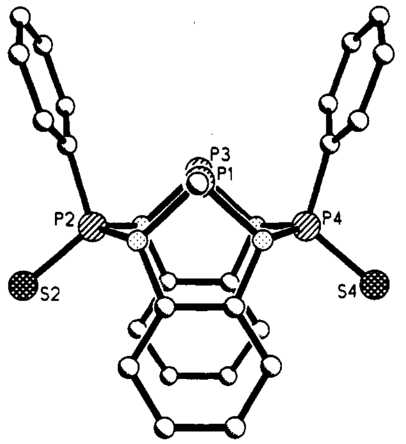


**Figure 3.** View of **6** down the P(1)···P(3) vector, showing the cavity between phenyl groups Ph(2) and Ph(4). Hydrogen atoms and phenyl groups Ph(1) and Ph(3) are omitted for clarity.

The cavity contained in molecules **4** and **6** (Figure 3), and that can be expected in other $[C_6H_4N_2(PhPX)(PhP)]_2$ compounds where X = O, Se, NPh, etc., could show novel coordination to both metal and non-metal atom species. Given that the van der Waals thickness of the cavity phenyl rings is about 3.7 Å,[31] there should be, without molecular distortion, around 3.0–3.5 Å of free space to allow coordination. With small but reasonable distortions of the $P_4N_4$ ring systems, cleft widths of at least 4.5 Å seem possible. This should make the cavity highly selective, allowing coordination/reactivity with only relatively small guest species. Cavity coordination in a myriad of other guest–host and cleft-containing systems is under investigation;[42] however, such behavior in diphosphorus systems would be new. This coordination, and the effect such coordination has on the coordinated species, is currently being studied in our laboratories.

**Acknowledgment.** Support of this work by National Science Foundation Grant CHE-8312856 and the Colorado Advanced Materials Institute is gratefully acknowledged.

**Supplementary Material Available:** Listings of all crystal collection and refinement data, hydrogen atom coordinates, anisotropic thermal displacement parameters, bond lengths and angles, least-squares planes, and interplane dihedral angles (22 pages); listings of calculated and observed structure factors (13 pages). Ordering information is given on any current masthead page.

---

(42) (a) Cram, D. J.; Karbach, S.; Kim, H.-E.; Knobler, C. A.; Maverick, E. F.; Ericson, J. L.; Helegeson, R. C. *J. Am. Chem. Soc.* **1988**, *110*, 2229. (b) Weber, D. E.; Vögtle, F. *Topics in Current Chemistry, Host Guest Complex Chemistry I*; Springer Verlag: Berlin, 1981; Vol. 98, p 1. (c) Rampradsad, D.; Lin, W.-K.; Goldsby, K. A.; Busch, D. H. *J. Am. Chem. Soc.* **1988**, *110*, 1480. (d) Collman, J. P.; Brauman, J. I.; Collins, T. J.; Iverson, B.; Sessler, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 2450. (e) Wilcox, C. S.; Greer, L. M.; Lynch, V. *J. Am. Chem. Soc.* **1987**, *109*, 1865.

---

# Notes

Contribution from the Department of Chemistry,
University of Southampton, Southampton SO9 5NH, U.K.

## Five-Coordinate Nickel(III) Phosphines: Spectroscopic and EXAFS Studies

Judith M. Corker, John Evans, William Levason,*
Mark D. Spicer, and Paul Andrews

*Received April 25, 1990*

Although once regarded as very rare, nickel(III) complexes have been shown by recent research to be obtainable with F, O, and particularly N donor ligands, the last including bi- and multidentate amines, peptides, oximes, and aza macrocycles.[1] A much smaller number of examples with second- and third-row p-block donors are known, including *trans*-$[Ni(L\text{-}L)_2X_2]^+$ (L-L = diphosphine or diarsine, X = Cl or Br).[2] All these complexes contain Ni(III) in a tetragonal-octahedral geometry, consistent with the Jahn–Teller distortion expected for a low-spin $d^7$ ion. In marked contrast to the isoelectronic Co(II), for which many five-coordinate complexes are known,[3] Ni(III) rarely exhibits five-coordination. Distorted square-pyramidal structures are established for two series of complexes, $[Ni(\text{diphosphine})X_3]$ (diphosphine = *o*-$C_6H_4(PPh_2)_2$, $Ph_2P(CH_2)_nPPh_2$ ($n$ = 2, 3), and *cis*-$Ph_2PCHCHPPh_2$),[4] and $[Ni\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}X_2]$ (X = Cl, Br, I, $NO_2$, $NO_3$).[5] The sole examples of trigonal-bipyramidal geometry are the very unstable $[Ni(PR_3)_2X_3]$, first reported in 1936[6] but relatively little studied since.[7–9] We recently reported a combined spectroscopic and EXAFS (extended X-ray absorption fine structure) study of the more stable Co(III) analogues $[Co(PR_3)_2X_3]$[10] and report here similar data for the Ni(III) complexes.

