(20) G. J. Long, Doctoral Dissertation, Syracuse University, 1968.
(21) J. R. DeVoe, Ed., *Natl. Bur. Stand.* (*U.S.*), *Tech. Note*, No. **404**, 108 (1966).
(22) B. W. Dale, personal communication.
(23) G. Lang and B. W. Dale, "Program for Least Squares Fitting of Mössbauer Spectra in Applied Fields", United Kingdom Atomic Energy Authority Research Group Report AERE-R7478, Nuclear Physics Division, AERE Harwell, Oxfordshire, England, 1973.
(24) D. P. C. Thackeray and B. C. Stace, *Spectrochim. Acta*, *Part A*, **30**, 1961 (1974).
(25) B. N. Figgis, "Introduction to Ligand Fields", Wiley-Interscience, New York, N.Y., 1966.
(26) A. Ludi and P. Schindler, *Angew. Chem., Int. Ed. Engl.*, **7**, 638 (1968).
(27) B. N. Figgis and J. Lewis, *Prog. Inorg. Chem.*, **6**, 40 (1964).
(28) B. N. Figgis, J. Lewis, F. E. Mabbs, and G. A. Webb, *J. Chem. Soc. A*, 442 (1967).
(29) G. J. Long and W. A. Baker, Jr., *J. Chem. Soc. A*, 2956 (1971).
(30) G. J. Long and J. T. Wrobleski, unpublished results.
(31) W. Kerler, *Z. Phys.*, **167**, 194 (1962).
(32) R. Ingalls, *Phys. Rev.* [*Sect.*] *A*, **133**, 787 (1964).
(33) T. C. Gibb, *J. Chem. Soc. A*, 1439 (1968).
(34) J. Chappert, *J. Phys.* (*Paris*), *Colloq.*, *Suppl.*, **35** (12), 71 (1974).
(35) W. M. Reiff, *Coord. Chem. Rev.*, **10**, 37 (1973).
(36) S. M. Condren, Doctoral Dissertation, University of Missouri—Rolla, 1971.
(37) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", 2nd ed, Wiley-Interscience, New York, N.Y., 1970, p 81.
(38) J. A. Thich, C. C. Ou, D. Powers, B. Vasiliou, D. Mastropaolo, J. A. Potenza, and H. J. Schugar, *J. Am. Chem. Soc.*, **98**, 1425 (1976).
(39) R. Savoie and P. A. Giguere, *J. Chem. Phys.*, **41**, 2698 (1964).
(40) R. L. Martin in "New Pathways in Inorganic Chemistry", E. A. V. Ebsworth, A. G. Maddock, and A. G. Sharpe, Ed., Cambridge University Press, Cambridge, England, 1968, p 175.
(41) A. Earnshaw and J. Lewis, *J. Chem. Soc.*, 396 (1961).
(42) D. M. Duggan, E. K. Barefield, and D. N. Hendrickson, *Inorg. Chem.*, **12**, 985 (1973); T. R. Felthouse, E. J. Laskowski, and D. N. Hendrickson, *ibid.*, **16**, 1077 (1977).
(43) P. J. Hay, J. C. Thibeault, and R. Hoffmann, *J. Am. Chem. Soc.*, **97**, 4884 (1975).
(44) A. V. Khedekar, J. Lewis, F. E. Mabbs, and H. Weigold, *J. Chem. Soc. A*, 1561 (1967); J. Lewis, F. E. Mabbs, and A. Richards, *ibid.*, 1014 (1967).
(45) W. M. Reiff, G. J. Long, and W. A. Baker, Jr., *J. Am. Chem. Soc.*, **90**, 6347 (1968).
(46) Y. Haven and R. E. Noftle, *J. Chem. Phys.*, **67**, 2825 (1977).
(47) H. H. Wickman and G. K. Wertheim in "Chemical Applications of Mössbauer Spectroscopy", V. I. Goldanski and R. H. Herber, Ed., Academic Press, New York, N.Y., 1968, p 548.
(48) H. H. Wickman, M. P. Klein, and D. A. Shirley, *Phys. Rev.*, **152**, 345 (1966).

