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Experimental and Theoretical Studies of the Bonding in $CpCoS_2N_2$

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The He I and He II gas-phase photoelectron spectra of $CpCoS_2N_2$ and $Cp^*CoS_2N_2$ ($Cp^* = C_5Me_5$) have been obtained. The first ionization energies (8.25 and 7.61 eV, respectively) are significantly larger than those reported for other analogous $CpCoL_2$ complexes. Extended Hückel and DV–Xα calculations both indicate that the HOMO is concentrated on the metal and lone pairs on the sulfur and nitrogen atoms coordinated to Co. There is substantial π delocalization in the CoS_2N_2 ring that makes the title compound different from other $CpCoL_2$ complexes.

Introduction

Although the preparation, reactivity,[6] and bonding[7] in cyclic sulfur–nitrogen compounds has been well-documented, far less is known about the chemistry of these molecules with transition metal complexes.[8,9] In this publication we report the He I and He II photoelectron spectra of $CpCoS_2N_2$ and $Cp^*CoS_2N_2$ ($Cp^* = C_5Me_5$) along with molecular orbital calculations at the extended Hückel and Hartree–Fock–Slater DV–Xα levels. The bonding model that emerges from this work is compared to other $CpCoL_2$ complexes.

Experimental Section

General Data. Although the products are moderately air-stable, the preparations were carried out under an inert atmosphere of dry nitrogen by using standard Schlenk techniques. Toluene was distilled from sodium benzophenone ketyl prior to use. Acetone was dried over molecular sieves (4 Å). S_4N_4,[10] $CpCo(CO)_2$,[11] $CpCo(COD)$,[12] and $Cp^*Co(CO)_2$[13] were prepared by literature methods. IR spectra were recorded as Nujol mulls on a Perkin-Elmer 467 grating spectrophotometer (4000–250 cm^{-1}). ^1H and ^{13}C NMR spectra were obtained with a Varian XL-200 spectrometer. Mass spectra were recorded with a Varian CH-5 instrument operating at 70 eV. Chemical analysis were performed by the Analytical Services of the Department of Chemsitry, University of Calgary. Melting points are uncorrected and were determined on a Mettler FPI apparatus.

Improved Preparation of $CpCoS_2N_2$.[8] S_4N_4 (1.74 g, 9.34 mmol), dissolved in 200 mL of toluene, was added to a solution of CpCo(COD) (4.35 g, 18.73 mmol) in toluene (50 mL), and the mixture was stirred for 3 h at 80 °C. The dark red solution was filtered and evaporated to dryness. The residue was washed with 2 × 50 mL of pentane to give 3.1 g (77% yield) of the product as a black microcrystalline solid: mp 140 °C dec; IR (Nujol) 1015 (m), 999 (m), 950 (s), 863 (s), 835 (vs), 818 (m), 737 (vs), 724 (s), 636 (s), 413 (m), 380 (s), 282 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.64 (C_5H_5); ^{13}C NMR ($CDCl_3$) δ 82.34 (C_5H_5); mass spectrum, *m/e* (relative intensity) 216 (53, M^+), 170 78, M^+–NS), 124 (100,

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Table I. DV–Xα Results for $CpCoS_2N_2$