## Experimental Section

The complexes $[Ni(PR_3)_2X_3]$ were made as described previously.[9] All measurements were made on samples that were <48 h old and that had been stored at −20 °C in the dark. UV–visible spectra were recorded from freshly prepared dichloromethane solutions, on Perkin-Elmer PE554 and Varian Cary 2300 spectrometers, and diffuse-reflectance spectra were recorded on a Beckman Acta M IV instrument using $BaSO_4$ as diluent and reference.

Nickel and bromine K-edge EXAFS measurements were made in transmission mode on Station 7.1 at the Daresbury Synchrotron Radiation Source (operating at 2 GeV with an average current of 150 mA), using a silicon (111) order-sorting monochromator. Data were collected from room-temperature samples diluted with boron nitride (ca. 10% Ni by weight) and held between Sellotape strips in 1 mm thick aluminum holders.

Background-subtracted spectra were obtained by using the program PAXAS.[11] Removal of the preedge background was achieved by using a polynomial of order 2. For the nickel K-edge data the postedge background was subtracted by fitting the postedge region with a polynomial of order 6; however, a similar treatment of the bromine K-edge data failed to remove low-frequency contributions in the spectra. A more satisfactory background was achieved by fitting coupled polynomials of order 7 to the postedge region. Curve-fitting analysis, by least-squares

---

(1) Lappin, A. G.; McAuley, A. *Adv. Inorg. Chem.* **1988**, *32*, 241. Nag, K.; Chakravorty, A. *Coord. Chem. Rev.* **1980**, *33*, 87.

(2) (a) Levason, W. *Comments Inorg. Chem.* **1990**, *9*, 331. (b) Bernstein, P. K.; Rodley, G. A.; Marsh, R.; Gray, H. B. *Inorg. Chem.* **1972**, *11*, 3040. (c) Mahadevan, C.; Seshasayee, M.; Ramakrishna, B. L.; Manoharan, P. T. *Acta Crystallogr.* **1985**, *C41*, 38.

(3) (a) Wood, J. S. *Prog. Inorg. Chem.* **1972**, *16*, 227. (b) Morassi, R.; Bertini, I.; Sacconi, L. *Coord. Chem. Rev.* **1973**, *11*, 343.

(4) Gray, L. R.; Higgins, S. J.; Levason, W.; Webster, M. *J. Chem. Soc., Dalton Trans.* **1984**, 459.

(5) Grove, D. M.; Van Koten, G.; Mul, P.; Zoet, R.; Van der Linden, J. G. M.; Legters, J.; Schmitz, J. E. J.; Murrall, N. W.; Welch, A. J. *Inorg. Chem.* **1988**, *27*, 2466.

(6) Jensen, K. A. *Z. Anorg. Allg. Chem.* **1963**, *229*, 275.

(7) Jensen, K. A.; Nygaard, B.; Pedersen, C. T. *Acta Chem. Scand.* **1963**, *17*, 1126.

(8) (a) Meek, D. W.; Alyea, E. C.; Stalick, J. K.; Ibers, J. A. *J. Am. Chem. Soc.* **1969**, *91*, 4920. (b) Stalick, J. K.; Ibers, J. A. *Inorg. Chem.* **1970**, *9*, 453.

(9) Higgins, S. J.; Levason, W.; Wilkes, D. J. *Inorg. Chim. Acta* **1984**, *84*, 1.

(10) Levason, W.; Ogden, J. S.; Spicer, M. D. *Inorg. Chem.* **1989**, *28*, 2128.

(11) Binsted, N. PAXAS. Program for the Analysis of X-ray Absorption Spectra. Southampton University, 1988.