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Electronic Spectral and Magnetochemical Studies of Aquo-μ-bis(*cyclo*-(L-histidyl-L-histidyl))-dicopper(II), a Copper(II) Complex with a Deprotonated Amide Nitrogen Ligand

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The title complex $Cu_2(C_{12}H_{13}N_6O_2)_2H_2O{\cdot}2ClO_4{\cdot}3.5H_2O$ (**1**) contains a pseudotetrahedral $Cu^{II}N_4$ unit which is joined by two deprotonated amide bridges to an about square-pyramidal $Cu^{II}N_2O_3$ unit. Ligation in the former chromophore is supplied by two imidazole and two deprotonated amide nitrogen donor atoms. Mull and single-crystal electronic spectra of **1** reveal a weak and very broad ligand field (LF) absorption at ~800 nm, which extends to ~1500 nm, and a stronger neighboring absorption at ~640 nm. These LF absorptions are mixed; the above spectral features cannot be unambiguously associated with the individual Cu(II) sites. Mull spectra of **1** include broad UV maxima at ~360, ~320, ~270, and ~230 nm. Nearly identical UV maxima were observed for a monomeric reference complex of the neutral ligand, $Cu(C_{12}H_{14}N_6O_2)_2{\cdot}2ClO_4{\cdot}6H_2O$ (**2**). Spectral features attributable to $\pi(N) \rightarrow Cu(II)$ ligand to metal charge transfer (LMCT) could not be located in the 360–640-nm region. The absorption of the type 1 blue copper proteins at ~450 nm is discussed in view of the spectral results reported here. Magnetic susceptibility studies of **1** reveal paramagnetic behavior ($1.90 \pm 0.02\ \mu_B$) over the temperature range 286–7.0 K and fix an upper limit of the exchange parameter $|J| < 0.5\ cm^{-1}$. However, a $|J|$ value $>0.02\ cm^{-1}$ is required by the triplet EPR spectrum of **1**; detailed analysis of the spectrum at Q band yielded the parameters $g_{\parallel} = 2.291$, $g_{\perp} = 2.040$, and $D_{\perp} = 0.5354\ cm^{-1}$. The spectrum of **2** at Q band is that of a monomeric complex having $g_{\perp} = 2.058$, $g_{\parallel} = 2.254$, and a parallel copper hyperfine spacing of 191 G.

The blue (type 1) copper proteins exhibit a characteristic electronic absorption at 610 ± 10 nm (ϵ >3000) along with weaker neighboring absorptions at ~800 and ~450 nm. Other workers have suggested that the detailed spectroscopic properties of these proteins may be rationalized in terms of a common, flattened tetrahedral, $Cu^{II}N_2$(imidazole)N*(deprotonated amide)S(cysteine) chromophore.[2] Recent studies[3] have indicated that the plastocyanins and azurins contain a somewhat different $Cu^{II}N_2$(imidazole)S(cysteine)S*(methionine) chromophore. Assignment[1] of the absorptions at ~610 and ~800 nm, respectively, to $\sigma(S) \rightarrow Cu(II)$ and $\pi(S) \rightarrow Cu(II)$ ligand to metal charge transfer (LMCT) remains consistent with these results and has received support from studies of model, approximately tetrahedral, mercaptoamine complexes.[4] Assignment of the absorption at ~450 nm to $\pi(N^*) \rightarrow Cu(II)$ LMCT cannot be correct for the plastocyanins and azurins. An absorption of this type remains possible for stellacyanin, a type 1 copper protein which is free of methionine residues,[3] and of course for simple Cu(II) complexes ligated in part by deprotonated amide nitrogen donors. Spectral studies of probably tetragonal Cu(II) complexes having one or more of these nitrogen donors have not revealed absorptions at ~450 nm which may be indicative of $\pi(N^*) \rightarrow Cu(II)$.[5] However, the position of this LMCT band should reflect the ligand field dependency of the copper d vacancy; the intensity of this band will depend upon factors such as the overlap between the π-symmetry orbitals of the Cu(II) and the deprotonated amide nitrogen and the extent of "borrowing" from highly allowed neighboring electronic transitions. Thus, appropriate structural models for detecting biologically relevant $\pi(N^*) \rightarrow Cu(II)$ LMCT should maintain an approximately tetrahedral arrangement of donor ligands. The title complex (Figure 1) is an attractive vehicle for such a test.[6] Cu(B) has a N_2(imidazole)N^*_2 donor set which approximates a flattened tetrahedron; the dihedral angle, N(4)–Cu(B)–N(5)/N′(4)–Cu(B)–N′(5), is 51.2°.[7a] More-