MO	eigenvalue, eV	atomic composition, %														IE[a]	character[b]
		Co			S_1			N_2		S_3			N_4				
		s	p	d	s	p	d	s	p	s	p	d	s	p	Cp		
10a″ (LUMO)	−2.958	0	0	41	0	19	1	0	8	0	0	4	0	8	19	(5.80)	d_{xz}
19a′ (HOMO)	−4.478	4	1	32	1	4	2	1	14	1	0	4	3	30	3	7.44	$d_{z^2} + n_s$
9a″	−5.143	0	0	63	0	5	2	0	13	0	7	2	0	3	5	8.11 (8.06)	d_{xy}
18a′	−5.177	3	2	75	0	4	1	0	2	0	2	0	2	2	7	(8.12)	$d_{x^2-y^2}$
8a″	−5.403	0	8	22	0	14	2	0	12	0	10	5	0	17	10	8.19 (8.24)	$d_{xz} + \pi_3$
17a′	−5.721	0	0	53	0	0	1	3	25	0	2	1	0	11	4	8.70 (8.71)	$d_{z^2} + n_s$
16a′	−6.081	1	2	9	3	35	2	3	1	0	4	1	0	8	31	(8.76)	$d_{yz} + n_a, n_{a'}$
7a″	−7.026	0	1	22	0	38	0	0	8	0	8	2	0	15	6	(9.74)	$d_{xy} + \pi_2$
15a′	−7.135	1	2	8	0	18	1	5	16	6	18	5	0	19	1	(9.91)	$d_{yz} + n_a, n_{a'}$
6a″	−7.159	0	2	29	0	1	0	0	0	0	1	0	0	0	67	(10.02)	π_{Cp}
14a′	−7.546	0	3	30	1	7	0	0	0	0	1	1	1	7	49	(10.25)	π_{Cp}
13a′	−9.327	0	1	10	3	13	1	1	11	0	13	2	1	15	29	(12.06)	
5a″	−9.406	0	1	2	0	11	1	0	23	0	47	2	0	13	0	(12.30)	π_1
12a′	−9.784	0	0	1	0	8	1	2	9	2	17	1	2	5	52	(12.48)	
4a″	−10.254	0	0	1	0	0	0	0	0	0	0	0	0	0	99	(12.67)	
11a′	−10.343	0	0	1	0	0	0	0	0	0	2	0	0	0	97	(12.75)	

[a] Calculated by the transition-state method. Values in parentheses are derived from a transition-state calculation for HOMO. [b] See text for a detailed description.

Table II. DV–Xα Results for S_2N_2

MO	eigenvalue, eV	atomic compositn, %										character
		S_1			N_2		S_3			N_4		
		s	p	d	s	p	s	p	d	s	p	
3a″ (LUMO)	−4.994	0	40	2	0	19	0	3	8	0	28	π_3
9a′ (HOMO)	−5.074	0	23	1	1	4	2	4	10	0	55	n_a
8a′	−5.340	0	53	1	3	22	1	3	1	0	16	n_s
2a″	−7.195	0	39	0	0	16	0	20	3	0	22	π_2
7a′	−7.240	0	19	0	3	16	2	19	1	8	32	$n_{a'}$
6a′	−9.389	3	13	0	5	32	1	10	4	16	16	σ
1a″	−10.055	0	10	1	0	32	0	47	1	0	9	π_1

$M^+-S_2N_2$), 105 (34, $CoNS^+$), 98 (22, $CoC_3H_3^+$), 91 (32, CoS^+), 59 (80, Co^+), 52 (24, $C_4H_4^+$), 46 (69, NS^+), 39 (97, $C_3H_3^+$). Anal. Calcd for $C_5H_5CoN_2S_2$: C, 27.78; H, 2.33; N, 12.96. Found: C, 27.78; H, 2.19; N, 13.35.

Preparation of $Cp^*CoS_2N_2$. S_4N_4 (2.10 g, 11.27 mmol) was added to a rapidly stirred solution of $Cp^*Co(CO)_2$ (5.60 g, 22.38 mmol) in 200 mL of toluene. The reaction mixture was allowed to stir overnight at room temperature and chromatographed directly on silica gel (column, 5 × 20 cm, Kieselgel 60 mesk, Merck). Unreacted starting materials were removed by elution with toluene. Further elution with acetone produced a broad purple band. Removal of the solvent followed by recrystallization from acetone/heptane gave 3.3 g (52% yield) of the product as purple plates: mp 139 °C; IR (Nujol) 1262 (m), 1159 (m), 1074 (m), 1022 (s), 962 (s), 800 (m), 726 (vs), 712 (s), 579 (m), 534 (m), 465 (m), 454 (m), 437 (m), 396 (m), 382 (s), 328 (m), 294 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.96 (CH_3); ^{13}C NMR ($CDCl_3$) δ 94.64 (C_5Me_5), 10.62 (C_5*Me_5*); mass spectrum, *m*/*e* (relative intensity) 286 (8, M^+), 240 (m, $M^+ - NS$), 134 (42, $C_5(CH_3)_4CH_2^+$), 119 (100, $C_5(CH_3)CH_2^+$), 105 (10, $CoNS^+$), 91 (36, CoS^+), 77 (14), 64 (18), 51 (14), 41 (21). Anal. Calcd for $C_{10}H_{15}CoN_2S_2$: C, 41.95; H, 5.28; N, 9.78. Found: C, 41.91; H, 5.58; N, 8.99.

