pathways that lead either to photoproducts or back to the starting material, as suggested by one model discussed in the beginning of the paper. Of course, it remains possible to invent even more complicated schemes that postulate two distinct transition states, one of which leads to such an intermediate (hot ground state), and thus preserve all features of both models, but it would be a formidable experimental task to obtain experimental evidence for such a complicated scheme in these compounds.

5. Even if one rightly emphasizes that the precision of transition-state thermodynamic parameters measured for short-lived excited states is not as good as one would expect for stable ground states, it is difficult to ignore the fact that a consistent pattern is emerging for Rh(III) complexes. In every case E_c exceeds E_n, and this result really only depends on the observation that the photochemistry is "more temperature sensitive" than is the phosphorescence lifetime, so that photochemical yield increases at higher temperatures despite the fact that the lifetime is reduced.

Table III invites further speculation. We caution against overinterpretation of the numerical quantities. However, the qualitative conclusions seem plausible: For both compounds, photosubstitution processes exhibit larger activation energies but smaller entropy changes in the activated state than do nonradiative decay processes. Dissociation apparently requires considerable enthalpy input, albeit far less than is required for the thermal substitution processes. For *trans*-[Rh(en)$_2$Br$_2$]$^+$, the activation entropy is negative: there is some increased ordering necessary to form the transition state, but the effect is not too restrictive. In that complex the photochemical substitution is Br$^-$ aquation. In contrast, in Rh(NH$_3$)$_5$Br^{2+}, the photochemical substitution is NH$_3$ aquation and for the latter process, which does not involve the same charge separation, the activation entropy appears to be positive, although the uncertainty is sufficiently large that one cannot be certain. In contrast, nonradiative decay, in these systems near room temperature, is dominated by a process that requires some enthalpy, but less than is needed for the photoaquation reaction; however, it occurs through a rather highly ordered transition state that involves a decrease of entropy that is significantly greater than what is required for photoaquation. Of course, much of the entropy contribution to both processes is expected to relate to ordering the surrounding solvent shell. When the two different complexes are compared, it seems that the difference in their nonradiative rates is predominately an enthalpic effect.

We conclude with the observation that excited electronic states with lifetimes as short as 1 ns are true metastable chemical species. They exhibit a chemistry that is distinctly different from that of the ground state of the same molecules, but that chemistry can be subjected to the same systematic investigation and thermodynamic interpretation.

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Two More Space Group Revisions

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The space groups (and atom coordinates) of two crystal structures reported in a recent issue of *Inorganic Chemistry* (Vol. 27, No. 4; Feb 24, 1988) should be revised. In both cases the structures were reported as triclinic, and the revised structures are *C*-centered monoclinic, one in space group $C2/m$ and the other in $C2/c$.

Table I. Coordinates (×10^4 for Cu, Cl, and N; ×10^3 for C) for TMCuC in Space Group $C2/m$[a]

	x'	y'	z'	x'	y'	z'
Cu(1)	0	0	0	0	0	0
Cu(2)	0	0	5000	0	0	5000
Cl(1)	1222 (2)	−4 (4)	2079 (4)	1222	0	2079
Cl(2a)	−550 (3)	−1628 (7)	2409 (8)	−551	1640	2358
Cl(3a)	−552 (4)	1651 (8)	2306 (9)			
Cl(2)	−640 (4)	−1945 (6)	3077 (7)	−632	1926	3050
Cl(3)	−623 (3)	1907 (6)	3024 (7)			
N	−1672 (4)	−4992 (7)	7500 (9)	−1672	5000	7500
C(1)	−202 (2)	−369 (4)	845 (6)	−204	370	843
C(2)	−205 (2)	−628 (3)	841 (6)			
C(3)	−186 (3)	−498 (6)	533 (3)	−186	500	533
C(4)	−77 (1)	−503 (6)	796 (7)	−77	500	796
C(1a)	−153 (2)	−498 (6)	970 (3)	−153	500	970
C(2a)	−214 (2)	−627 (2)	687 (7)	−215	372	687
C(3a)	−216 (2)	−372 (4)	687 (7)			
C(4a)	−88 (2)	−497 (5)	652 (6)	−88	500	652

[a] The values on the left are obtained by transforming the coordinates in Table III, ref 1, as described in the text; values on the right are obtained by symmetrizing and averaging according to $C2/m$.

(1) Tetramethylammonium Trichlorocuprate(II) (TMCuC) at 323 K.[1] The structure was described in space group $P\bar{1}$, with a = 9.082 (5) Å, b = 9.073 (5) Å, c = 6.442 (3) Å, α = 90.05 (4)°, β = 92.40 (4)°, γ = 119.99 (3)°, and Z = 2. The lattice vectors [210], [010], and [001] define a *C*-centered cell with a' = 15.732 Å, b' = 9.073 Å, c' = 6.442 Å, α' = 90.05°, β' = 92.80°, γ' = 90.02°, and Z = 4; the corresponding transformations $x' = {}^1/_2x$, $y' = y - {}^1/_2x$, and $z' = z$ lead to the coordinates in the left-hand columns of Table I. When these coordinates are symmetrized and, in some cases, averaged so as to conform to space group $C2/m$, the values in the right-hand columns of Table I result.