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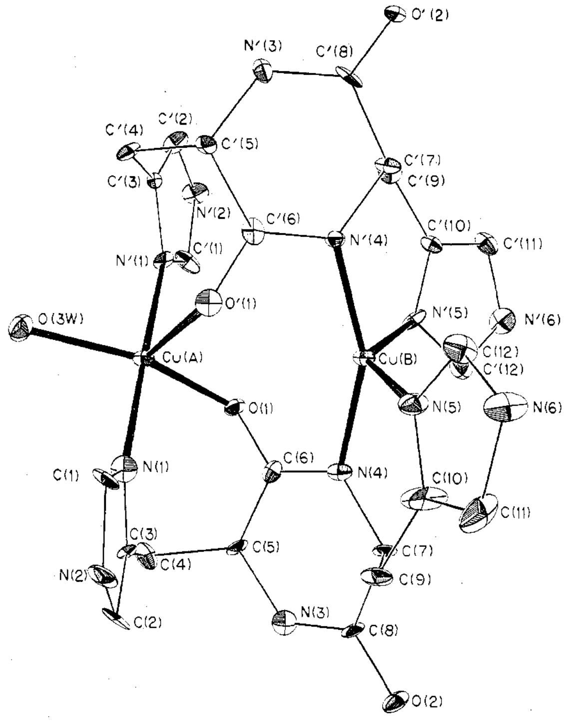

Figure 1. ORTEP view of **1**.

over, the possibility of interesting magnetic phenomena arises from the linking of Cu(B) by the two deprotonated amide bridges to a second Cu(II) species, Cu(A), which has an approximately square-pyramidal N_2O_3 ligand donor set. The Cu(A)–Cu(B) separation is 3.539 (3) Å.[7b] We report here the electronic-spectral and magnetic properties of the title complex and their comparison, in part, with those obtained for a reference monomeric complex.

Experimental Section

Preparation of $Cu_2(C_{12}H_{13}N_6O_2)_2H_2O\cdot 2ClO_4\cdot 3.5H_2O$ (1). The dropwise addition of 6 mL of 1 N NaOH to a solution of 2.22 g of $Cu(ClO_4)_2\cdot 6H_2O$ (6 mmol) and 1.65 g of *cyclo*-(L-histidyl-L-histidyl) (6 mmol) in 20 mL of hot water raised the pH from 4.0 to 7.0. After cooling the mixture to 25 °C, the solution deposited **1** as rectangular dark blue plates whose long dimension corresponded to the crystallographic *b* axis.[6]

Anal. Calcd for $Cu_2(C_{12}H_{13}N_6O_2)_2H_2O\cdot 2ClO_4\cdot 3.5H_2O$: Cu, 13.33; C, 30.23; H, 3.70; N, 17.63. Found: Cu, 13.57; C, 30.93; H, 3.60; N, 17.15.

Preparation of $Cu(C_{12}H_{14}N_6O_2)_2\cdot 2ClO_4\cdot 6H_2O$ (2). When NaOH was omitted from the preparation of **1**, the hot solution deposited pale blue plates of a complex containing 2 molecules of the neutral cyclic dipeptide ligand/Cu(II) ion. Complex **2** also was obtained when the NaOH and half of the $Cu(ClO_4)_2\cdot 6H_2O$ were omitted from the preparation of **1**.

Anal. Calcd for $Cu(C_{12}H_{14}N_6O_2)\cdot 2ClO_4\cdot 6H_2O$: Cu, 6.91; C, 31.36; H, 4.39. Found: Cu, 6.78; C, 32.19; H, 4.25.

Magnetic Measurements. X-band and Q-band EPR spectra of powdered **1** and **2** were obtained using instrumentation and procedures described previously.[8] Variable-temperature (7.0–286 K) magnetic susceptibilities of **1** were measured using a vibrating-sample magnetometer. Observed molar susceptibility data were corrected for atomic diamagnetism (-343×10^{-6} cgsu), which was estimated using Pascal's constants.[9] Complexes **1** and **2** were purified for magnetic studies by recrystallization (2×) from hot solutions that were filtered through a Millipore membrane (0.22-μm pore size).

