ceptibility above 350 K is only weakly temperature dependent, it appears that some V atoms develop magnetic moments below 345 K and that these couple antiferromagnetically or are lost again below 140 K.

The presence of these distorted phases gives rise to unusual electrochemical behavior as lithium is intercalated and deintercalated.[22]

Summary

We have prepared Li_xVS_2 for $0 \le x \le 1$, this being the first report of the existence of VS_2. All of the compositions show evidence for phase transitions near or below room temperature. These transitions are due, at least in part, to electronic instabilities of the V d band.

Acknowledgment. We are indebted to P. K. Gallagher for the TGA results and B. G. Bagley for assistance with the DSC data.

Registry No. VS_2, 12166-28-8; $Li_{1.0}VS_2$, 12218-74-5; $Li_{0.10}VS_2$, 64175-20-8; $Li_{0.25}VS_2$, 64175-16-2; $Li_{0.33}VS_2$, 64175-14-0; $Li_{0.40}VS_2$, 64175-18-4; $Li_{0.50}VS_2$, 64175-13-9; $Li_{0.55}VS_2$, 64175-22-0; $Li_{0.60}VS_2$, 64175-19-5; $Li_{0.66}VS_2$, 64175-15-1; $Li_{0.75}VS_2$, 64175-17-3; $Li_{0.90}VS_2$, 64175-21-9.

References and Notes

(1) M. S. Whittingham, *J. Electrochem. Soc.*, **123**, 315 (1976).
(2) D. W. Murphy and F. A. Trumbore, *J. Cryst. Growth*, **39**, 185 (1977).
(3) J. A. Wilson and A. D. Yoffe, *Adv. Phys.*, **18**, 193 (1969).
(4) M. B. Dines, *Mater. Res. Bull.*, **10**, 287 (1975).
(5) D. W. Murphy, F. J. Di Salvo, G. W. Hull, Jr., and J. V. Waszczak, *Inorg. Chem.*, **15**, 17 (1976).
(6) M. S. Whittingham and F. R. Gamble, *Mater. Res. Bull.*, **10**, 363 (1975).
(7) G. A. Wiegers and C. F. van Bruggen, *Physica*, **86–88B**, 1009 (1977).
(8) B. van Laar and D. J. W. Ijdo, *J. Solid State Chem.*, **3**, 590 (1971).
(9) J. Rouxel, *J. Solid State Chem.*, **17**, 223 (1976).
(10) S. Brunie and M. Chevreton, *C. R. Hebd. Seances Acad. Sci.*, **258**, 5847 (1964).
(11) M. Danot, J. Bichon and J. Rouxel, *Bull. Soc. Chim. Fr.*, 3063 (1972).
(12) J. A. Wilson, F. J. Di Salvo, and S. Mahajan, *Adv. Phys.*, **24**, 117 (1975).
(13) J. P. Pouget, P. Lederer, D. S. Schreiber, H. Launois, D. Wohlleben, A. Casalot, and G. Villeneuve, *J. Phys. Chem. Solids*, **33**, 1961 (1972).
(14) A. C. Gossard, F. J. Di Salvo, L. R. Erick, J. P. Remeika, H. Yasuoha, K. Kosuge, and S. Kachi, *Phys. Rev. B.*, **10**, 4178 (1974).
(15) A. C. Gossard, J. P. Remeika, T. M. Rice, H. Yasuoha, K. Kosuge, and S. Kachi, *Phys. Rev. B.*, **9**, 1230 (1974).
(16) A. C. Gossard, A. Menth, W. W. Warren, and J. P. Remeika, *Phys. Rev. B*, **12**, 1187 (1975).
(17) F. J. Di Salvo and J. V. Waszczak, *J. Phys. (Paris), Colloq.*, **C4**, 157 (1976).
(18) P. M. Williams in "Crystallography and Crystal Chemistry of Materials with Layered Structures", Vol. 2, F. Levy, Ed., Reidel, Holland, 1976.
(19) C. F. van Bruggen and C. Haas, *Solid State Commun.*, **20**, 251 (1976).
(20) A. H. Thompson, *Phys. Rev. Lett.*, **34**, 520 (1975).
(21) J. R. Bloembergen, R. Haange, G. A. Wiegers, and C. F. van Bruggen, Extended Abstracts, Vth International Conference on Solid Compounds of Transition Elements, Uppsala, 1976, p 60.
(22) D. W. Murphy, J. N. Carides, F. J. Di Salvo, C. Cros, and J. V. Waszczak, *Mater. Res. Bull.*, **12**, 825 (1977).