Photoelectron Spectra. He I (21.217 eV) and He II (40.814 eV) gas-phase photoelectron spectra were recorded on a Perkin-Elmer PS-18 spectrometer modified for He II measurements by inclusion of a hollow cathod discharge lamp which gives a high photon flux at He II wavelengths (Helectros Developments). A heated inlet system was adopted in the 80–100 °C temperature range. The spectrometer was connected on-line with a Minc-23 computer (Digital Equipment) by an interface build in our laboratory at Padova. Data acquisition was carried out by several sweeps (4–6) over 500 distinct channels. Typical sweep time amounts to 5 min. The ionization energy (IE) scale was calibrated by reference to peaks due to admixed inert gases (Xe, Ar) and to the He $1s^{-1}$ self-ionization.

Theoretical Methods. Hartree–Fock–Slater (HFS) calculations were performed by using the discrete variational (DV) procedure.[14] The molecular electronic density was approximated with an s-wave expansion (overlapping spherical functions on every center), and the SCF equations were converged by a self-consistent-charge (SCC) procedure.[15] Numerical atomic orbitals from atomic HFS calculations were used as basis functions, and the corelike basis functions have been kept frozen during the SCF procedure. The 3d AOs have been included in the valence basis set for sulfur atoms since it is well-known that they are necessary to account for the behavior of such hypervalent compounds.[7b,h] A total of 4924 integration points (DV procedure) were used to determine the molecular Hamiltonian and overlap matrix in the SCF procedure. The Xα exchange parameter was set equal to $^2/_3$ throughout the calculations. All of the calculations were performed on a VAX-730 computer and required 40 SCF cycles to achieve convergence. The solid-state geometry[8] was idealized to C_s symmetry, the mirror plane being coincident with the S_2N_2 one. The calculation on the S_2N_2 neutral fragment has been carried out by maintaining the same geometrical parameters of the whole molecule.

Transition-state (TS) calculations[16] on ground-state MOs have been carried out in order to partially account for the reorganization process occurring during ionization. However, the IE values obtained employing the TS calculation on the HOMO are not significantly different from those computed by explicit TS cacualtions (see Table I) so that we have limited the TS procedure only to four MOs.

The extended Hückel calculations[17] utilized the modified Wolfsberg–Helmholz formula.[18] Standard[19] orbital exponents and H_{ii} values were employed.

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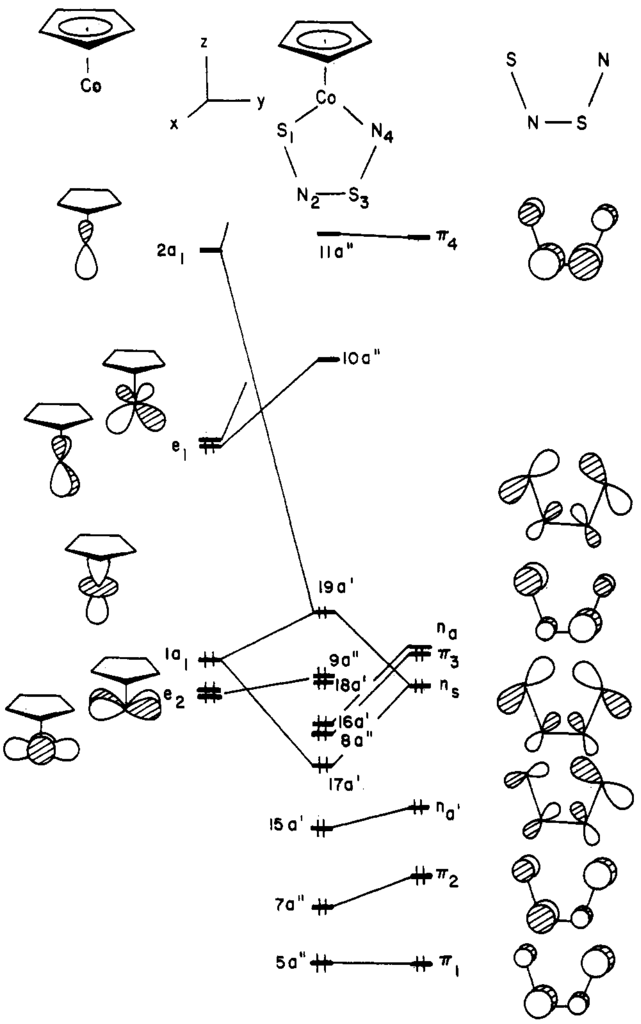

