

Table IV. Differences between M-CO and M-CS Bond Distances in Carbonyl-Thiocarbonyl Complexes

compd	$\nu(\text{CS})^a$	M-CO ^b	M-CS ^b	Δ^b
[CpFe(CO) ₂ (CS)]PF ₆ ^c	1348	1.803 (4), 1.816 (4)	1.788 (4)	0.022
(η -C ₆ H ₅ CO ₂ Me)Cr(CO) ₂ (CS) ^d	1225	1.847 (3), 1.850 (2)	1.792 (2)	0.057
(η^6 -tetralone)Cr(PPh ₃)(CO)(CS) ^e	1170-1201 ^f	1.85 (1)	1.75 (1)	0.10

^acm⁻¹. ^bÅ. ^cThis work. ^dSaillard, J.-Y.; LeBorgne, G.; Grandjean, D. *J. Organomet. Chem.* **1975**, *94*, 409. ^eKorp, J. D.; Bernal, I. *Cryst. Struct. Commun.* **1980**, *9*, 821. ^fNot reported for this compound. Values given are for the similar compounds: (η -C₆H₅CO₂Me)Cr(PPhMe₂)(CO)(CS), 1170 cm⁻¹ (Jaouen, G.; Meyer, A.; Simonneaux, G. *Tetrahedron* **1975**, *31*, 1889); (η -C₆H₅CO₂Me)Cr[P(OEt)₃](CO)(CS), 1201 cm⁻¹ (Jaouen, G.; Dabard, R. *J. Organomet. Chem.* **1974**, *72*, 377).

are two symmetry-independent PF₆⁻ groups, each with one phosphorus and two fluorines lying on twofold axes. The PF₆⁻ group containing P(1) is clearly resolved, with fluorine thermal parameters comparable to those for carbon and oxygen atoms. The other group is more disordered but approximated by the four independent positions F(5), F(6), F(7), and F(8). The cyclopentadienyl ring is planar within experimental error.

The Fe-CS bond distance (1.788 (4) Å) in **1** is considerably longer than that (1.662 (3) Å) in the more electron-rich Fe(CS)(OEP)¹⁶ (OEP = octaethylporphyrin), consistent with the idea that there is more π -bonding to the CS in the latter compound. The shorter C-S distance in **1** (1.521 (4) Å) as compared with that (1.559 (3) Å) in Fe(CS)(OEP) is also expected because of reduced π -electron donation from the Fe to the π^* orbitals of CS in **1**. Even though the Fe-CS distance (1.788 (4) Å) in **1** is relatively long, it is still much shorter than Fe-CS distances in the bridging thiocarbonyl complexes [(C₅H₅)Fe(CO)(μ -CS)]₂ (1.90-1.91 Å)¹⁷ and [(C₅H₅)Fe(CO)]₂(μ -CO)(μ -CS) (1.889 (8) Å).¹⁸

The Fe-CO distances (1.816 (4) and 1.803 (4) Å) in **1** are relatively long and comparable to those (1.802 (6), 1.831 (7), and 1.815 (6) Å) in [(C₅H₅)Fe(CO)₃]PF₆;¹⁹ thus, CS does not measurably affect the Fe-CO distances as compared with those in (C₅H₅)Fe(CO)₃⁺. In contrast, the Fe-CO distances (1.767 (4) and 1.775 (4) Å) in [(C₅H₅)Fe(CO)₂(PPh₃)]Cl,²⁰ containing the more electron-donating PPh₃ ligand, are significantly shorter than those in **1**.

Comparison of M-CS and M-CO Bond Distances. As discussed in the introduction, Andrews⁷ concluded that the CS ligand should have a higher π -acceptor/ σ -donor ratio than CO in electron-rich complexes but a lower ratio than CO in electron-poor complexes. If the π -acceptor/ σ -donor ratio is largely determined by the π -acceptor character of the CX ligand, then in electron-rich complexes M-CS bonds should be shorter than M-CO bonds; this is what is observed in all known structures of carbonyl-thiocarbonyl complexes.³⁻⁶ However, as the electron richness of the complex decreases, it is expected that CO and CS will become comparable π -acceptors and the M-CS and M-CO distances should become more equivalent.