0020-1669/91/1330-0331$02.50/0

**Table I.** UV–Visible Spectroscopic Data[a]

| complex | $e'' \rightarrow e_a'$ | $e_a' \rightarrow a_1$ | $P(\sigma) \rightarrow Ni(e_a')$ | $P(\sigma) \rightarrow Ni(a_1)$ | $X(\pi) \rightarrow Ni(e_a')$ | $X(\pi) \rightarrow Ni(a_1)$ |
|---|---|---|---|---|---|---|
| $[Ni(PEt_3)_2Cl_3]$[b] | 10600 (20) | 14300 (sh) | 16780 (2400) | 24500 (1730) | 27030 (9780) | 37000 (4200) |
| $[Ni(PEt_3)_2Br_3]$ | 10100 (45) | 14700 (sh) | 16340 (2850) | 25250 (14720) | 21710 (2300) | 32500 (9200) |
| $[Ni(PMe_2Ph)_2Cl_3]$ | 10400 (35) | 14280 (sh) | 17120 (3770) | 24510 (3520) | 27170 (7040) | 38400 (10100) |
| $[Ni(PMe_2Ph)_2Br_3]$ | 9700 (55) | 14500 (sh) | 16950 (2820) | 25510 (8480) | 21100 (1300) | 31250 (2370) |

[a] $E_{max}$/cm$^{-1}$ ($\epsilon_{mol}$/dm$^3$ mol$^{-1}$ cm$^{-1}$) in freshly prepared $CH_2Cl_2$ solution. $\epsilon_{mol}$ values are approximate due to solution instability of the complexes. [b] $e_b' \rightarrow e_a'$ transitions seen in the diffuse-reflectance spectra at ca. 5800 cm$^{-1}$ (vw).

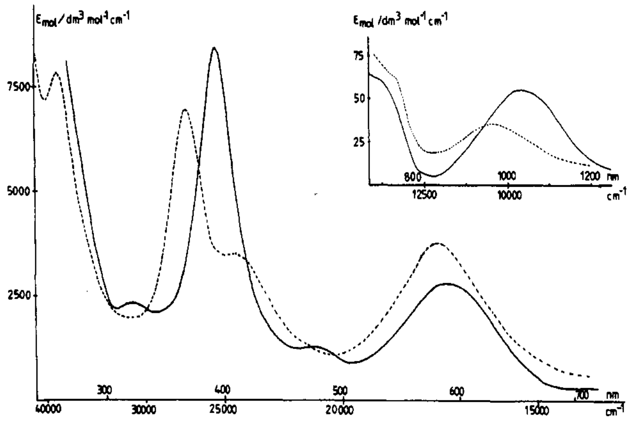


**Figure 1.** UV-visible spectra of $[Ni(PMe_2Ph)_2X_3]$ (X = Cl (---), Br (—)).

refinement of the non-Fourier filtered $k^3$-weighted EXAFS spectra, was carried out within EXCURVE;[12] this program employs spherical wave methods with ab initio phase shifts and backscattering factors calculated in the usual manner from relativistic HF–SCF derived atomic charge densities. The results are summarized in Table II. Various model compounds with known first coordination sphere bond lengths were used to assess the transferability of phase shift parameters.[13] Satisfactory agreement with X-ray data was found in each case without modification of the calculated phase shifts.

## Results and Discussion

The $[Ni(PR_3)_2X_3]$ complexes ($PR_3$ = $PEt_3$, $PMe_2Ph$; X = Cl, Br) are intensely colored, dichroic materials, which decompose in a few hours at room temperature and more rapidly in solution. The structure of $[Ni(PMe_2Ph)_2Br_3]$ was established by a single-crystal X-ray study[8] (on a crystal of composition $Ni(PMe_2Ph)_2Br_2 \cdot 2Ni(PMe_2Ph)_2Br_3 \cdot 2C_6H_6$) to be distorted trigonal bipyramidal with axial phosphines, and similar geometries may be assigned to the other complexes from the similarity of their far-IR and UV–visible spectra.[9] Limited-range UV–visible spectra have been reported previously and the bands tentatively assigned as d–d transitions,[8,9] but from our recent study[10] of $[Co(PR_3)_2X_3]$ complexes, it appeared that the charge-transfer transitions may occur at unusually low energies, and thus a detailed reinvestigation of the spectra of four examples over the range 5000–35000 cm$^{-1}$ has been undertaken. Compared with those of the Co(III) analogues, spectra of the Ni(III) complexes are more difficult to obtain due to their much lower stability and are more complex as a result of the Jahn–Teller distortion. The results are listed in Table I, and Figure 1 shows typical examples. Two intense transitions in each complex are essentially independent of the halogen present and are provisionally assigned as $P(\sigma) \rightarrow Ni$ charge transfer (CT) bands, while two other intense features in each complex have energies that vary with the halogen and are probably $X(\pi) \rightarrow Ni$ CT bands. The remaining very much weaker features are likely to be d–d in origin.