Figure 1. An orbital interaction diagram for $CpCoS_2N_2$.

Results and Discussion

Before we present the photoelectron spectra, it is useful to construct the valence orbitals of $CpCoS_2N_2$. The qualitative features of bonding are essentially identical at the extended Hückel and DV–Xα levels. Figure 1 shows an *idealized* interaction diagram for building the molecular orbitals of $CpCoS_2N_2$ at the extended Hückel level. A charge density analysis of these orbitals from the DV–Xα calculations is given in Table I (the numbering system used is defined in Figure 1). An analogous listing for the S_2N_2 fragment (at the geometry of $CpCoS_2N_2$) is given in Table II. The valence orbitals of a CpCo fragment, on the left side of figure 1, are well-known.[20] At low energy there are three nonbonding metal d orbitals, $1a_1$ + e_2. At higher energy the e_1 set is primarily metal d antibonding to Cp π orbitals. Furthermore, metal p mixes into e_1 in a way to hybridize these orbitals away from the Cp ligand. Finally, the high-lying $2a_1$ orbital is primarily a metal sp hybrid. For a neutral CpCo fragment the e_1 set is half-filled. On the right side of Figure 1 are the four π-type orbitals of the S_2N_2 fragment. They are topologically analogous to the π levels of butadiene except that the coefficients on the atoms are weighted with respect to the electronegativity of nitrogen and sulfur; i.e., π_1 and π_2 are concentrated more on nitrogen while π_3 and π_4 are more sulfur-based. The n_s and n_a levels are two lone-pair orbitals that will be used to form the Co–S and Co–N bonds. In terms of the S_2N_2 *molecule*, n_s represents the N–S σ bond that is broken on going to the geometry of the fragment and n_a is the σ* orbital. Notice that the DV–Xα calculations reverse the energy ordering (and hence electron occupation) of n_a and π_3. However, both methods are in agreement with the fact that n_s, n_a, and π_3 are close in energy and widely separated from the other valence π levels of S_2N_2.

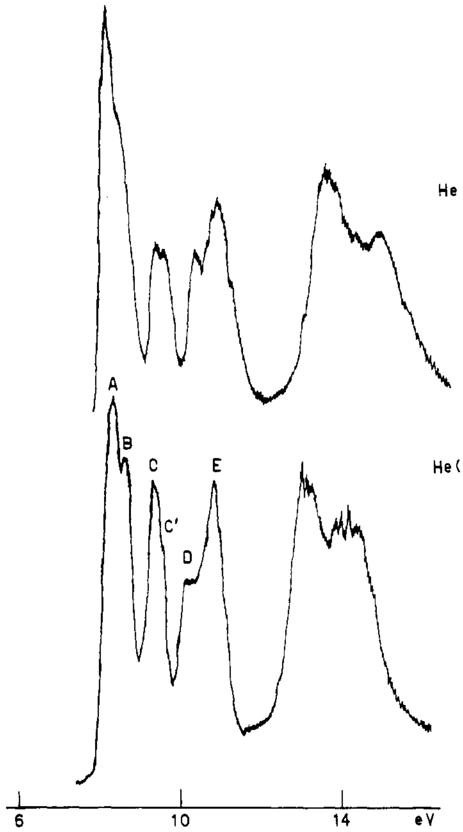

Figure 2. The He I and He II spectra of $CpCoS_2N_2$.

