

incorrect, as such a premise fails to take account of the weaker σ polarization brought about by coordination and also fails to take account of π back-bonding deactivation, which is inherently greater than π -bonding activation.

Acknowledgment. The author gratefully acknowledges the award of a CSIRO Postdoctoral Fellowship and helpful discussions with Dr. W. H. F. Sasse concerning this paper.

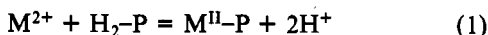
Contribution from the Department of Chemistry,
Howard University, Washington, D.C. 20059

Equilibrium Constants and Electrophilic Exchange Reaction Kinetics of Lead(II) Porphyrins

Shirleyanne E. Haye and Peter Hambright*

Received July 10, 1984

Although over 50 metal ions react with free-base (H_2 -P) porphyrins to form metalloporphyrins (M-P),¹ equilibrium constants for these reactions have been measured only in the cases of Zn^{2+} , Cd^{2+} , and Hg^{2+} . Zinc(II)² and cadmium(II)³ produce 1:1 metal to porphyrin species (eq 1), while 1:1, 2:1,



and 3:2 adducts have been demonstrated for $Hg(II)$.⁴⁻⁷ Such reversible equilibria allow for detailed kinetic studies of electrophilic exchange reactions, where one metal can displace another from its porphyrin complex. A number of exchange studies have been run in nonaqueous media,⁸⁻¹¹ while only cadmium^{7,12} and zinc^{10,13,14} porphyrins have been examined in aqueous solution.

We report equilibrium and rate constants for lead(II) reactions with water-soluble porphyrins and the kinetics of the exchange of Zn^{2+} and Co^{2+} with lead and cadmium porphyrins. Since high concentrations of zinc protoporphyrin are found in individuals with lead poisoning,¹⁵ the facile $Zn^{2+}/Pb^{II}-P$ exchange reactions might be one possible pathway for the production of this complex in vivo.

Experimental Section

The porphyrins tetrakis(*N*-methyl-4-pyridyl)porphyrin (H_2 -TMPyP(4)), its 2-pyridyl analogue (H_2 -TMPyP(2)), and tetrakis(*N,N,N*-trimethyl-4-aniliniumyl)porphyrin (H_2 -TAP) prepared before³ were converted by ion-exchange techniques into their nitrate salts. The transition-metal nitrates were analyzed by EDTA titrations.¹⁶ All reactions were run at 25 °C, at an ionic strength of 0.2 (NaNO₃),

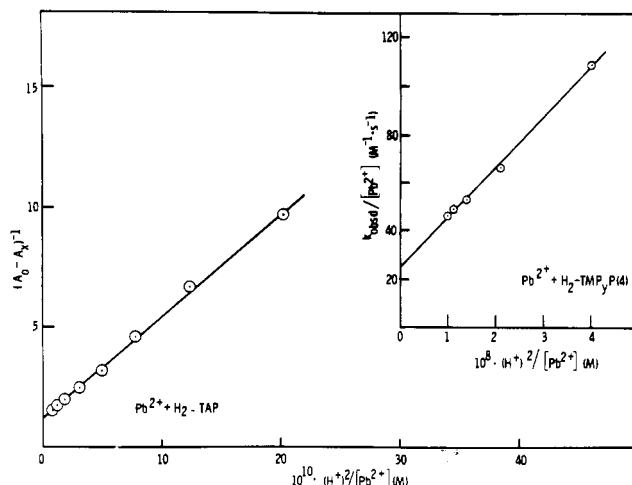


Figure 1. Left side: Graphical determination of the equilibrium constant K_{Pb} for the Pb^{2+}/H_2 -TAP reaction, from eq 3. Inset: Plot of $k_{obsd}/[Pb^{2+}]$ vs. $[H^+]^2/[Pb^{2+}]$ for the approach to equilibrium of the Pb^{2+}/H_2 -TMPyP(4) reaction.

Table I. Equilibrium and Formation Rate Constants for Metalloporphyrins at 25 °C

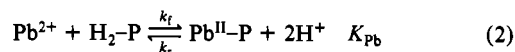
porphyrin	pK_3^a	K_{Pb}^b (k_{Pb}) ^{b,c}	$K_{Cd}^{b,d}$ (k_{Cd}) ^{b,d}	$K_{Zn}^{b,e}$ (k_{Zn}) ^{b,e}
H_2 -TMPyP(2)	-0.9	9.5×10^{-8} (20)	7.9×10^{-7} (7)	1.9×10^2 (4.9×10^{-4})
H_2 -TMPyP(4)	+1.4	3.2×10^{-8} (28)	2.0×10^{-8} (40)	4.4 (3.7×10^{-2})
H_2 -TAP	+3.6	3.0×10^{-10} (128)	1.7×10^{-10} (87)	

^a pK_3 for the H_3 -P⁺/ H_2 -P reaction; see ref 3. ^b K_M in units of M; k_M in units of $M^{-1} s^{-1}$. ^c This paper. ^d Data from ref 3.