The interpretation of these spectra are based for the d–d bands upon the strong-field model of Norgett et al.[14] The magnetic moments of the complexes correspond to one unpaired electron[9] and hence a low-spin state. For a low-spin $d^7$ ion in a trigonal-bipyramidal geometry, the d-orbital ordering is $(d_{xz}, d_{yz})$ $(e'')$ < $(d_{x^2-y^2}, d_{xy})$ $(e')$ < $(d_{z^2})$ $(a_1)$, and since the Jahn–Teller effect will lift the degeneracy of the e′ level, the ground-state configuration is $(e'')^4(e_b')^2(e_a')^1(a_1)^0$. From the assignments of the Co(III) spectra,[10] the broad weak features in the region 9500–10500 cm$^{-1}$ are assigned as $e'' \rightarrow e_a'$, and the shoulders evident on the low-energy side of the first intense absorption to $e_a' \rightarrow a_1$. No lower energy features were evident in the solution spectra, but the diffuse-reflectance spectra all show very weak bands at ca. 5800–6200 cm$^{-1}$, which are assignable to the transition between the Jahn–Teller split e′ orbitals ($e_b' \rightarrow e_a'$). From this energy and the $e_a' \cdots a_1$ separation, one can predict the $e_b' \rightarrow a_1$ transition at ca. 20000 cm$^{-1}$. This region is obscured by CT transitions in the bromides, but in $[Ni(PEt_3)_2Cl_3]$ a weak feature is seen at 19700 cm$^{-1}$, and a shoulder at similar energy is present in $[Ni(PMe_2Ph)_2Cl_3]$. The highest energy transition expected from $e'' \rightarrow a_1$ is also obscured by the charge-transfer bands.

The charge-transfer bands can be assigned by using Jorgensen's concept[15] of optical electronegativity, which relates the energy of the CT transition to the electronegativity differences between the ligand donor and metal acceptor orbitals. The optical electronegativity of Ni(III) was estimated from the energy of the lowest charge-transfer transition[16] in $[Ni\{o\text{-}C_6H_4(PMe_2)_2\}_2Cl_2]^+$, which after correction for the ligand field splitting and spin-pairing energy gives a value of 2.4, compared with 2.3 for Co(III). The usual values were used for $P(\sigma)$ (2.4), $Br(\pi)$ (2.8), and $Cl(\pi)$ (3.0).[14]

For $[Ni(PR_3)_2Cl_3]$ the lowest energy charge-transfer transition is $P(\sigma) \rightarrow Ni(e_a')$, for which the predicted energy is

$$E_{obs} = 30000[\chi_{opt}(P) - \chi_{opt}(Ni)] + E(e_a'\text{–}e'') + SPE$$

putting $E(e_a'\text{–}e'')$, the energy separation between the two d orbitals, as ca. 10000 cm$^{-1}$ and SPE, the spin-pairing energy correction ($+^1/_3D$), as ca. 1000 cm$^{-1}$.[16] This predicts the energy as ca. 17000 cm$^{-1}$. Similarly, the prediction for $P(\sigma) \rightarrow Ni(a_1)$ energy is

$$E_{obs} = 30000[\chi_{opt}(P) - \chi_{opt}(Ni)] + E(a_1\text{–}e'') + SPE$$

In this case the spin-pairing energy corresponds to a change from $S = {}^1/_2$ to $S = 1$ and is $-^5/_3D$ (ca. 5000 cm$^{-1}$). Taking $E(a_1\text{–}e'')$ as ca. 25000 cm$^{-1}$, this predicts a value of ca. 26000 cm$^{-1}$. The energies of the charge-transfer bands from $Cl(\pi) \rightarrow Ni(e_a')$ and $Cl(\pi) \rightarrow Ni(a_1)$ are similarly predicted as ca. 29000 and ca. 38000 cm$^{-1}$, respectively, and for the bromide analogues that for $Br(\pi) \rightarrow Ni(e_a')$ is predicted as ca. 23000 cm$^{-1}$ and that for $Br(\pi) \rightarrow Ni(a_1)$ as ca. 32000 cm$^{-1}$. Within the limitations of the model, these values are in good agreement with the experimentally determined values in Table I, and support the assignments.

## EXAFS Data

Nickel K-edge EXAFS data, supplemented by bromine K-edge data, were used to obtain structural information.

**Bromide Complexes.** A two-shell model based on two phosphorus and three bromine atoms produced an excellent fit to the

---

(12) Gurman, S. J.; Binsted, N.; Ross, I. *J. Phys. C* **1984**, *17*, 143; **1986**, *19*, 1845.