Results and Discussion

The mull spectrum of **1** at 293 K exhibits a weak and very broad LF absorption at ≈800 nm, which extends to ≈1500 nm, and a stronger absorption at ≈640 nm. The LF absorptions for the low-symmetry Cu(A) and Cu(B) units appear to be broad and mixed; we were not able unambiguously to associate any spectral features with the individual copper sites. Although polarized spectra (Figure 2) of the monoclinic **1** may be distorted somewhat by dispersion effects, we include these data to demonstrate gross band shapes and intensity features of the LF spectra. We were unable to detect any near-UV band having a λ_{max} >370 nm in either polarization studied. Mull spectra of **1** also include broad UV maxima at ≈360, ≈320, ≈270, and ≈230 nm. Since nearly identical mull spectra were obtained for **2**, we are unable to identify any features in the near-UV spectral range which can be attributed to $\pi(N^*) \rightarrow$ Cu(II) LMCT. This result implies that the spectroscopic role of the extra lone electron pairs of N(4) and N′(4) is not important. Moreover, coordination by deprotonated amides produces ligand fields appropriate for a medium-field σ-only donor.[10] These results parallel those obtained for thioether sulfur which also acts like a medium-field purely σ-donor ligand; $\pi(S) \rightarrow$ Cu(II) LMCT is at best a barely detectable spectral feature.[13]

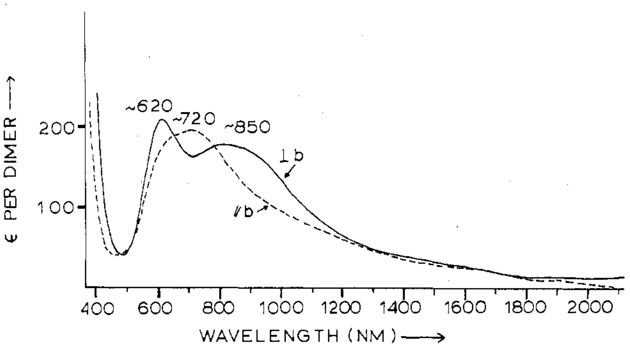

Figure 2. Polarized single-crystal spectra of **1** at 298 K with the electric vector either parallel (---) or perpendicular (—) to the crystallographic *b* axis.

Since Cu(II)–S*(methionine) bonding appears to be a feature common to plastocyanins and azurins,[3] their electronic absorption at ~450 nm likely corresponds to the $\sigma(S^*) \rightarrow$ Cu(II) LMCT observed for model copper(II)–thioether chromophores.[13,14] For the methionine-free protein, stellacyanin,[3,15] absorption at ~450 nm may originate from $\pi(N) \rightarrow$ Cu(II) LMCT which has borrowed considerable intensity from the highly allowed "blue band" at 600 nm. Another plausible explanation is that this absorption originates from copper(II)–disulfude bonding in stellacyanin.[16]

The corrected magnetic moment per Cu(II) of **1** was observed to be 1.90 ± 0.02 μ_B over the temperature range 286–7.0 K.[17] Thus, despite the two deprotonated amide pathways linking Cu(B) to apical O(1) and equatorial O′ (1) sites on Cu(A), the susceptibility measurements do not detect any magnetic interaction between the copper sites and fix an upper limit of the exchange parameter of $|J| < 0.5$ cm^{-1}. However, the EPR spectra of **1** (Figure 3) are those of a triplet-state species and require $|J|$ to be larger than ≈0.02 cm^{-1}, the normal magnitude of the copper hyperfine interaction. Measurements on different samples of **1** indicate that the Q-band signal at ≈11 750 G ($g \cong 2.1$) arises from an impurity. If the dimer effectively is axial, five EPR signals are expected from the single $\Delta M_s = 2$ signal, the zero field split $g_\perp$ signals, and the relatively weak zero field split $g_\parallel$ signals. Comparison of the Q-band spectrum with those of dimeric copper(II) carboxylates[18] indicates that the signals at 8945 and 14 730 G are the two $g_\perp$ zero-field split signals; the signal at 4895 G then may be assigned as the $\Delta M_s = 2$ transition.