There are few structural studies in the literature that allow a comparison of M-CO and M-CS distances in the same molecule to test this idea. However, three examples where the distances are sufficiently precise for such a comparison are given in Table IV. As the electron richness increases down the table, as measured by the decreasing $\nu(\text{CS})$ values, the M-CS bond does indeed become shorter relative to the M-CO bond, as indicated by the difference (Δ) between the M-CS distance and the average of the M-CO bond distances. Even though k_{CO} for CpFe(CO)₂(CS)⁺ is 17.4 mdyne/Å, which is above the point where Andrews suggests the π -acceptor/ σ -donor ability of CO should be larger than that of CS, the M-CS distance is still slightly shorter than M-CO. However, the trend is in the direction predicted by Andrews' analysis.

While it would be desirable to substantiate the above trend with more data, one might nevertheless consider the chemical conse-

quences of the relative change in CS and CO bonding with electron density on the complex. In electron-rich L_xM(CO)_y(CS) complexes, the CS ligand should be bonded more strongly than CO, and substitution reactions with phosphines and other ligands should result in replacement of CO, rather than CS. That this is true is documented in numerous substitution reactions.^{3-6,21} The only reactions where some CS substitution occurs are those of (C₅H₅)Fe(CO)₂(CS)⁺. Thus, (C₅H₅)Fe(CO)₂(CS)⁺ reacts with phosphines and related ligands to give a mixture of products, (C₅H₅)Fe(CO)(L)(CS)⁺ and (C₅H₅)Fe(CO)₂(L)⁺;²² it also reacts with halides (X⁻) to give both (C₅H₅)Fe(CO)(X)(CS) and (C₅H₅)Fe(CO)₂X.²³ In general, one might expect CS substitution to be a likely reaction in complexes where the $\nu(\text{CS})$ value is as high as or higher than that (1348 cm⁻¹) of (C₅H₅)Fe(CO)₂(CS)⁺.

Acknowledgment. This research was supported by the U.S. Department of Energy under Contract No. W-7405-Eng-82, Office of Basic Energy Sciences, Materials Science Division.

Supplementary Material Available: Listings of thermal parameters and least-squares planes (2 pages); a table of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

(21) Dombek, B. D.; Angelici, R. J. *Inorg. Chem.* **1976**, *15*, 1089.

(22) Bussetto, L.; Palazzi, A. *Inorg. Chim. Acta* **1976**, *19*, 233.

(23) Angelici, R. J.; Dunker, J. W. *Inorg. Chem.* **1985**, *24*, 2209.

Contribution from the Departments of Chemistry,
Los Angeles Pierce College,
Woodland Hills, California 91371,
and California State University,
Los Angeles, California 90032

Phosphorus(V) Oxides

B. D. Sharma*

Received July 11, 1986

Among oxides of phosphorus it is believed that phosphorus pentoxide (named according to its empirical formula, P₂O₅) is best understood.¹ Furthermore, it is stated that in addition to amorphous and glassy forms it exists in three crystalline polymorphs.^{2,3} We wish to suggest that the so-called crystalline polymorphs are in fact three distinct compounds with different structural characteristics but with the same empirical formula, P₂O₅.

Structural data for the three crystalline forms based upon X-ray diffraction studies are given in Table I. There are no spectroscopic studies on any of the three solid forms.

The so-called H form¹⁻³ (based upon the erroneous belief that the crystals belong to the hexagonal crystal system) contains discrete P₄O₁₀ molecules.^{4,7} Unfortunately, the crystal structure studies^{4,7} do not provide precise structural parameters even though the existence of discrete P₄O₁₀ molecules is not in doubt. The reliable structural parameters of the P₄O₁₀ molecule are based

(16) Scheidt, W. R.; Geiger, D. K. *Inorg. Chem.* **1982**, *21*, 1208.

(17) Dunker, J. W.; Finer, J. S.; Clardy, J.; Angelici, R. J. *J. Organomet. Chem.* **1976**, *114*, C49.

(18) Beckman, D. E.; Jacobson, R. J. *J. Organomet. Chem.* **1979**, *179*, 187.