(13) Corker, J. M.; Evans, J.; Leach, H.; Levason, W. *J. Chem. Soc., Chem. Commun.* **1989**, 181.

(14) (a) Norgett, M. J.; Thornley, J. K. M.; Venanzi, L. M. *J. Chem. Soc. A* **1967**, 540. (b) Norgett, M. J.; Venanzi, L. M. *Inorg. Chim. Acta* **1968**, *2*, 105.

(15) Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: Amsterdam, 1984; Chapter 5.

(16) Chandramouli, G. V. R.; Manoharan, P. T. *Inorg. Chem.* **1987**, *26*, 3291.

**Table II**

| complex | technique | $d$(Ni–P), Å | $d$(Ni–X), Å | $2\sigma^2$, Å$^2$ | $E_0$, eV | FI[a] | $R$,[b] % |
|---|---|---|---|---|---|---|---|
| $[Ni(PEt_3)_2Cl_3]$ | EXAFS | 2.25 | 2.19 | 0.012, 0.010 | 24.6 | 0.85 | 13.7 |
| $[Ni(PMe_2Ph)_2Cl_3]$ | EXAFS | 2.27 | 2.19 | 0.006, 0.008 | 18.5 | 0.89 | 13.7 |
| $[Ni(PEt_3)_2Br_3]$ | EXAFS | 2.29 | 2.35 | 0.010, 0.009 | 20.0 | 2.14 | 14.3 |
| $[Ni(PEt_3)_2Br_3]$ | EXAFS[c] |  | 2.36 | 0.008 | 13.6 | 0.26 | 20.6 |
| $[Ni(PMe_2Ph)_2Br_3]$ | EXAFS | 2.27 | 2.35 | 0.010, 0.009 | 17.1 | 2.63 | 14.3 |
|  | x-ray[d] | 2.268 (3) | 2.354 (2) |  |  |  |  |
| $[Ni(PMe_2Ph)_2Br_3]$ | EXAFS[e] |  | 2.36 | 0.009 | 13.9 | 0.25 | 20.5 |

[a] Fit index defined as $\sum_i[(\chi_i^T - \chi_i^E)(k_i)^3]^2$. [b] $R$ factors defined as $(\int|\chi^T - \chi^E|k^3\,dk/\int|\chi^E|k^3\,dk) \times 100\%$. [c] Bromine K-edge; also $d$(Br···P) = 3.25 Å. [d] Reference 8; average values. [e] Bromine K-edge; also $d$(Br···P) = 3.24 Å.

