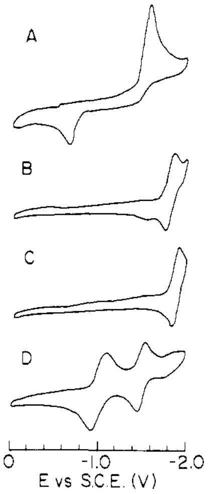

Figure 1. Cyclic voltammograms of 3-mM solutions in 0.1 M $(C_2H_5)_4NClO_4$ vs. SCE in DMF at a platinum button electrode, scan rate 0.4 V/s. (A) $[(C_2H_5)_4N]_2[Mo_2S_4(SC_6H_5)_4]$, (B) $[(C_2H_5)_4N]_2[Mo_2S_4(C_6H_4SNH)_2]$, (C) $[(C_2H_5)_4N]_2[Mo_2S_4(SCH_2CH_2S)_2]$, (D) $Mo_2S_4(CH_3NHCH_2C(CH_3)_2S)_2$.

core. Complex **6** has been found only in the syn isomeric form[14] while complex **7** has been crystallographically characterized in both isomeric forms.[8c,15] The infrared spectra of complexes **3**–**8** (Table I) all contain a strong Mo–S_t stretching vibration and in most cases a second, much weaker, absorption at lower wavenumbers, consistent with the predominant or exclusive formation of the syn isomer.[17] The dianionic complexes display lower Mo–S_t stretching frequencies than the neutral complexes, presumably due to additional electron density on the $Mo_2S_4^{2+}$ core. Comparison of the neutral and dianionic complexes of the *o*-aminobenzenethiol ligand, **4** and **5**, where ν(Mo–S_t) occurs at 542 and 510 cm^{-1}, respectively, illustrates this effect.

The cyclic voltammograms of complexes **3**, **5**, **7**, and **8**, shown in Figure 1, illustrate the effect of different ligands and donor atoms on the electrochemical behavior of the $Mo_2S_4^{2+}$ core. All complexes, with the exception of **3**, display reversible one-electron transfers. This behavior is consistent with that observed previously for complexes with the $Mo_2O_{4-x}S_x^{2+}$ (x = 0–4) core where electrochemical reversibility increases with the number of sulfide ligands.[16,18] The irreversibility observed for **3**, which contains monodentate thiophenoxide ligands, suggests that bidentate ligands may be required to stabilize the reduced $Mo_2S_4^{2+}$ complexes. The more negative reduction potentials found for the dianionic complexes **3**, **5**, and **7** relative to the neutral complexes **4**, **6**, and **8** may result from the additional electron density on the $Mo_2S_4^{2+}$ core in the dianionic complexes. In addition, electrolysis of **4**, at potentials more negative than its two irreversible waves, results in a quantitative conversion to **5**. A more detailed discussion of the electrochemical behavior will appear in a forthcoming publication.

The reduction of the disulfide complex, **1**, to give the molybdenum sulfide complexes reported here should be viewed in light of a recently reported redox reaction in which the reverse process occurs, i.e., the conversion of a molybdenum sulfide to a molybdenum disulfide complex (eq 4).[9d] Further, a recent study shows

$$2MoO_2S_2^{2-} \rightarrow Mo_2O_2S_2(S\text{–}S)_2^{2-} \qquad (4)$$

that a partial disulfide bond can be formed in the Mo^{VI} coordination sphere from two nominally noninteracting *cis*-thiolate ligands.[21] These results point to previously unrecognized intramolecular redox behavior associated with sulfur coordinated to molybdenum in its higher oxidation states.

The general procedures reported here for the preparation of a variety of $Mo_2S_4^{2+}$ complexes have allowed for the first time the isolation of this core with nonsulfur-donor and nonchelating ligands. Varying the ligand is found to have profound effects on the spectroscopic and, especially, the electrochemical properties of $Mo_2S_4^{2+}$ complexes. Further, we have found these complexes to be reactive toward a variety of divalent first-row transition-metal ions. As in the thiomolybdate series,[3,4] the terminal sulfides in $Mo_2S_4^{2+}$ complexes appear to function as donors toward the appropriate metal ions. Full characterization of the products of these reactions is under way. However, initial results indicate that $Mo_2S_4^{2+}$ complexes represent new molybdenum sulfide starting materials for the preparation of heteronuclear molybdenum sulfide containing complexes and materials.