Contribution No. 5609 from the Arthur Amos Noyes Laboratory of Chemical Physics,
California Institute of Technology, Pasadena, California 91125

Emission Spectra and Lifetimes of $Re_2Cl_8^{2-}$, $Re_2Br_8^{2-}$, and $Mo_2Cl_8^{4-}$ at 1.3 K upon Excitation of the $\delta \rightarrow \delta^*$ Transition

WILLIAM C. TROGLER, EDWARD I. SOLOMON, and HARRY B. GRAY*

Received May 10, 1977 AIC70341A

Excitation (650 nm) of $(n\text{-}Bu_4N)_2[Re_2Cl_8]$ and $(n\text{-}Bu_4N)_2[Re_2Br_8]$ in KBr disks at 1.3 K gives broad emission centered at 13 020 and 12 530 cm^{-1}, respectively. Emission lifetimes are as follows: $Re_2Cl_8^{2-}$, 150 ns; $Re_2Br_8^{2-}$, 110 ns. Luminescence was also recorded for the $Mo_2Cl_8^{4-}$ ion doped into a crystal of $(enH_2)Cl_2$. Again a broad, structureless emission band was observed (14 950 cm^{-1}, τ = 75 ns, 1.3 K). Owing to the lack of overlap of the emission with the 0–0 transition in absorption, it is proposed that the luminescent state is one of the spin–orbit components of $^3A_{2u}$. This places the $\delta \rightarrow \delta^*$ singlet–triplet splitting in the range 1000–3000 cm^{-1}.

Absorption spectroscopy has been employed to characterize the lowest spin-allowed transitions in compounds that contain a quadruple metal–metal bond.[1] With the exception of dimolybdenum(II) carboxylates,[2] the lowest singlet excited state in binuclear complexes of Mo(II) and Re(III) is $^1A_{2u}$ (in D_{4h} microsymmetry) derived from the one-electron excitation $\delta \rightarrow \delta^*$. The location of $^3A_{2u}(\delta \rightarrow \delta^*)$ (or, more properly, its A_{1u} and E_u spin–orbit components) in these complexes, however, has been the subject of some speculation. And, although scattered-wave Xα calculations have been performed for $Re_2Cl_8^{2-}$,[3] $Mo_2Cl_8^{4-}$,[4] and $Mo_2(O_2CH)_4$,[5] it is now recognized[5] that singlet–triplet splittings cannot be predicted reliably from this type of theory.

Clark and Franks[6] noticed a weak, structured absorption at 6250 cm^{-1} in the diffuse-reflectance spectra of some but not all of the $Mo_2Cl_8^{4-}$ salts they examined, and the suggestion was made that this near-IR band might be attributable to the $^1A_{1g} \rightarrow {}^3A_{2u}(\delta \rightarrow \delta^*)$ transition. However, it has been pointed out[7] that the 12 000-cm^{-1} singlet–triplet splitting that follows from such an interpretation is unexpectedly large, and the possibility of near-IR impurity absorption has been raised.[7,8] An alternative placement of $^1A_{1g} \rightarrow {}^3A_{2u}$ in $Mo_2Cl_8^{4-}$ could be 17 500 cm^{-1}, where Fanwick et al.[7] found a weak shoulder in one polarized absorption spectrum of a single crystal of $K_4Mo_2Cl_8 \cdot 2H_2O$ at 4 K.

In an attempt to gather more evidence concerning the position of the $^3A_{2u}$ state in quadruply bonded binuclear complexes, we have measured the emission spectra and lifetimes at 1.3 K of $(n\text{-}Bu_4N)_2[Re_2Cl_8]$, $(n\text{-}Bu_4N)_2[Re_2Br_8]$, and 0.2% $Mo_2Cl_8^{4-}$ in a single crystal of $(enH_2)Cl_2$. The results reported herein support a relatively small singlet–triplet splitting of the $\delta \rightarrow \delta^*$ excited states.