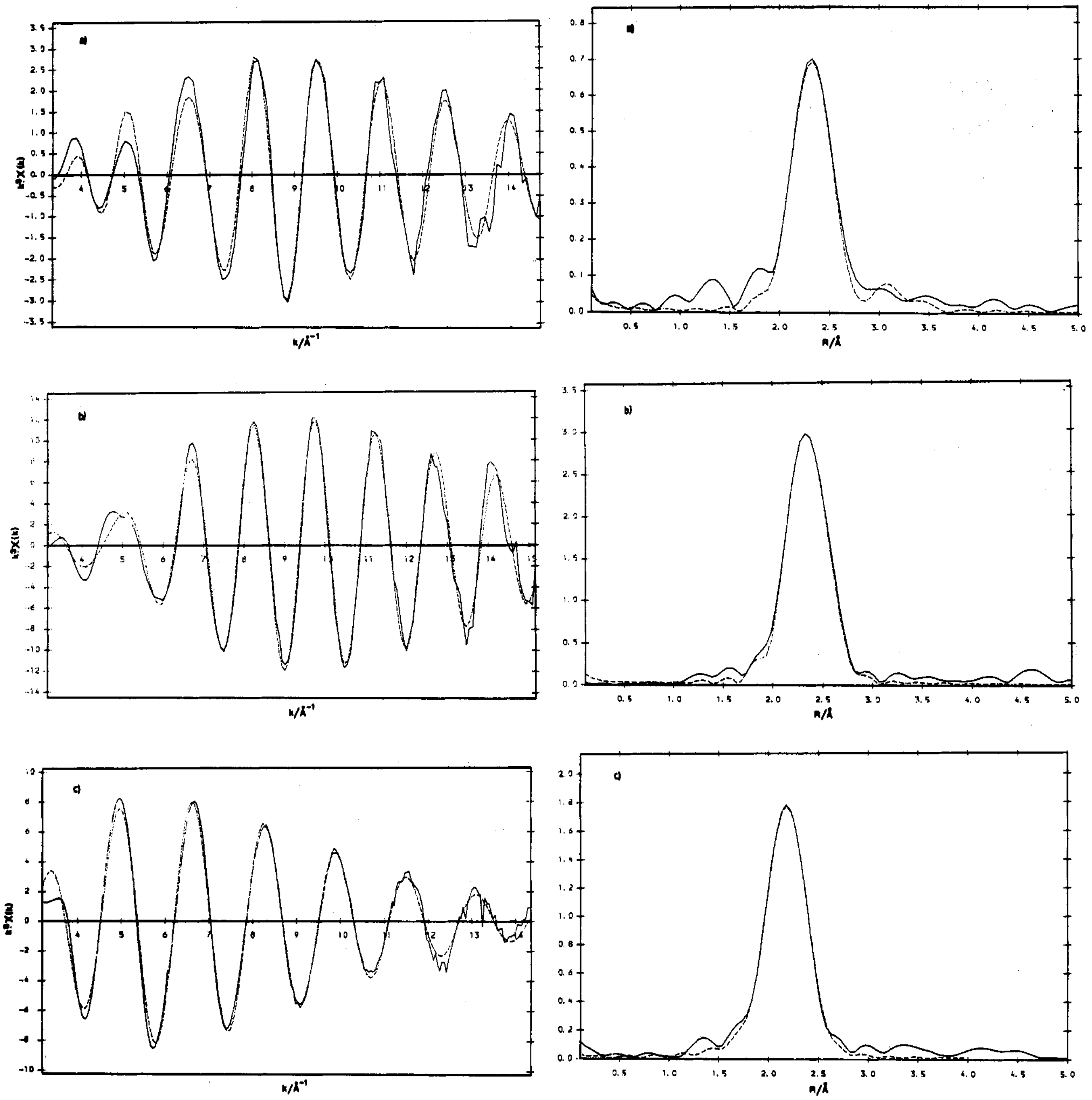


**Figure 2.** Background-subtracted EXAFS spectra and the Fourier transforms phase-shifted for the first shell of (a) $[Ni(PEt_3)_2Br_3]$ (Br K-edge), (b) $[Ni(PEt_3)_2Br_3]$ (Ni K-edge), and (c) $[Ni(PEt_3)_2Cl_3]$ (Ni K-edge): —, experimental; - - -, theory.

nickel K-edge data for both complexes, with the stronger backscattering bromine shell dominating the EXAFS as expected. The bromine K-edge EXAFS for the $PMe_2Ph$ complex was initially modeled by using a single nickel shell, producing a Br–Ni distance of within 0.02 Å of that derived from the nickel K-edge data, but it was felt that a better fit could be achieved. A second shell of two phosphorus atoms was therefore included, resulting in a significant reduction[17] in $R$ factor (20%) and a more consistent Br–Ni bond length. The bromine K-edge data for the $PEt_3$ complex were also subjected to a similar analysis procedure. The Br···P distance derived for the $PMe_2Ph$ complex (3.24 Å) is consistent with an average value of 3.27 Å calculated from the X-ray data.[8] Similarly, comparison of the Ni–Br and Ni–P bond

---

[17] Joyner, R. W.; Martin, K. J.; Meehan, P. *J. Phys. C* **1987**, *20*, 4005.

lengths determined by EXAFS with the X-ray distances shows excellent agreement. Little change in first coordination sphere bond lengths would be expected when $PMe_2Ph$ is replaced with $PEt_3$; thus, the similar results obtained for $[Ni(PEt_3)_2Br_3]$ can be viewed with some confidence.

**Chloride Complexes.** Distinguishing phosphorus from chlorine in EXAFS analyses often presents difficulties because of the very similar backscattering powers of the two elements. Fits produced by using a single shell of phosphorus or chlorine atoms were therefore compared to that derived from the two-shell model. For both complexes, a significant decrease[17] in $R$ factor (12%) was observed for the two-shell fit, and no unacceptably high correlations between the two shells were observed. Thus, the bond lengths quoted in Table II are believed to be reliable to within ±0.03 Å.

**Acknowledgment.** We thank the SERC (J.M.C. and M.D.S.) and BP Research (J.M.C.) for support, the Director of The Daresbury Laboratory for the provision of facilities, and Professor C. D. Garner and Dr. D. A. Rice for the use of the Varian Cary 2300 and Beckman Acta spectrometers, respectively.