We used a least-squares procedure to fit these three peak positions to the theoretical equations[19] describing the field dependency for the expected five signals and obtained the result $g_\parallel = 2.291$, $g_\perp = 2.040$, and $D_\perp = 0.5354$ cm^{-1}. The observed

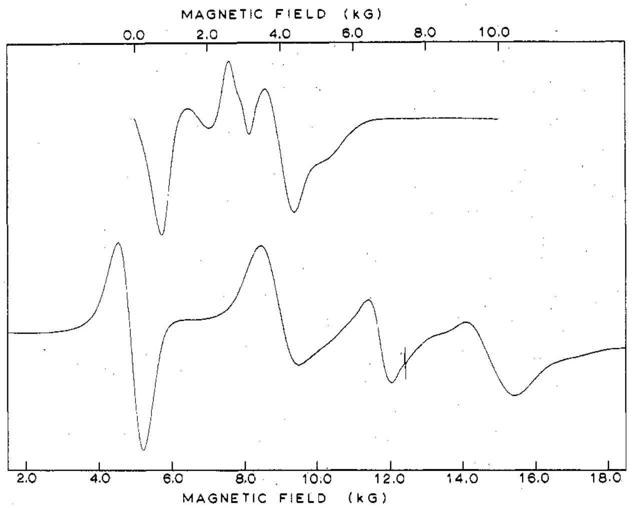

Figure 3. X-band (upper) and Q-band (lower) EPR spectra of powdered **1** at liquid-nitrogen temperature. The narrow resonance in the Q-band spectra is due to DPPH ($g = 2.0036$).

Cu–Cu separation of ≈3.6 Å fixes the maximum dipole–dipole zero-field splitting at 0.06 cm^{-1} or about 10% of the observed value. As has been presented in detail for another Cu(II) dimer, this difference in observed zero-field splitting and calculated maximum dipolar zero-field splitting is the result of an appreciable pseudo-dipolar zero-field interaction.[20] The ground electronic state of **1** is coupled with an excited state having a much larger value of J. The Q-band EPR spectrum (not shown) at ≈110 K for **2** is that of a magnetically dilute monomeric complex[21] having $g_\perp = 2.058$, $g_\parallel = 2.254$, and parallel copper hyperfine spacing of 191 G.

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Registry No. $Cu_2(C_{12}H_{13}N_6O_2)_2H_2O{\cdot}2ClO_4$, 60583-90-6; $Cu(C_{12}H_{14}N_6O_2)_2{\cdot}2ClO_4$, 67421-38-9.