Experimental Section

The compounds $(n\text{-}Bu_4N)_2[Re_2Cl_8]$ and $(n\text{-}Bu_4N)_2[Re_2Br_8]$ were prepared by the literature method.[9] Crystals of $(enH_2)Cl_2$ doped with $Mo_2Cl_8^{4-}$ were prepared by the following modification of the literature synthesis[10] of $(enH_2)_2[Mo_2Cl_8]$. $Mo_2(O_2CCH_3)_4$[11] was added to a 6 N HCl solution saturated with $(enH_2)Cl_2$. The solution was filtered before slowly cooling to 5 °C, yielding a crop of translucent purple crystals. Anal. Calcd for $C_2H_{10}N_2Cl_2$: C, 17.9; H, 8.22; N, 20.9; Cl, 52.9. Found: C, 17.8; H, 7.48; N, 20.5; Cl, 54.1; Mo, 0.35. The Mo analysis corresponds to a mole fraction of $Mo_2Cl_8^{4-}$ of ca. 0.2% (assuming $Mo_2Cl_8^{4-}$ is the only Mo species present). The C, H, N, and Cl analyses were obtained from Chemalytics, Inc., Tempe, Ariz., and the Mo analysis was performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

Emission spectra were obtained at the λ point of liquid He in an optical Dewar. A pulsed nitrogen laser was used to pump a dye laser (output pulse width of 32 ns) and excitation wavelengths of 650 and 540 nm were used for the Re(III) and Mo(II) compounds, respectively. Emission lifetimes were recorded at the wavelength of maximum

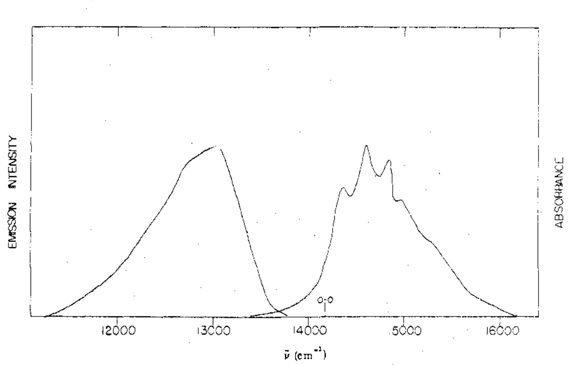


Figure 1. Corrected emission (1.3 K) and absorption (15 K) spectra of $(n\text{-}Bu_4N)_2[Re_2Cl_8]$ in a KBr disk.

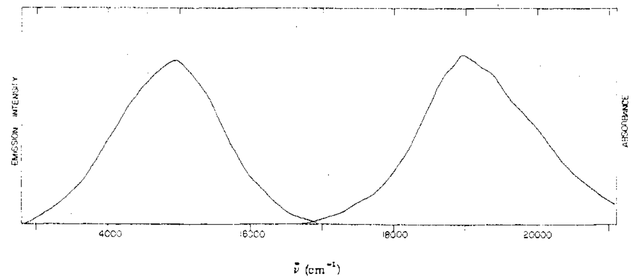


Figure 2. Corrected emission (1.3 K) and absorption (15 K) spectra of a single crystal of $(enH_2)Cl_2$ doped with $Mo_2Cl_8^{4-}$ (0.2 mol %).

emission intensity. Boxcar integration techniques were applied to the signal from a GaAs phototube for data collection. A resolution of 0.6 nm was maintained for the emission spectra. Emission spectra were corrected for phototube and monochromator response before plotting. Samples of $(n\text{-}Bu_4N)_2[Re_2Cl_8]$ and $(n\text{-}Bu_4N)_2[Re_2Br_8]$ consisted of crystals suspended in 13-mm diameter KBr pressed disks. The low-temperature single-crystal polarized absorption spectra of the crystal doped with $Mo_2Cl_8^{4-}$ (vide supra) were recorded employing experimental conditions as previously described.[1] Parallel polarization is for the long axis[12] (*c*), which was also an extinction direction of the $(enH_2)Cl_2$ crystal. The crystal was mounted over a pinhole on a copper disk with heat-conducting copper grease.

Results

Upon 650-nm excitation of the $^1A_{1g} \rightarrow {}^1A_{2u}(\delta \rightarrow \delta^*)$ transition of $(n\text{-}Bu_4N)_2[Re_2Cl_8]$, a broad emission centered at 13 020 cm^{-1} is observed (Figure 1) with a lifetime of 150 ns at 1.3 K. Two features of the emission spectrum are extremely important. First, it is evident that a mirror-symmetry relationship does not exist between the emission band and the $^1A_{1g} \rightarrow {}^1A_{2u}$ absorption system. Notably, the sharp vibronic structure observed in absorption is not present in emission. Second, and more importantly, there is no overlap between the emission band and the 0–0 transition of $^1A_{1g} \rightarrow {}^1A_{2u}$ that has been positioned from single-crystal polarized absorption measurements.[13]