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Kenneth F. Miller, Alice E. Bruce, James L. Corbin
Scot Wherland, Edward I. Stiefel*
Charles F. Kettering Research Laboratory
Yellow Springs, Ohio 45387

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[17] Two infrared-active Mo–S_t stretching vibrations are expected for complexes in the syn isomeric form while only one is predicted for the anti isomer. Although both stretching modes have been identified for **6**[16] it may not always be possible to observe the weaker, lower-energy absorption for the syn isomer. We attribute the Mo–S_t stretching vibration observed at 522 cm^{-1} in **7** to the syn isomeric form. The shoulder observed at 510 cm^{-1} is due to either the second stretching vibrational mode of the syn isomer or the presence of small quantities of the anti isomer. The syn and anti isomers of **7** have been reported to give rise to single Mo–S_t stretching vibrations of 508 and 493 cm^{-1}, respectively.[8c] The discrepancy between our finding of 522 cm^{-1} and the previously reported 508 cm^{-1} is not understood. The voltammetry of **7** is in good agreement with that reported previously[8c] for the syn isomer of **7**.

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A Quintet-State Triplet-Triplet Radical Pair

Sir:

Radical pairs having triplet multiplicity–and only triplet multiplicity–have been detected in many chemical reactions in the past decade and a half by using ESR spectroscopy.[1,2] Even among stabilized organic radicals, multiplicities higher than triplet are scarce. Trozzolo, Wasserman, and co-workers[3] observed complex ESR spectra in the low-temperature matrix photolysate of 1,3-bis(α-diazobenzyl)benzene and 1,3-diazidobenzene and assigned them to the quintet ground states of *m*-dicarbene and *m*-dinitrene, respectively. Itoh[4] also succeeded in stabilizing the quintet state of *m*-dicarbene in the precursor single crystal. There are also reports on the detection of septet-state organic radicals

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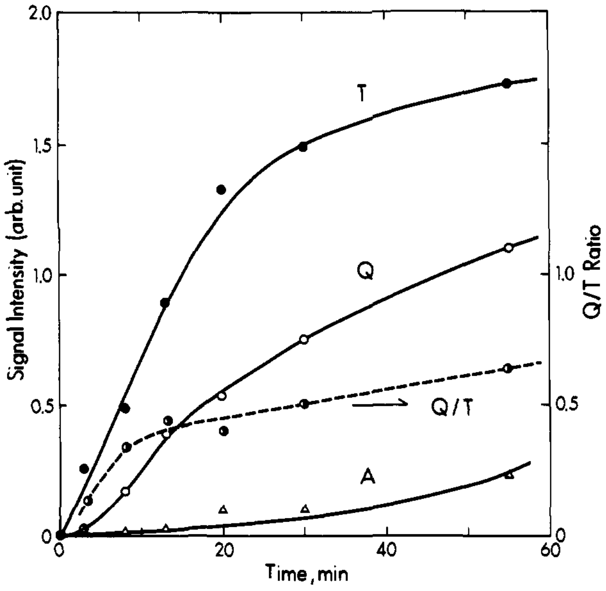

Figure 1. Time dependence of the ESR signals during photolysis of azibenzil powder at 77 K. T = **1a**; Q = quintet state species; A = doublet radical; Q/T = intensity ratio of the quintet signal vs. the triplet signal (**1a**).

produced in the photolysis of 1,3,5-triazido-2,4,6-tricyanobenzene[5] and 1,3,5-tris(α-diazobenzyl)benzene.[6] More recently, Weissman and Kothe[7] reported the quartet ESR spectrum of the stable molecule 1,3,5-(2,4,6-tricyanobenzenetriyl)tris(N^1,N^1-diphenylhydrazyl). Using an L-band spectrometer, these authors were able to observe the $\Delta m = 3$ transition, making the assignment of the spectrum unambiguous.

The purpose of the present communication is to report the first observation of a quintet state triplet–triplet radical pair formed in the pairwise interaction of two triplet-state benzoylphenylmethylenes. The latter were produced by the photolysis of azibenzil powder with uranium glass filtered light at 77 K.

Irradiation produced a complex ESR spectrum which ultimately could be resolved into four different spectra: (1) a signal with no hfs at $g = 2.003$ which is assigned to an unidentified doublet radical;[8] (2) a set of strong absorptions which is assigned to the trans conformer of triplet benzoylphenylmethylene (**1a**);[8] (3) another set of weak absorptions, assigned to the cis isomer of **1a**, (**1b**);[8] and (4) a set of complex absorptions consisting of at least 11 lines of varying intensity which appeared in the 0–6400-G range.