^e Data from ref 2.

with 1×10^{-2} M 4-morpholineethanesulfonic acid (MES) as the buffer.

Formation Constants. The lead porphyrin formation constants (eq 2) were studied between pH 4 and 6.2, with total lead concentrations less than 10^{-3} M. This pH range avoids $PbOH^+$ ($pK_a = 7.7$)¹⁷ and



is such that the porphyrins are in their free-base states.³ The low lead levels ensure that Pb^{2+} (rather than polynuclear¹⁷ $Pb_2(OH)^{3+}$ or $Pb_4(OH)_4^{4+}$) is the reactant.

At pH 4 with ca. 10^{-6} M H_2 -TMPyP(4) and 1×10^{-4} M Pb^{2+} , the typical free-base spectrum of the porphyrin is observed. As the pH is raised, Pb^{II} -TMPyP(4) appears, with bands at 476 nm ($\epsilon 1.5 \times 10^3$), 609 nm ($\epsilon 9.7 \times 10^3$), and 660 nm ($\epsilon 1.4 \times 10^4$). Isobestic points are found at 390, 445, 590, and 503 nm, indicating that H_2 -P and Pb^{II} -P are the only absorbing species. This porphyrin spectrum is similar to those of Pb^{II} -TMPyP(4) (containing an impurity) reported by Harriman and co-workers¹⁸ ($\lambda_{max} = 469, 606,$ and 658 nm) and lead(II) tetraphenylporphyrin in benzene ($\lambda_{max} = 467, 607,$ and 657 nm). With pHs higher than 6.5, lead in the 10^{-4} M concentration range precipitates.

At 424 nm, the Soret peak for H_2 -TMPyP(4), we can define A_0 as the absorbance of H_2 -P, A_{00} as that of Pb^{II} -P, and A_x as the absorbance of mixtures of the two species. The solution is buffered, and with $[Pb^{2+}]_0 \gg [H_2-P]_0$, then $[Pb^{2+}]_0 = [Pb^{2+}]$. It¹⁹ has been shown that K_{Pb} for eq 2 can be derived from linear graphs of $(A_0 - A_x)^{-1}$ vs. $[H^+]^2/[Pb^{2+}]$, from eq 3. Such a plot for the Pb^{2+}/H_2 -TAP

reaction is shown in Figure 1, and the resulting equilibrium constants are listed in Table I. The same K_{Pb} values could be obtained from

(17) Baes, C. F.; Mesmer, R. E. "The Hydrolysis of Cations"; Wiley: New York, 1976; p 358.

(18) Harriman, A.; Richoux, M. C.; Neta, P. *J. Phys. Chem.* **1983**, *87*, 4957.

(19) Miller, J. R.; Dorough, G. D. *J. Am. Chem. Soc.* **1952**, *74*, 3977.

- Buchler, J. W. In "Porphyrins and Metalloporphyrins"; Smith, K. M., Ed.; Elsevier: Amsterdam, 1975; Chapter 5.
- Hambright, P. *Inorg. Chem.* **1977**, *16*, 2987.
- Shamim, A.; Hambright, P. *Inorg. Chem.* **1980**, *19*, 564.
- Adeyemo, A.; Krishnamurthy, M. *Inorg. Chem.* **1977**, *16*, 3355.
- Adeyemo, A.; Krishnamurthy, M. *Inorg. Chim. Acta* **1984**, *83*, L41.
- Hudson, M. F.; Smith, K. M. *Tetrahedron* **1976**, *32*, 597.
- Shamin, A.; Hambright, P. *J. Inorg. Nucl. Chem.* **1980**, *42*, 1645.
- Grant, C.; Hambright, P. *J. Am. Chem. Soc.* **1969**, *91*, 4195.
- Barnes, J. W.; Dorough, G. D. *J. Am. Chem. Soc.* **1950**, *72*, 4045.
- Baker, H.; Hambright, P.; Ross, L. *Inorg. Chem.* **1973**, *12*, 2200.
- Reid, J.; Hambright, P. *Inorg. Chim. Acta* **1979**, *33*, L135.
- Tabata, M.; Tanaka, M. *J. Chem. Soc., Dalton Trans.* **1983**, *9*, 1955.
- Cheung, S. K.; Dixon, L. F.; Fleischer, E. B.; Jeter, D. K.; Krishnamurthy, M. *Bioinorg. Chem.* **1973**, *2*, 281.
- Das, R. R. *J. Inorg. Nucl. Chem.* **1972**, *34*, 1263.
- Lamola, A. A.; Yamane, T. *Science (Washington, D.C.)* **1974**, *186*, 936.
- Welcher, F. J. "The Analytical Uses of Ethylenediamine Tetraacetic Acid"; Van Nostrand: Princeton, NJ, 1957.