Similar 650-nm excitation of $(n\text{-}Bu_4N)_2[Re_2Br_8]$ results in broad emission centered at 12 530 cm^{-1} with a lifetime of 110 ns at 1.3 K. The 490-cm^{-1} red shift of the emission maximum from that in $Re_2Cl_8^{2-}$ is reasonable for a $\delta \rightarrow \delta^*$ type transition, considering the fact that $^1A_{1g} \rightarrow {}^1A_{2u}(\delta \rightarrow \delta^*)$ in $Re_2Br_8^{2-}$ is red-shifted in absorption by 586 cm^{-1}.[14]

The related species $Mo_2Cl_8^{4-}$ behaves analogously to the Re(III) compounds, as excitation at 540 nm gives a broad, structureless emission centered at 14 950 cm^{-1} (Figure 2) with a 75-ns lifetime at 1.3 K; however, the separation between the emission and absorption systems is nearly twice that in the Re(III) compounds. It is also evident in this case that the emission band does not overlap the 0–0 transition reported[7] at 18 083 cm^{-1} for a single crystal of $K_4Mo_2Cl_8{\cdot}2H_2O$. As the polarization of this band has been established[7] to be parallel to Mo–Mo, the polarized spectra of the doped crystal (Figure 3) prove that the $Mo_2Cl_8^{4-}$ ion orients with Mo–Mo directed primarily along the needle axis of the crystal.

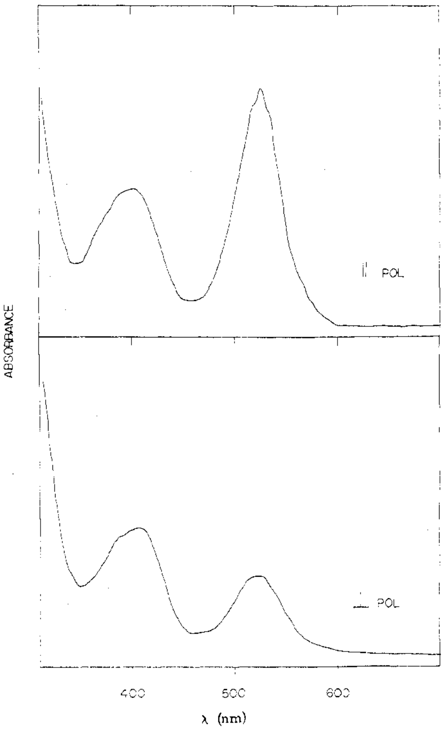


Figure 3. Single-crystal polarized absorption spectra at 15 K of a single crystal of $(enH_2)Cl_2$ doped with $Mo_2Cl_8^{4-}$ (0.2 mol %). Polarizations are denoted parallel and perpendicular to the crystal needle axis.

A broad absorption centered at 405 nm, which is not attributable to $Mo_2Cl_8^{4-}$, is present in the doped crystal. This absorption does not occur in a pure $(enH_2)Cl_2$ crystal. When a 6 N HCl solution containing $K_4Mo_2Cl_8$ is allowed to stand overnight under anaerobic conditions, the 530-nm absorption decreases at the same time a new band grows in at 418 nm. The latter absorption is present in solutions of $Rb_3Mo_2Cl_8H$ prepared[15] from oxidation of the $Mo_2Cl_8^{4-}$ ion in concentrated HCl. Therefore it is likely that $Mo_2Cl_8H^{3-}$ or a related species is trapped during growth of the doped crystals. Because the 405-nm band was found not to be polarized, it appears that this species is randomly incorporated into the $(enH_2)Cl_2$ lattice. Emission related to this second component was not observed, as only the lowest absorption was pumped using 540-nm radiation. Observation of emission in a doped crystal, where the rate of resonance energy transfer should be small, shows that impurity emission from an exciton trap probably does not occur.