Except for the four disordered atoms Cl(2a), Cl(3a), Cl(2), and Cl(3), none of the symmetrizing shifts is larger than expected from the reported esd's. For these four chlorine atoms, the necessary shifts are much greater than the esd's, ranging up to 0.035 Å. However, the proposed disorder[1] is such that pairs of disordered atoms are separated by only 0.53 Å; the electron density associated with these sites is undoubtedly diffuse and can probably be modeled in several ways. (The carbon atoms are also disordered, but for them the separations are about 1.0 Å or more so resolution is complete.)

Space group $C2/m$ is more attractive than $P\bar{1}$ on the general grounds of symmetry relationships in phase transitions. The structure represents an intermediate-temperature (323 K) phase that undergoes a transition (probably first order) at 319 K to a low-temperature phase with space group $P2_1$ and another transition (probably second order) at about 373 K to a high-temperature phase with space group $P6_3/mmc$.[1] Symmetry $C2/m$ for the intermediate phase is then far more logical than symmetry $P\bar{1}$, in view of the transition to the low-temperature and (presumably) lower symmetry phase with space group $P2_1$: a 2_1 axis is contained within the symmetry elements of $C2/m$ but not of $P\bar{1}$.

(2) Fe(C$_6$H$_8$N$_2$S$_2$)$_2$(NCS)$_2$. Polymorph B.[2] The structure of this crystalline form of bis(2,2′-bis-2-thiazoline)bis(thiocyanato)iron(II) was also described in space group $P\bar{1}$, with a = 10.846 (3) Å, b = 10.847 (3) Å, c = 12.526 (4) Å, α = 115.72 (2)°, β = 93.92 (2)°, γ = 119.97 (2)°, and Z = 2. The vectors [210], $[0\bar{1}0]$, $[\bar{1}\bar{1}\bar{1}]$ define a *C*-centered cell with a' = 18.792 Å, b' = 10.847 Å, c' = 11.754 Å, α' = 90.03°, β' = 116.65°, γ' = 90.03°, and Z = 4; the corresponding transformations $x' = {}^1/_2(x - z) + 0.25$, $y' = -y + {}^1/_2(x + z) - 0.25$, and $z' = 1 - z$ (the translations of 0.25 in x' and y' are necessary to place the origin at a conventional center of symmetry) lead to coordinates that are compatible with space group $C2/c$ within their esd's. These

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(1) Willett, R. D.; Bond, M. R.; Haije, W. G.; Soonieus, O. P. M.; Maaskant, W. J. A. *Inorg. Chem.* **1988**, *27*, 614.

(2) Ozarowski, A.; McGarvey, B. R.; Sarkar, A. B.; Drake, J. E. *Inorg. Chem.* **1988**, *27*, 628.

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Table II. Coordinates (×10^4) for $Fe(C_6H_8N_2S_2)_2(NCS)_2$ in Space Group *C*2/*c*[a]

atom	*x*′	*y*′	*z*′
Fe	0 [0]	1542 [–]	2500 [1]
S(1,3)	1704 [0]	4282 [2]	5573 [1]
S(2,4)	92 [1]	3556 [1]	6037 [0]
S(5,6)[b]	–1919 [0]	–1460 [1]	2319 [1]
N(1,3)	899 [3]	3004 [1]	3499 [0]
N(2,4)	–112 [2]	1977 [1]	4255 [1]
N(5,6)	–908 [0]	252 [1]	2038 [4]
C(1,7)	930 [1]	3346 [2]	4562 [6]
C(2,8)	2002 [1]	4488 [4]	4316 [2]
C(3,9)	1578 [2]	3499 [1]	3328 [8]
C(4,10)	312 [0]	2878 [3]	4888 [2]
C(5,11)	–762 [2]	2556 [4]	5557 [2]
C(6,12)	–707 [2]	1601 [0]	4685 [0]
C(13,14)	–1327 [0]	–463 [2]	2161 [0]

[a] Numbers in square brackets are the shifts necessary to achieve the asymmetry of *C*2/*c* from the $P\bar{1}$ coordinates in Table IV, ref 2. [b] The *x* coordinate for S(6) in Table IV, ref 2, 0.6258, is undoubtedly a misprint and should probably be 0.6158; otherwise, both the S(6)–C(14) bond length and the S(6)–C(14)–N(6) bond angle reported in ref 2 are incorrect. The S(3)–(7) distance given in Table V, 2.078 Å, is also misprinted; I calculate 1.741 Å from the triclinic parameters and 1.734 Å from the averaged, *C*2/*c* parameters above (S(1,3)–C(1,7)).

coordinates, after appropriate symmetrizing or averaging, are given in Table II.