Supplementary Material Available: A table of experimental magnetic susceptibility data for **1** (1 page). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Rutgers. (b) University of Illinois.
(2) E. I. Solomon, J. W. Hare, and H. B. Gray, *Proc. Natl. Acad. Sci. U.S.A.*, **73**, 1389 (1976).
(3) P. M. Coleman, H. C. Freeman, J. M. Guss, M. Murata, V. A. Norris, J. A. M. Ramshaw, and M. P. Venkatappa, *Nature (London)*, **272**, 319 (1978).
(4) D. Mastropaolo, J. A. Thich, J. A. Potenza, and H. J. Schugar, *J. Am. Chem. Soc.*, **99**, 424 (1977).
(5) (a) E. W. Wilson, Jr., M. H. Kasperian, and R. B. Martin, *J. Am. Chem. Soc.*, **92**, 5365 (1970). (b) G. F. Bryce and F. R. N. Gurd, *J. Biol. Chem.*, **241**, 1439 (1966).
(6) Figure 1 was constructed from atomic positional parameters reported by Y. Kojima, K. Hirotsu, and K. Matsumoto, *Bull. Chem. Soc. Jpn.*, **50**, 3222 (1977).
(7) (a) The unit cell of this complex contains a second crystallographically unique dimer which structurally is nearly identical with Figure 1. The corresponding dihedral angle of this other pseudotetrahedral CuN_4 site is 48.8°. (b) The copper–copper separation in the latter dimer is 3.600 (3) Å.
(8) C. C. Ou, D. A. Powers, J. A. Thich, T. R. Felthouse, D. N. Hendrickson, J. Potenza, and H. J. Schugar, *Inorg. Chem.*, **17**, 34 (1978).
(9) A. Earnshaw, "Introduction to Magnetochemistry", Academic Press, New York, N.Y., 1968.
(10) For example, the tetragonal[11] CuN_4O_2 chromophore present in $K_2(Cu(NH_2CHC({=}O)NCH_2CO_2)_2){\cdot}6H_2O$ exhibits LF absorption at ≈535 nm.[12] Structurally analogous tetragonal $Cu(H_2NCH_2CH_2NH_2)_2X_2$ units where X is apically bound H_2O, Cl^-, Br^-, etc., exhibit LF absorption in the 520–535-nm range.[13]
(11) A. Sugihara, T. Ashida, Y. Sasada, and M. Kakudo, *Acta Crystallogr., Sect. B*, **24**, 203 (1968).
(12) Y. Nakao, K. Sakurai, and A. Nakahara, *Bull Chem. Soc. Jpn.*, **39**, 1608 (1966).
(13) V. M. Miskowski, J. A. Thich, R. Solomon, and H. J. Schugar, *J. Am. Chem. Soc.*, **98**, 8344 (1976).
(14) A. R. Amundsen, J. Whelan, and B. Bosnich, *J. Am. Chem. Soc.*, **99**, 6730 (1977).
(15) C. Bergman, E. Gandvik, P. O. Nyman, and L. Strid, *Biochim. Biophys. Res. Commun.*, **77**, 1052 (1977), and references cited therein.
(16) Copper(II)–disulfide bonding in low-molecular weight complexes is uncommon. Weak (apical) copper(II)–disulfide bonding has been reported by J. A. Thich, D. Mastropaolo, J. A. Potenza, and H. J. Schugar, *J. Am. Chem. Soc.*, **96**, 726 (1974).
(17) Supplementary material.
(18) For example, see G. F. Kokoszka and R. W. Duerst, *Coord. Chem. Rev.*, **5**, 209 (1970), and references therein. Similar Q-band EPR spectra have been observed in complexes with short Cu–Cu distances: C. J. Doumit, G. L. McPherson, R. L. Belford, S. B. Lenoux, and H. B. Jonassen, *Inorg. Chem.* **16**, 565 (1977).
(19) E. Wasserman, L. C. Snyder, and W. A. Yager, *J. Chem. Phys.*, **41**, 1763 (1964).
(20) T. T. Felthouse and D. N. Hendrickson, *Inorg. Chem.*, **17**, 444 (1978).
(21) A dihydrate form of **2**, $Cu(C_{12}H_{14}N_6O_2)_2{\cdot}2ClO_4{\cdot}2H_2O$, contains discrete $Cu(C_{12}H_{14}N_6O_2)_2{}^{2+}$ cations; puckered CuN_4 units arise from the ligation of Cu(II) by the four imidazole residues. Private communication from Dr. Keiji Matsumoto, Osaka City University, Osaka, Japan.

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Xα Scattered-Wave Calculations of the Electronic Structures of SO_2 and SO_2F_2. Relationship to π Bonding in the Cyclic Phosphazenes

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The overlapping-spheres Xα scattered-wave method has been used for investigating the chemical bonding and the electronic structures of SO_2 and SO_2F_2. Excellent agreement is obtained for SO_2 both with the experimental photoelectron spectrum and with the charge distributions obtained previously with near-Hartree–Fock calculations. For SO_2F_2, there is also good agreement with the observed He I and He II spectra, and molecular orbital contour maps have been used for discussing the vibrational structure in the He I spectrum. These new calculations demonstrate a close connection between the level ordering and π bonding in SO_2F_2 and the corresponding quantities obtained in earlier Xα scattered-wave calculations on the cyclic phosphazene fluorides $(NPF_2)_3$ and $(NPF_2)_4$.

Introduction

There is a continuing interest in the nature of the chemical bonding in molecules of phosphorus or sulfur in which the second-row atom is in a high formal oxidation state, and previous discussions have tended to center on the role of 3d orbitals.[1,2] More recently a number of important computational methods have become sufficiently developed to allow the quantitative investigation of the electronic structures of

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