Discussion

For $Re_2Cl_8^{2-}$ and $Mo_2Cl_8^{4-}$ the lack of overlap between the emission band and the 0–0 peak in absorption strongly rules against an assignment of simple fluorescence from the $^1A_{2u}$ state. Unfortunately, the emission lifetimes are not definitive in this respect, as they are consistent with either fluorescence and little radiationless decay[16] or "phosphorescence" with a large contribution from nonradiative deactivation pathways. However, two additional observations are inconsistent with a $^1A_{2u}$ emitting state, namely, the absence of vibronic structure for the $Re_2Cl_8^{2-}$ emission and the increased emission–absorption separation in $Mo_2Cl_8^{4-}$. Ligand substitution effects in the Re(III) complexes, as well as the similarity of the absorption and emission half-bandwidths and the overall band profiles, suggest that luminescence occurs from a state that is bonding to the same extent as is $^1A_{2u}$. For the reasons just stated, then, we believe the emitting state is one of the spin-orbit components of $^3A_{2u}$ (A_{1u} or E_u). Assignment of the emission to $^1A_{2u} \rightarrow {}^1A_{1g}$, however, is not entirely out of the question, as a large geometrical distortion in the $^1A_{2u}$ state of $M_2X_8{}^{n-}$ complexes could lead to nonoverlapping emission and absorption systems. The Duschinsky effect[17] could then operate to give an emission band shape that is considerably distorted from that of the corresponding absorption.[18] For the $M_2X_8{}^{n-}$ (M = Re, Mo; X = Cl, Br; n = 2 or 4) compounds, the excited-state distortion most likely would involve an eclipsed (D_{4h}) to noneclipsed (D_{4d}) conformational change. Even if this type of distortion occurs, it apparently does not affect the a_1 vibrational modes to a large extent, as the ground to excited state frequency shifts of a_1(ReRe) and a_1(ReReCl) are small.[13] Additionally, the calculations of Norman and Kolari[4,5] for $Mo_2Cl_8{}^{4-}$ suggest that chloride–chloride attractions contribute to the stabilization of the eclipsed geometry. Thus there is doubt whether the $^1A_{2u}$ state would distort at all from the eclipsed configuration.

The evidence favors assignment of the emission to one of the transitions $A_{1u}(^3A_{2u})$ or $E_u(^3A_{2u}) \rightarrow {}^1A_{1g}$. This interpretation places the singlet–triplet ($^1A_{2u}$–$^3A_{2u}$) separation in the range 1000–3000 cm^{-1}. This range is quite in line with the only documented singlet–triplet splitting in a binuclear Re(III) or Mo(II) compound, which is 1800 cm^{-1} for the $^{3,1}E_g(\delta \rightarrow \pi^*)$ excited states of $Mo_2(O_2CCF_3)_4$.[2] Further elucidation of the nature and position of the low-lying triplet excited states in $M_2X_8{}^{n-}$ complexes will require much additional theoretical and experimental effort.

Acknowledgment. We thank Ib Trajberg for experimental assistance and Professors F. A. Cotton and D. S. Martin, Jr., for communication of their results[7] prior to publication. Professor W. A. Goddard III is acknowledged for helpful discussions. W.C.T. held an IBM fellowship for 1976–1977. This research was supported by the National Science Foundation (Grant CHE-7519086).

Registry No. $(n\text{-}Bu_4N)_2[Re_2Cl_8]$, 14023-10-0; $(n\text{-}Bu_4N)_2[Re_2Br_8]$, 14049-60-6; $K_4Mo_2Cl_8$, 25448-39-9; $(enH_2)Cl_2$, 333-18-6.