(19) Gress, M. E.; Jacobson, R. A. *Inorg. Chem.* **1973**, *12*, 1746.

(20) Riley, P. E.; Davis, R. E. *Organometallics* **1983**, *2*, 286.

* Address correspondence to Los Angeles Pierce College.

Table I. Structural Data for Three Crystalline Forms of Phosphorus(V) Oxides^a

cryst form	P-O _{ext}	P-O _{bridge}	∠POP	∠OPO _{ext}	∠OPO _{bridge}	ref
rhombohedral (trigonal) (H form) ^c	1.46 (3)	1.58 (3)	124 (2)	117 (2)	101 (2)	4
face-centered O form ^b (O form) ^c	1.4 ₀	1.6 ₅	124	117	96	5
primitive O form (O' form) ^c	1.49 (3)	1.56 (3)	145 (2)	116	104 (2)	6

^a Distances are in angstroms and angles in degrees. The esd's are enclosed in parentheses. The values are averages of the values in the asymmetric units unless indicated otherwise. ^b The values quoted are those assumed by deDecker.⁵ The angles are calculated by this author on the basis of the assumed (by deDecker) P...P and O...O distances. ^c Previous label.

upon an electron diffraction study⁸ of gaseous phosphorus(V) oxide, of which there is just one form. The crystals of this phosphorus(V) oxide containing discrete P₄O₁₀ molecules belong to the rhombohedral crystal system (space group *R3c*, *C*_{3v}⁶, No. 161) and should be correctly called the rhombohedral or trigonal form. The distinction between the hexagonal crystal system and the rhombohedral (trigonal) crystal system has been presented recently.^{9,10} A reasonable name for this compound is "clovo tetraphosphorus decoxide" in any state. The Greek word "clovo" means cage. The existence of the discrete molecule P₄O₁₀ cannot be overemphasized.

A second crystalline form of phosphorus(V) oxide has been labelled the O form,¹⁻³ based upon its orthorhombic crystal system as shown by single-crystal X-ray diffraction study.⁵ The structure determination is the least precise among all the known crystalline phosphorus(V) oxides.^{4-7,11} The space group is *Fdd2* (*C*_{2v}¹⁹, No. 43). The only definitive result is that there are 20-membered rings containing alternating P and O. The rings share POP linkages with other 20-membered rings to give a *three-dimensional network*; there are *no* discrete molecules. Hence, the crystals of the "clovo tetraphosphorus decoxide" and the crystalline form with the face-centered orthorhombic crystal system cannot be polymorphs. Just because two crystalline products show the same elemental composition does not mean that these are polymorphs. A precise definition of the term "polymorphs" has been presented elsewhere.¹² It is, therefore, necessary to name this orthorhombic crystalline form to distinguish it from the rhombohedral (trigonal) form. We name it "diktyo-icosogonol phosphorus(V) oxide". The Greek word "diktyo" means network. The crystals should be referred to as the face-centered O form.

The third crystalline form, labeled as O' form, thought to be tetragonal by Hill, Faust, and Hendricks,² belongs in fact to the orthorhombic crystal system, space group *Pnam* (*D*_{2h}¹⁶, No. 62).^{6,11} We suggest that this crystalline form be called the primitive O form. In this structure we have 12-membered rings with alternating P and O jointed with other 12-membered rings with common POP sides to give a pseudo-hexagonal-packed *layer* structure. Again, there are no discrete molecular entities. The POP angle linking the atoms in the ring and between rings is 145° as shown in Table I. This is clearly a different structural feature of significance compared to other similar values in the other two crystal forms. Hence, this crystal represents a different compound and is not a polymorph of either of the other two crystal forms. This requires that we give it a separate name. We suggest "phyllo-dodecagonal phosphorus(V) oxide". The Greek word "phyllo" means layer.

The distinctions suggested above are also supported by the fact that the three solids give different liquids upon melting.^{2,3} In addition, the reaction of water with the rhombohedral (trigonal) form gives a clear solution with sudden evolution of heat, whereas the face-centered O form gives a suspension that dissolves slowly even at steam-bath temperature.^{2,3} The electrical conductivities of the solutions of the rhombohedral (trigonal) form and face-centered O form in water, based upon the calculation of moles of the solute in terms of the formula P₄O₁₀ in both cases, are different.¹³ The primitive O form reacts with water to give a gel.^{2,3}

There are other systems in inorganic chemistry that require the same kind of treatment. We hope to present these in the future.

