen atoms have been positioned by geometrical considerations. The ordered hydrogen atoms were located on a ΔF map. Full-matrix least-squares refinement, with all nonhydrogen atoms anisotropic and hydrogens isotropic, with the exceptions noted above, has led to a final R value of 0.043 (4202 intensities above zero) and a final weighted R value of 0.052.

The cobalt is octahedrally coordinated with the six coordination sites occupied by the four nitrogens of the two ethylenediamine groups, a chlorine atom, and N-7 of the theophylline moiety. The chlorine ligand and N-7 have assumed trans positions in the coordination sphere (Figure 1). In the previously determined

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