The latter spectrum was analyzed by using the Hamiltonian

$$\mathcal{H} = g\beta\vec{H}\cdot\vec{S} + D\left\{S_z^2 - \frac{S(S+1)}{3}\right\} + E(S_x^2 - S_y^2)$$

The exact energy levels of $\mathcal{H}$ obtained by a numerical iteration method were used to determine the zero-field splitting parameters from the two highest steplike absorption fields. When $S = 2$ and $g = 2.002$, the values of D and E were found to be 0.0943 and 0.0077 cm^{-1}, respectively. The equation then satisfactorily reproduces the observed spectrum, which clearly belongs to a quintet-state radical. The lowest absorption, between ~0 and 100 G, is found to be the $\Delta m = 2$ transition because the energy separation of one of the three $\Delta m = 2$ transitions at zero field is comparable to the microwave energy. The lowest absorption of the $\Delta m = 1$ transition predicted by the D and E values is observed in the tail portion of the strong H_z absorption of **1a**.

Exposure time studies (Figure 1) showed that the ESR absorption of **1a** was linear with time while the intensity of the quintet spectrum was higher than first order in the initial stages. The temporal variations observed are consistent with the postulate that the quintet species is formed from the interaction of two molecules of **1a**. It was also observed that the quintet signal intensity kept growing in the dark for several minutes after cessation of irradiation. This phenomenon is probably due to some physical relaxation involving a slight reorientation of the radical pairs in the lattice.

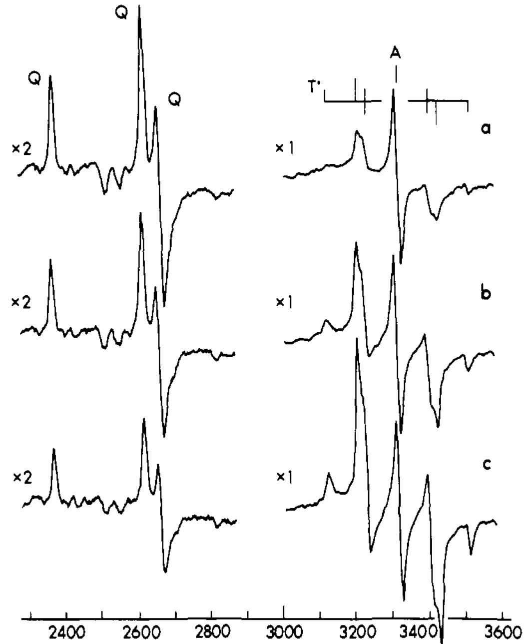

Figure 2. ESR spectra of the quintet state (Q), new triplet state (T′), and the doublet radical (A) generated in the uranium glass filtered light photolysis of azibenzil powder at 77 K recorded (a) immediately after warming to 91 K, (b) after 18 min at 91 K, and (c) after 60 min at 91 K. The klystron frequency was 9.330 GHz.

All these ESR signals are stable for hours at 77 K, but upon the photolysate's being warmed to 90 K, the quintet-state spectrum is converted irreversibly to a new triplet spectrum having small zero-field splitting parameters ($D = 0.0189$ cm^{-1} and $E = 0.0008$ cm^{-1}) (Figure 2). The $\Delta m = 2$ transition for this triplet is also observed at half magnetic field. This quintet → triplet conversion follows a good first-order kinetics. The new triplet signal decays above 120 K while the signal of **1a** is stable up to 150 K. The quintet signal is not observed when photolysis is carried out in organic glass matrixes.

The alternative possibility of assigning the quintet spectrum to a single radical instead of a radical pair is highly remote. The carrier of the new triplet spectrum generated upon decay of the quintet is postulated to be a diradical formed as a result of spin inversion and single covalent bond formation in the radical pair. The mean separation of the two unpaired electrons in terms of point-spin approximation in the new triplet is ~5.2 Å, indicating that bond formation probably occurs between the carbene carbon and the carbonyl linkage.

The zero-field splitting parameters of the quintet are given as averages of six interactions of four electrons.[9] Since the main contribution to the D value must come from the two triplet **1a** radicals ($D = 0.3916$ cm^{-1}), the observed D value of the quintet is in satisfactory agreement with the triplet-pair model proposed. Preliminary temperature studies seem to suggest that the ground state of **1a** is triplet and that the quintet is also the ground state of the radical pair.

In summary, the quintet ESR spectrum reported here is assigned to the novel radical pair formed from the interaction of two triplet benzoylphenylmethylenes. As far as can be ascertained, this is the first known example of a quintet-state radical pair.