References and Notes

(1) W. C. Trogler, C. D. Cowman, H. B. Gray, and F. A. Cotton, *J. Am. Chem. Soc.*, **99**, 2993 (1977), and references therein.
(2) W. C. Trogler, E. I. Solomon, I. Trajberg, C. J. Ballhausen, and H. B. Gray, *Inorg. Chem.*, **16**, 828 (1977); F. A. Cotton, D. S. Martin, T. R. Webb, and T. J. Peters, *ibid.*, **15**, 1199 (1976); F. A. Cotton, D. S. Martin, P. E. Fanwick, T. J. Peters, and T. R. Webb, *J. Am. Chem. Soc.*, **98**, 4681 (1976).
(3) A. P. Mortola, J. W. Moskowitz, N. Rosch, C. D. Cowman, and H. B. Gray, *Chem. Phys. Lett.*, **32**, 283 (1975).
(4) J. G. Norman and H. J. Kolari, *J. Am. Chem. Soc.*, **97**, 33 (1975).
(5) J. G. Norman, H. J. Kolari, H. B. Gray, and W. C. Trogler, *Inorg. Chem.*, **16**, 987 (1977).
(6) R. J. H. Clark and M. L. Franks, *J. Am. Chem. Soc.*, **97**, 2691 (1975).
(7) P. E. Fanwick, D. S. Martin, F. A. Cotton, and T. R. Webb, *Inorg. Chem.*, **16**, 2103 (1977).
(8) In this connection, it should be mentioned that the spectrum of the one-electron oxidation product of $Mo_2(SO_4)_4{}^{4-}$ exhibits a structured $\delta \rightarrow \delta^*$ absorption band at 7100 cm^{-1}: D. K. Erwin, G. L. Geoffroy, H. B. Gray, G. S. Hammond, E. I. Solomon, W. C. Trogler, and A. A. Zagars, *J. Am. Chem. Soc.*, **99**, 3620 (1977).
(9) F. A. Cotton, N. F. Curtis, B. F. G. Johnson, and W. R. Robinson, *Inorg. Chem.*, **4**, 329 (1965).
(10) J. V. Brencic and F. A. Cotton, *Inorg. Chem.*, **8**, 2698 (1969).
(11) T. A. Stephenson, E. Bannister, and G. Wilkinson, *J. Chem. Soc.*, 2538 (1964).
(12) T. Ashida and S. Hirokawa, *Bull. Chem. Soc. Jpn.*, **36**, 704 (1963).
(13) C. D. Cowman and H. B. Gray, *J. Am. Chem. Soc.*, **95**, 8177 (1973).
(14) C. D. Cowman, Ph.D. Thesis, California Institute of Technology, 1974.
(15) M. J. Bennett, J. V. Brencic, and F. A. Cotton, *Inorg. Chem.*, **8**, 1060 (1969); F. A. Cotton and B. J. Kalbacher, *ibid.*, **15**, 522 (1976).
(16) J. B. Birks, "Photophysics of Aromatic Molecules", Wiley-Interscience, New York, N.Y., 1970, pp 87–88.
(17) F. Duschinsky, *Acta Physiochim. URSS*, **1**, 551 (1937).
(18) C. J. Ballhausen and A. E. Hansen, *Annu. Rev. Phys. Chem.*, **23**, 15 (1972).

Contribution from the Department of Chemistry,
Texas Tech University, Lubbock, Texas 79409

^{31}P NMR Study of Some Coordination Complexes of the Phosphorus Cage Molecule Tetraphosphorus Heptaoxide[1]

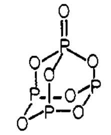
MICHAEL L. WALKER and JERRY L. MILLS*

Received December 1, 1976 AIC60862I

The molecule P_4O_7 is a structural derivative of the phosphorus cage molecule P_4O_6, and, as such, can potentially behave as a nonchelating, tridentate ligand. Complexes formed between P_4O_7 and the metal carbonyls $Ni(CO)_4$, $Fe_2(CO)_9$, $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ are characterized by ^{31}P NMR spectroscopy. A two-to-one complex is formed between BF_3 and P_4O_7, while borane and trimethylborane do not react with P_4O_7. A comparison between the ligative properties of P_4O_6 and P_4O_7 is discussed in terms of ^{31}P NMR spectral data.

Introduction

Earlier we communicated the preparation of P_4O_7, giving



spectroscopic evidence for the compound retaining the adamatane-like structure of P_4O_6, with the addition of an exocyclic oxygen atom to the cage.[2] Since P_4O_6 had been shown to react with $Ni(CO)_4$,[3] iron carbonyls,[4] group 6B metal carbonyls,[5] and diborane,[6] it was expected that P_4O_7 should behave in a similar manner and act as a tridentate, nonchelating ligand. Also of interest was the effect of oxidation of one phosphorus atom of the P_4O_6 cage on the potential Lewis basicity of the other three phosphorus Lewis base sites. The present paper reports the details of preparation and ^{31}P NMR characterization of several P_4O_7 metal carbonyl complexes, with comparison to the P_4O_6 analogues.

Results

Due to the extreme air sensitivity of P_4O_7 and its derivative metal carbonyl adducts, attempts to isolate the compounds in pure form were unsuccessful. The use of ^{31}P NMR allowed the study of reaction mixtures with the identification of the compounds by hyperfine splitting patterns and chemical shift data. In all cases the reaction of metal carbonyls with P_4O_7 followed the general scheme

$$nM(CO)_m + P_4O_7 \rightarrow [M(CO)_{m-1}]_n(P_4O_7) + nCO$$

For nickel carbonyl an entirely closed system was used to exclude air and water. Progressive addition of $Ni(CO)_4$ to P_4O_7 from a mole ratio of about 0.7 to 4.0 favored saturative ligation of the P_4O_7 cage, with a mixture of products [Ni-