---

Contribution from the Department of Chemistry
and Biochemistry, The University of Texas,
Austin, Texas 78712

# Synthesis and Characterization of a Tetranuclear Iron(III) Complex Derived from a New *m*-Xylyl-Bridged Tetraimidazole Ligand

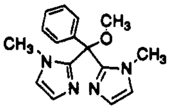
Jonathan L. Sessler,* Jeffrey D. Hugdahl, Vincent Lynch, and Brian Davis

*Received May 30, 1990*

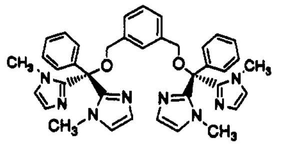
Binuclear iron–oxo centers have been found to be a common structural element at the active sites of numerous proteins, including hemerythrin,[1-4] purple acid phosphatase,[5] ribonucleotide reductase,[6] ruberythrin,[7] and methane monooxygenase.[8] These centers perform a wide variety of important biological processes, including oxygen transport, methane oxidation, and oxygen atom transfer. While many models of the bimetallic site exist, relatively few of the models employ imidazoles as the sole N-donors.[9,10] Such biomimetic models may ultimately prove important in reproducing the chemical and physical properties of the histidine-dominated cores found in the protein systems.[11] Recently, Lippard et al. has succeeded in crystallizing both an unsymmetrical iron(II) and a symmetrical iron(III) dimer utilizing the diimidazole ligand ($L_1$) as the sole capping subunit.[9] This success suggests that further studies with related imidazole-containing ligands might also be informative. In this note, we report the synthesis of a new xylyl-bridged tetraimidazole ligand, $L_2$, and the results of iron binding and X-ray structural studies carried out with this system. We have found that this new ligand, with its rigid xylyl bridge, serves to stabilize the formation of a tetranuclear $\mu$-oxo iron(III) complex in the solid state.[12]

**Table I.** Crystallographic Data for **2**

| | | | |
|---|---|---|---|
| chem formula | $C_{90}H_{102}N_{16}O_{26}Fe_4Cl_6$ | space group | $P2_1/n$ (No. 14) |
| fw | 2260.00 | $T$, °C | −80 |
| $a$, Å | 14.192 (3) | $\rho_{calc}$, g cm$^{-3}$ | 1.49 |
| $b$, Å | 16.557 (3) | $\mu$, cm$^{-1}$ | 8.029 |
| $c$, Å | 21.856 (6) | transm coeff | 0.8012–0.9376 |
| $\beta$, deg | 101.25 (2) | $R(F_o)$ | 0.0747 |
| $V$, Å$^3$ | 5037 (2) | $R_w(F_o)$ | 0.0656 |
| $Z$ | 2 | | |



$L_1$



$L_2$

## Experimental Section

NMR spectra were obtained in $CDCl_3$ with $Me_4Si$ as an internal standard and recorded on a General Electric QE-300 spectrometer. Chemical ionization mass spectrometric analyses (CI MS) were made by using a Finnigan MAT 4023. Infrared spectra were recorded, as KBr pellets, from 4000 to 400 cm$^{-1}$ on a Bio-Rad FTS-40 spectrophotometer. Electronic spectra were recorded in chloroform on a Beckman DU-7 spectrophotometer.

**Bis(1-methylimidazol-2-yl)phenylcarbinol (1).** A solution of *N*-methylimidazole (5.0 g, 60.9 mmol) in 200 mL of THF under nitrogen was cooled to −78 °C and treated with 42 mL of 1.6 M *n*-butyllithium in hexanes for 1 h. Benzoyl chloride (4.28 g, 30.4 mmol) was dissolved in 25 mL of THF and added dropwise. The solution was warmed to room temperature over 4 h, and 50 mL of water was added. THF was removed in vacuo. The aqueous solution was extracted with methylene chloride, dried over $MgSO_4$, filtered, and concentrated. Addition of ether to the methylene chloride solution afforded a white precipitate that was filtered and dried, affording **1** (6.3 g), which was used without further purification: yield 78%. $^1$H NMR: $\delta$ 3.39 (6 H, s, N*C*$H_3$), 6.5 (1 H, br, –O*H*), 6.88 (2 H, s, Im4*H*), 6.95 (2 H, s, Im5*H*), 7.09 (2 H, m, phenyl), 7.34 (3 H, m, phenyl). $^{13}$C NMR: $\delta$ 30.71, 74.98, 123.49, 125.98, 127.45, 128.36, 148.45. CI MS *m/e* 269 (MH$^+$).