The π system of the CoS_2N_2 ring is easily constructed. π_1 and π_4 are essentially unperturbed. The π_2 level is slightly stabilized by the *xy* component of e_2 (see the top of Figure 1 for the coordinate system used). The major interaction in the π system occurs between π_3 and the *xz* component of e_1 for energy gap and overlap reasons. A filled bonding (8a″) and empty antibonding (10a″) molecular orbital is produced by this union. The Co–N and Co–S σ bonds are formed by the interaction of n_a and a S_2N_2 lone-pair orbital, labeled $n_{a'}$ in Figure 1, with the *yz* component of e_1 to yield 15a′ and 16a′. Likewise, n_s combines with $1a_1$ and $2a_1$ to give a bonding (17a′) and effectively nonbonding (19a′) molecular orbital. The DV–Xα and extended Hückel calculations differ somewhat here. The DV–Xα results place the 16a′ orbital slightly lower in energy than 17a′. For reasons to be mentioned shortly concerning the PE spectra, we suspect that this level ordering is more reliable. Finally the e_2 set is destablized slightly by π_2 and n_s to produce 18a′ and 9a″.

The He I and He II PE spectra of $CpCoS_2N_2$ and $Cp^*CoS_2N_2$ are reproduced in Figures 2 and 3, respectively. The pertinent IE values are listed in Table III along with their proposed assignments. Two experimental criteria proved to be very useful for making the assignments: (i) The He I vs. He II relative intensity changes provide information concerning the participation of ligand and/or

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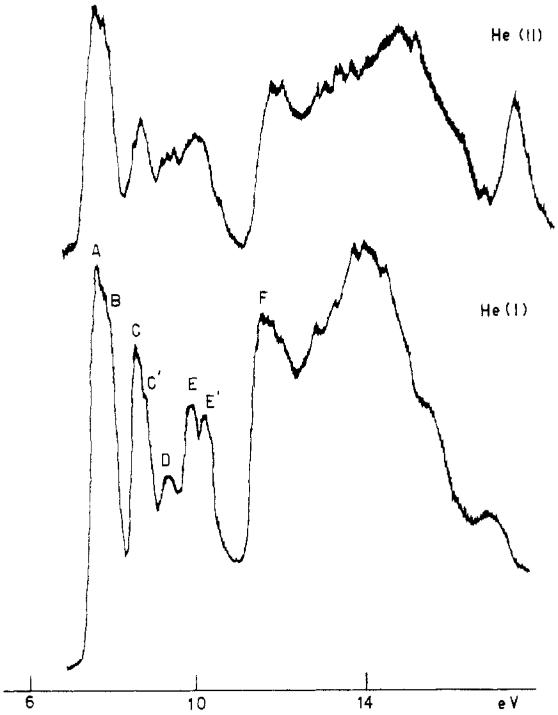

Figure 3. The He I and He II spectra of $Me_5C_5CoS_2N_2$.

Table III. Ionization Energies (eV) and Spectral Assignments for $CpCoS_2N_2$ and $Cp^*CoS_2N_2$

band label	$CpCoS_2N_2$	$Cp^*CoS_2N_2$	assignments[a]
A	8.25	7.61	19a′, 9a″, 18a′
B	8.55	7.9	8a″
C	9.23	8.54	16a′
C′	9.4	8.8	17a′
D	10.2	9.22	7a″, 15a′
E	10.73	9.86	6a″, 14a′
E′		10.21	
F		11.58	$\sigma(CH_3)$

[a] see Table I or Figure 1 for MO labeling.