Acknowledgment. I am grateful to the reviewers for suggestions that have made the presentation clearer.

(13) Boratynski, K.; Nowakowski, A. *C. R. Hebd. Seances Acad. Sci.* **1932**, *194*, 89.

Contribution from the Institut für Anorganische Chemie und Analytische Chemie, Johannes Gutenberg-Universität, D-6500 Mainz, FRG

Light-Induced Excited-Spin-State Trapping (LIESST) in [Fe(2-Y-phen)₃]X₂ Spin-Crossover Compounds

P. Poganiuch[†] and P. Gülich*

Received July 22, 1986

About 2 years ago we observed the first case of "light-induced excited-spin-state trapping (LIESST)" in the iron(II) spin-crossover compound [Fe(ptz)₆](BF₄)₂ (ptz = 1-propyltetrazole). This compound shows a thermally induced low-spin (LS) ⇌ high-spin (HS) transition.¹⁻³ The ¹A_{1g}(O_h) ground state can be quantitatively converted into the ⁵T_{2g}(O_h) state by irradiating the sample into the spin-allowed ¹A₁ → ¹T₁ absorption band at temperatures much below the thermal transition temperature T_c ~ 130 K.^{4,5} It could be shown that the trapped HS state has practically infinite lifetime below T_c^L ~ 50 K. We could also show that the mechanism of this LS → HS spin-state conversion involves a double intersystem crossing after the first spin-allowed transition, ¹A₁ → ¹T₁ → ³T₁ → ⁵T₂. The back-relaxation from the trapped ⁵T₂ state to the ¹A₁ ground state is thermally hindered.

More recently, we have reported on the occurrence of the LIESST effect in other iron(II) spin-crossover complexes such as [Fe(phen)₂(NCS)₂] (phen = 1,10-phenanthroline) and [Fe(2-pic)₃]Cl₂·EtOH (2-pic = 2-picolyamine).⁶ The critical temperature T_c^L for the ⁵T₂ → ¹A₁ back-relaxation was found to be ca. 55 K in the former and ca. 30 K in the latter case.

It is not clear as yet which conditions are to be fulfilled in order to see the LIESST effect. One important factor is the energetically favorable position of the spin-triplet levels,⁵ which "catalyze" the population of the metastable spin-quintet state through spin-orbit coupling. Another important factor is the relative position, re-

- (1) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; Interscience: New York, 1980.
- (2) Hill, W. L.; Faust, G.; Hendricks, S. B. *J. Am. Chem. Soc.* **1943**, *65*, 794.
- (3) Van Wazer, J. R. *Phosphorus and its Compounds*; Interscience: New York, 1958; Vol. 1.
- (4) Cruickshank, D. W. J. *Acta Crystallogr.* **1964**, *17*, 677.
- (5) deDecker, H. C. J. *Recl. Trav. Chim. Pays-Bas* **1941**, *60*, 413.
- (6) Cruickshank, D. W. J. *Acta Crystallogr.* **1964**, *17*, 679.
- (7) deDecker, H. C. J.; MacGillavry, C. H. *Recl. Trav. Chim. Pays-Bas* **1941**, *60*, 153.
- (8) Beagley, B.; Cruickshank, D. W. J.; Hewitt, T. G.; Haaland, A. *Trans. Faraday Soc.* **1967**, *63*, 836.
- (9) Sharma, B. D. *J. Chem. Educ.* **1982**, *59*, 742.
- (10) Schomaker, V.; Lingafelter, E. C. *J. Chem. Educ.* **1985**, *62*, 219.
- (11) MacGillavry, C. H.; deDecker, H. C. J.; Nijland, L. M. *Nature (London)* **1949**, *164*, 448.
- (12) Sharma, B. D. *J. Chem. Educ.*, in press.

* To whom correspondence should be addressed.

[†] In partial fulfillment of the Ph.D. thesis.