Both of these space group changes involve only a change in Laue group—from $\bar{1}$ to 2/*m*—and hence there are no significant changes in the bond lengths and angles[3] except where the disordered Cl atoms in TMCuC are involved. (Note that the disorder was present in the triclinic description, and was not introduced upon going to the monoclinic description.) However, in both cases the molecular symmetry required by the space group has increased. In TMCuC, the Cu atoms lie on sites of symmetry 2/*m* (C_{2h}) and the tetramethylammonium groups lie on mirror planes; the $Fe(C_6H_8N_2S_2)_2(NCS)_2$ molecule lies on a 2-fold axis. For the latter compound the original authors noted that the "the results of the X-ray investigations do not confirm the presumption of the pseudoaxial molecular symmetry suggested by the small *E*/*D* ratio" (from EPR measurements); the revised monoclinic description does indeed require axial symmetry.

In both of these cases the original, triclinic unit cells show three coplanar lattice vectors—[100], [010], and [110]—that are equal in length and subtend angles of 120° (within experimental error). It is probable that this coincidence caused difficulties in the computer-directed cell-reduction process. (The software may have been similar in both cases, one diffractometer being a Syntex $P2_1$ instrument and the other a Nicolet R3m/E instrument. A reviewer reports the same failure to find the monoclinic cells when the triclinic cell dimensions were presented to his CAD4 system, so the problem seems to be fairly general.) Relying on a computer to choose the most appropriate lattice type from merely the setting angles of a number of reflections is indeed a dangerous procedure, particularly when the setting angles are subject to (usually unknown) errors, both random and systematic, and when cell edges may be approximately equal only by coincidence.[4] On the other hand, examination of the atom coordinates usually leads rapidly to hints of trouble. Thus, for the first compound, both the *x* and *z* coordinates of atoms C(1) and C(2) and of atoms C(2a) and C(3a) are effectively equal;[1] for the second compound, the Fe atom has the suspicious coordinates $x = 0.2501$ (1), $z = 0.7501$ (1).[2] It was these coincidences that led me to explore (on a hand-held calculator) alternative unit cells, and the monoclinic descriptions were immediately apparent.

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Appendix

Comments by the Author of Syntex/Nicolet Diffractometer Software: Robert A. Sparks, 2085 Sandalwood Court, Palo Alto, CA 94303. For the Bravais lattice program provided by Syntex/Nicolet it is necessary first to obtain the reduced primitive lattice. The autoindexing program that precedes the Bravais lattice program does have the option of producing the correct reduced primitive lattice. In one case the authors did not have this software (they were using an early Syntex instrument). In the other case the authors report that they did not use this software feature. In both cases the authors manually chose primitive lattices that were not reduced. We have determined that in both cases the correct Bravais lattices are obtained with the correct use of these programs.

It must be emphasized, however, that these programs provide necessary but not sufficient information for the determination of the correct Bravais lattice. The correct Bravais lattice must have the proper Laue symmetry, which can only be obtained by comparison of the intensities of certain classes of reflections. The axial photograph program provides information of this kind about the presence or absence of mirrors in the Laue group. It does not provide information about the presence or absence of 3-, 4-, or 6-fold axes. Therefore, the determination of the correct Laue symmetry and hence the correct Bravais lattice does require some manual interpretation of the data.

Comments Regarding the Enraf-Nonius Software: Graheme J. B. Williams, Enraf-Nonius, 390 Central Avenue, Bohemia, NY 17716. When the reduced forms of the two triclinic cells are presented to the extant CAD4 software, the "best" lattice representation is unambiguously identified as *C*-centered monoclinic in both cases. From the published cells, the standard reduced form of the first cell can be produced trivially by the users' CAD4 software and obtained interactively for the second. All CAD4 systems yield standard reduced cells by default when working with unknown specimens. The summer 1988 release of the CAD4 software smoothly produces the (metrically) suggested monoclinic *C*-centered cell from the published (nonreduced) triclinic cells for both examples without operator input. As always, confirmation of the metrically suggested symmetry by methods such as those suggested by Marsh and Sparks must be obtained. The interchange of ideas with Marsh and Sparks is appreciated, as is the opportunity to see the note before publication.

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(3) Schomaker, V.; Marsh, R. E. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1979**, *B35*, 1933. Marsh, R. E.; Herbstein, F. H. *Acta Crystallogr., Sect. B: Struct. Sci.* **1988**, *B44*, 77.

(4) In both of these cases, a careful application of the rules given in ref 5 leads to the correct monoclinic cell; the care is necessary because neither triclinic cell as reported corresponds to the "true" reduced cell as defined in ref 5.

(5) *International Tables for Crystallography*; Reidel: Dordrecht, The Netherlands, 1983; Vol. A, pp 739–742.