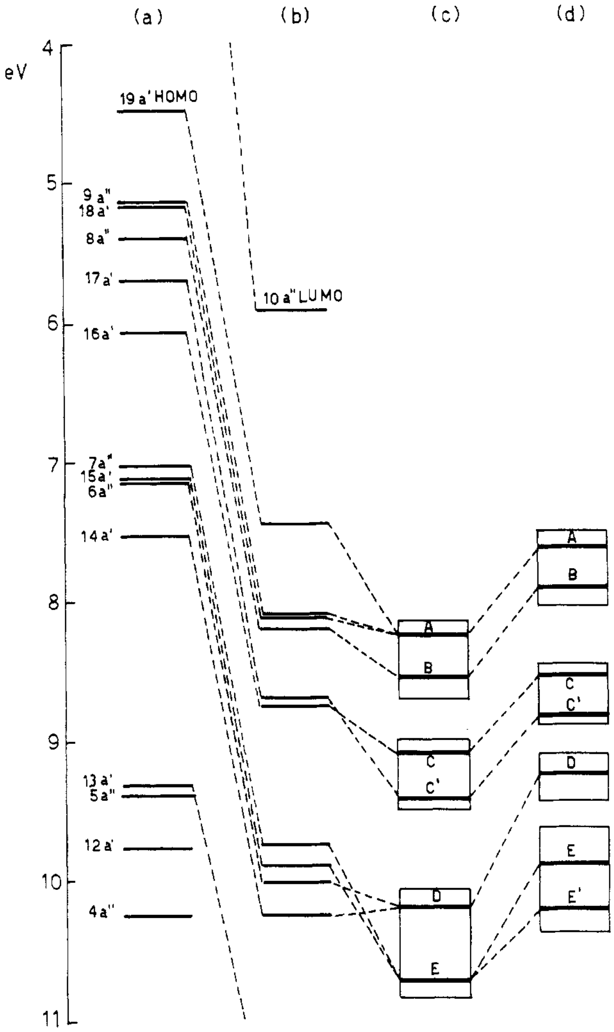

Figure 4. Theoretical DV-Xα and UV-PE results for studied molecules: (a) ground-state eigenvalues (sign changed); (b) transition-state theoretical IEs; (c) PE of $CpCoS_2N_2$; (d) PE of $Cp^*CoS_2N_2$.

metal based AOs to the corresponding MOs.[21] Using the Gelius model[22] for the photoionization cross sections, the MOs based on ligand 2p and 3p AOs decrease in intensity with respect to 3d metal based ones on going from the He I to the He II source. A similar trend is usually observed when 2p and 3p based MOs are compared, the latter has a more pronounced intensity fall-off. (ii) Pentamethylation of the Cp ring shifts all valence ionizations to lower values, particularily to those pertaining to the Cp π ionizations.[23] Both of these considerations lead us to associate the band envelopes labeled A and B in Figures 2 and 3 mostly with 3d based ionizations while the higher IE bands are associated the MOs of mixed metal–ligand character. A more detailed assignment is primarily derived from the DV–Xα calculations.

The theoretical IEs computed adopting the TS formalism (Table I) are compared in Figure 4 with the experimental values. The agreement between theory and experiment is satisfactory for all ionizations except for the HOMO, which is predicted to be a distinct band at a lower IE in contrast to the experimental evidence.

We propose that band A corresponds to ionizations from three MOs, namely, 19a′, 9a″, and 18a′. The marked decrease of intensity for band B on going to the He II spectra is consistent with the assignment of this ionization from 8a″, an orbital which contains only 30% metal character. B and C (which exhibits a shoulder on the high IE side labeled C′) we take to represent ionizations from the 17a′ and 16a′ MOs, i.e., from the Co–S and Co–N σ bonds. The C′ component gains intensity with respect to C in the He II spectra of $CpCoS_2N_2$ and $Cp^*CoS_2N_2$. This suggests that C′ represents ionization from 17a′ (see in Table I that 16a′ is concentrated more on the sulfur 3p AO, whereas 17a′ contains a higher participation of nitrogen 2p). For the D–E band envelope, the calculations predict four closely spaced ionizations from the 7a″, 15a′, 6a″, and 14a′ MOs which represent ligand-based π_2, a S_2N_2 lone pair/Co–N σ orbital, and two CpCo π-bonding MOs, respectively. We can propose only tentative assignments for this ionization region. The D band shows the largest IE shift upon pentamethylation which is consistent with ionization from 6a″ and 14a′ MOs. The E band in both molecules decreases with respect to D at the He II wavelength (especially for the E′ resolved component in $Cp^*CoS_2N_2$). This suggests ionization from a sulfur 3p based MOs—7a″ and/or 15a′.