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H. Murai, M. Torres, O. P. Strausz*
Department of Chemistry, University of Alberta
Edmonton, Alberta, Canada T6G 2G2

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Intense Satellites in the N 1s X-ray Photoelectron Spectra of Certain Metalloporphyrins

Sir:

Satellite features associated with core-electron photoelectron photoionization, as observed in X-ray photoelectron spectroscopy (XPS), have attracted considerable interest over the last 10 years.[1-3] These features, commonly called shake-up satellites but perhaps better called correlation-state structure, following Shirley,[5] arise because photoionization may leave the final system in a valence excited state. This is due physically to the rearrangement of valence electronic structure upon core ionization. The interest in such features in transition-metal compounds has been especially intense,[2,4,6,7] partly because of their intensity in some of these systems and partly because it is felt that they may provide useful information not readily obtained otherwise about the excited-state manifolds of these compounds. Most recently, attention has focused upon satellite structures arising from ligand levels in transition-metal compounds.[8,9] We report here rather striking N 1s satellites in certain metalloporphyrins, satellites which are strongly metal dependent and thus reflect properties of the metals involved.

Weak N 1s satellites are ubiquitous in porphyrins and have been reported by various workers.[10-12] They depend weakly, if at all, on the metal and probably represent a $\pi \rightarrow \pi^*$ transition localized on the porphyrin. We have found quite different behavior, however, in the metal porphyrins containing Zn, Ag, Cd, and Mg and in four metalloporphyrins of trivalent lanthanides (Gd, Ho, Er, and Tm). The lanthanide compounds are believed to contain hydroxide as an axial ligand.[13] N 1s spectra of four of these compounds appear in Figure 1, along with the N 1s spectrum of Ni(OEP) (OEP = octaethylporphyrin) for comparison. Spectra similar to some of those in Figure 1 have appeared previously; in particular, spectra of magnesium porphyrins and of chlorophylls[12] have appeared. The satellites have been attributed to radiation-induced demetalation of the porphyrin. The intensity of the satellite is constant from sample to sample, however, and does not change with time of irradiation. The positions and relative intensities of the satellites shown in Figure 1 appear in Table I.

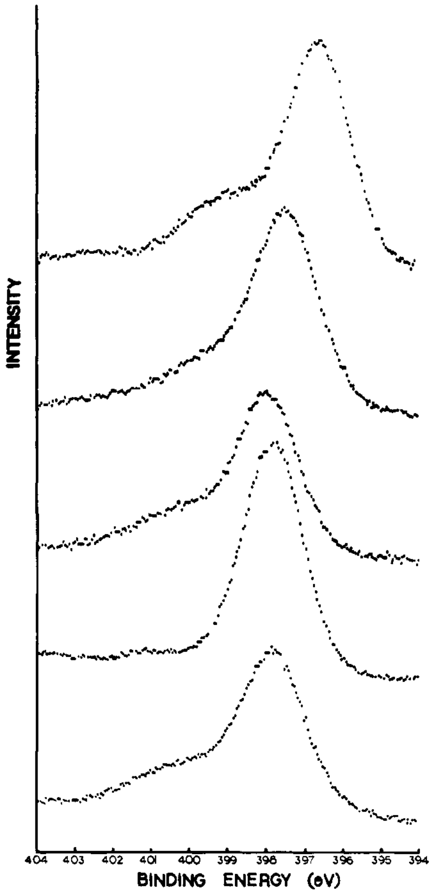

Figure 1. N 1s spectra of (top to bottom): MgTPP, AgOEP, GdOEP, NiOEP, and ZnOEP (TPP = tetraphenylporphyrin, OEP = octaethylporphrin).

Table I. Positions and Intensities of the N 1s Satellites of Several Porphyrins

compound	satellite position, eV from main line	intensity, % of main line
NiOEP	3.1	4.7
ZnOEP	2.3	16.3
AgOEP	2.1	20.6
MgTPP	2.2	29.7
GdOEP	1.7	39

None of these compounds display any structure on the metal core ionizations. Various sources of the features we observe must be considered. (1) They may be due to the presence of more than one nitrogen-containing species on the sample, due, for instance, to sample degradation. (2) They may be due to irregular geometries of the compounds involved, leading to the presence of more than one electronically distinct type of nitrogen atom. (3) The features are genuine correlation-state structures, due to population of excited final states of the systems involved.

We have eliminated the first possibility by observing the intensity distribution in the N 1s region of several samples of each compound as a function of time of irradiation. In all the cases at hand, the intensities were independent of sample and time of irradiation. We could obtain spectra after as little as 3-min irradiation at 100 K.

The second possibility is hardly likely for such compounds as magnesium porphyrins, in which the geometry is known[14] but cannot be excluded in such compounds as the lanthanide porphyrins, in which the geometry is really quite unknown. The intensities of the features (see Table I) militate against such an explanation, however, since they should be approximately in the ratio of multiples of one-fourth, i.e., 1:3 or 1:1, and these intensity

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