**1,3-Bis((bis(1-methylimidazol-2-yl)phenylmethoxy)methyl)benzene ($L_2$).** A stirred solution of **1** (1.52 g, 5.67 mmol) in 50 mL of dry dimethylformamide (DMF) under nitrogen was treated with sodium hydride (156 mg, 6.5 mmol). $\alpha,\alpha'$-Dibromo-*m*-xylene (0.75 g, 2.83 mmol) was added all at once, and the solution was stirred overnight. The DMF was removed in vacuo, and the resulting solid was dissolved in 20 mL of water and extracted chloroform. The chloroform extracts were dried over magnesium sulfate, filtered, and removed in vacuo, leaving a white foam ($L_2$) (1.70 g): yield 94%. $^1$H NMR: $\delta$ 3.34 (12 H, s, N*C*$H_3$), 4.42 (4 H, s, Ph*C*$H_2$O–), 6.78 (4 H, s, Im4*H*), 6.97 (4 H, s, Im5*H*), 7.30 (10 H, m, phenyl), 7.53 (4 H, d, phenyl). $^{13}$C NMR: $\delta$ 34.20, 67.47, 81.54, 122.84, 125.58, 126.40, 126.45, 127.49, 127.55, 127.83, 127.94, 138.03, 138.25, 146.32. IR (KBr, cm$^{-1}$, selected peaks): 3386 (w), 3102 (m), 1677 (m), 1486 (s), 1446 (s), 1400 (m), 1279 (s), 1057 (s), 904 (m), 893 (m), 754 (vs), 721 (s), 700 (s). CI MS: *m/e* 639 (MH$^+$). HR CI MS: found, *m/e* 638.312 026; calcd, *m/e* 638.311 773.

**Preparation of $[Fe_2(L_2)(\mu\text{-}O)(\mu\text{-}HCO_2)_2(HCO_2)_2]_2$ (2).** The metal complex has been prepared by two methods.

---

(1) Wilkins, R. G.; Harrington, P. C. *Adv. Inorg. Biochem.* **1983**, *5*, 51–86.

(2) Sheriff, S.; Hendrickson, W. A.; Smith, J. L. *J. Mol. Biol.* **1987**, *197*, 273–296.

(3) Garbett, K.; Darnall, D. W.; Klotz, I. M.; Williams, R. J. P. *Arch. Biochem. Biophys.* **1969**, *135*, 419–434.

(4) Wilkins, P. C.; Wilkins, R. G. *Coord. Chem. Rev.* **1987**, *79*, 195–214.

(5) Antanaitis, B. C.; Aisen, P. *Adv. Inorg. Biochem.* **1983**, *5*, 111–136.

(6) Sjoberg, B.-M.; Graslund, A. *Adv. Inorg. Biochem.* **1983**, *5*, 87–110.

(7) LeGall, J.; Prickril, B. C.; Moura, I.; Xavier, A. V.; Mouira, J. J. G.; Huynh, B.-H. *Biochemistry* **1988**, *27*, 1636–1642.

(8) Fox, B. G.; Froland, W. A.; Dege, J. E.; Lipscomb, J. D. *J. Biol. Chem.* **1989**, *264*, 10023–10033.

(9) Tolman, W. B.; Bino, A.; Lippard, S. J. *J. Am. Chem. Soc.* **1989**, *111*, 8522–8523.

(10) Structurally characterized iron complexes employing imidazole or benzimidazole in addition to other nitrogen donors have been reported: (a) Suzuki, M.; Oshio, H.; Uehara, A.; Endo, K.; Yanaga, M.; Kida, S.; Saito, K. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 3907–3913. (b) Gomez-Romero, P.; Casan-Pastor, J.; Ben-Hussein, A.; Jameson, G. B. *J. Am. Chem. Soc.* **1988**, *110*, 1988–1990. (c) Mashuta, M. S.; Webb, R. J.; Oberhausen, K. J.; Richardson, J. F.; Buchanan, R. M.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1989**, *111*, 2745–2746. (d) Adams, H.; Bailey, N. A.; Crane, J. D.; Fenton, D. E.; Latour, J.-M.; Williams, J. M. *J. Chem. Soc., Dalton Trans.* **1990**, 1727–1735.

(11) Tolman, W. B.; Rardin, R. L.; Lippard, S. J. *J. Am. Chem. Soc.* **1989**, *111*, 4532–4533.

(12) Two similar complexes have been reported: (a) Toftlund, H.; Murray, K. S.; Zwack, P. R.; Taylor, L. F.; Anderson, O. P. *J. Chem. Soc., Chem. Commun.* **1986**, 191–193. (b) Sessler, J. L.; Sibert, J. W.; Lynch, V. *Inorg. Chem.* **1990**, *29*, 4143–4146.

0020-1669/91/1330-0334$02.50/0