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[21] Rabalais, J. W. *Principles of UV Photoelectron Spectroscopy*; Wiley-Interscience: New York, 1977.

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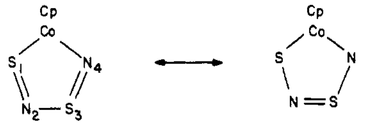
[23] See, for example: Calabro, D. C.; Hubbard, J. L.; Blevins II, C. H.; Campbell, A. C.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1981**, *103*, 6839.

There is an unusual feature in the electronic structure of $CpCoS_2N_2$. Theoretical[24] as well as experimental[25] studies on $CpCoL_2$ complexes, where L = CO, PR_3, olefin, etc., show the existence of a high-lying HOMO. In fact, it is this orbital that makes $CpCoL_2$ compounds strong bases.[26] The first ionization energy for $CpCo(CO)_2$, for example, was found to be 7.6 eV.[25a,b] The HOMO in these d^8 complexes is highly localized in the CpCo region of the molecule and corresponds to the xz component of e_1 in Figure 1. When L is a π-acceptor ligand like CO, this orbital is stabilized somewhat by donation to the appropriate combination of empty CO π^* levels. In $CpCoS_2N_2$ the situation is drastically altered. The corresponding molecular orbital, labeled 8a″ in Figure 1, we have assigned to an ionization energy of 8.55 eV. Both the extended Hückel and DV-Xα calculations indicate that this MO is concentrated more on the S_2N_2 portion of the molecule (approximately 60% on S_2N_2 at both levels of theory). The S_2N_2 π_3 fragment orbital lies at a lower energy than the e_1 set of CpCo; therefore, 8a″, the bonding combination of the two fragment orbitals is more concentration on S_2N_2 π_3. In valence bond terms one can write two *limiting* resonance structures, A and B. In A π_3 is formally empty and some back-donation into it can occur from the xz component of e_1. In B π_3 is filled. Our calculations would indicate that B is somewhat more favored. S_2N_2 is a noninnocent ligand, analogous to dithiolene,[27] diazabutadiene and tetraazabutadiene.[29] Notice that there is a difference in the electron count assigned to the metal in the two resonance structures. In structure A the electron count is 18 whereas it is 16 for B. The involvement of both resonance structures will tend to equalize the three S–N bond lengths, and this is indeed apparent from the crystal structure of $CpCoS_2N_2$.[8] What is interesting is that a related $(dppen)_2IrS_2N_2^+$ complex (dppen = *cis*-1,2-bis(diphenylphosphino)ethylene) has recently been isolated.[9b] The molecule is close to an octahedral geometry and has two more valence electrons. In valence bond terms, a resonance structure akin to A will be of the energetically unfavorable 20-electron type while that analogous to B will have 18 electrons. Therefore, we predict that there should be a more pronounced S–N bond alternation in this complex with the S_1–N_2 and S_3–N_4 distances longer than N_2–S_3. In molecular orbital terms the MO analogous to the LUMO, 10a″ in Figure 1, will be filled so the first ionization energy should be much smaller than in $CpCoS_2N_2$. Furthermore, the net occupation of π_3 in the molecule will be close to two electrons and consequently the S–N bond lengths should alternate in the aforementioned direction. Unfortunately, the S_2N_2 group is disordered in $(dppen)_2IrS_2N_2^+$[9b] so this prediction cannot be tested. We look forward to further experimental work on related molecules.



A B

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Registry No. $Cp^*CoS_2N_2$, 109975-51-1; S_4N_4, 28950-34-7; $Cp^*Co(CO)_2$, 12129-77-0; CpCo(COD), 12184-35-9; $CpCoS_2N_2$, 82066-57-7.

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