Table II. Metal Ion-Metalloporphyrin Exchange Rate Data at 25 °C

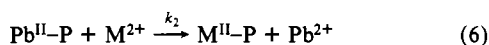
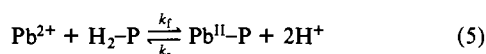
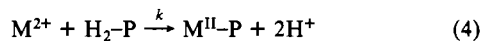
	M* + Pb ^{II} -TMPyP(4)		M* + Cd ^{II} -TMPyP(4)	
	Zn ²⁺	Co ²⁺	Zn ²⁺	Co ²⁺
$k_f(\text{Pb}^{2+}/\text{H}_2\text{-P})^a$	22	19	47	33
$k_2(\text{M}^*/\text{M}^{\text{II}}\text{-P})^a$	14	0.27	79	0.93
$k(\text{M}^*/\text{H}_2\text{-P})^a$	4.9×10^{-2}	1.0×10^{-3}	4.9×10^{-2}	1.0×10^{-3}
k_2/k	285	270	1620	925

^a Rate constants in units of M⁻¹ s⁻¹; ionic strength 0.2. See eq 4-6 for definitions of k_f , k_2 , and k .

data analyzed at the Pb^{II}-P Soret peaks.

Formation Rates. Due to the necessity of using low lead concentrations and working at moderate pHs, it was not possible to study the Pb^{II}-P formation kinetics under conditions that drive eq 2 completely to the products. We thus studied the kinetics of the rate of approach of lead porphyrin solutions to equilibrium, where the rate law is of the form $k_{\text{obsd}} = k_f[\text{Pb}^{2+}] + k_r[\text{H}^+]^2$. Figure 1 shows linear plots of $k_{\text{obsd}}/[\text{Pb}^{2+}]$ vs. $[\text{H}^+]^2/[\text{Pb}^{2+}]$, from which k_f and k_r can be evaluated. Although $K_{\text{Pb}} = k_f/k_r$, such kinetically derived K_{Pb} values differed (by no more than a factor of 2, either larger or smaller) from those derived from equilibrium studies. This problem has precedent in other porphyrin systems,²⁰ and no explanation is apparent at this time. However, such k_f values could be independently determined from the electrophilic exchange kinetics, and both sets of rate constants are in reasonable agreement.

Exchange Reactions. For labile cadmium porphyrins exchanging with Zn²⁺ or Co²⁺, we previously⁷ postulated the following mechanism, which is also suggested for the lead porphyrins:



The direct k pathway (eq 4) is several hundred times slower than the exchange reaction and can be neglected. Assuming that Pb^{II}-P is a steady-state intermediate, the rate law is of the form

$$k_{\text{obsd}} = k_f k_2 [\text{Pb}^{2+}] [\text{M}^{2+}] / (k_r [\text{H}^+]^2 + k_2 [\text{M}^{2+}]) \quad (7)$$

This can be rearranged into $[\text{Pb}^{2+}]/k_{\text{obsd}} = k_2^{-1} K_{\text{Pb}}^{-1} [\text{H}^+]^2 / [\text{M}^{2+}] + k_f^{-1}$. For the Zn²⁺/Pb^{II}-TMPyP(4) reaction, the pH was varied from 4.6 to 5.4, the lead concentration from 1.2×10^{-4} to 8.8×10^{-4} M, and the zinc concentration from 4.3×10^{-4} to 3.3×10^{-3} M. Figure 2 shows the linear relationship between $[\text{Pb}^{2+}]/k_{\text{obsd}}$ and $[\text{H}^+]^2/[\text{Zn}^{2+}]$ under these conditions, and a similar plot for the Zn²⁺/Cd^{II}-TMPyP(4) reaction is also presented. With either Zn²⁺ or Cd²⁺ as the displacing ion, the k_f values are similar to one another (Table II) and to those measured from the approach to equilibrium study (Table I).

Discussion

The equilibrium constants for lead(II) and cadmium³ porphyrins shown in Table I are of a similar magnitude, and both are about 10⁸ times smaller than those for the corresponding zinc porphyrins.² For all three ions, the most stable metalloporphyrins have the least basic (lower pK₃) free-base-porphyrin forms. Such stability ($K = k_f/k_r$) is primarily due to the marked decrease in the rate constants of the reverse, acid solvolysis reaction k_r , as porphyrin basicity decreases.³ The formation rate constants k_f increase less sharply with an increase in porphyrin basicity.^{3,21} While Pb²⁺ (radius = 118 pm) is larger¹ and has a higher Pauling electronegativity ($E_n = 2.33$) than Cd²⁺ (radius = 95 pm; $E_n = 1.69$), both are too large to fit into the porphyrin plane and their intrinsic differences appear to be leveled. At $I = 0.2$, the metalloporphyrin formation²² rate constants k_f are in the order Cd²⁺ > Pb²⁺ > Cu²⁺ > Zn²⁺ > Co²⁺ > Mn²⁺ > Ni²⁺ and span a 10⁷-fold

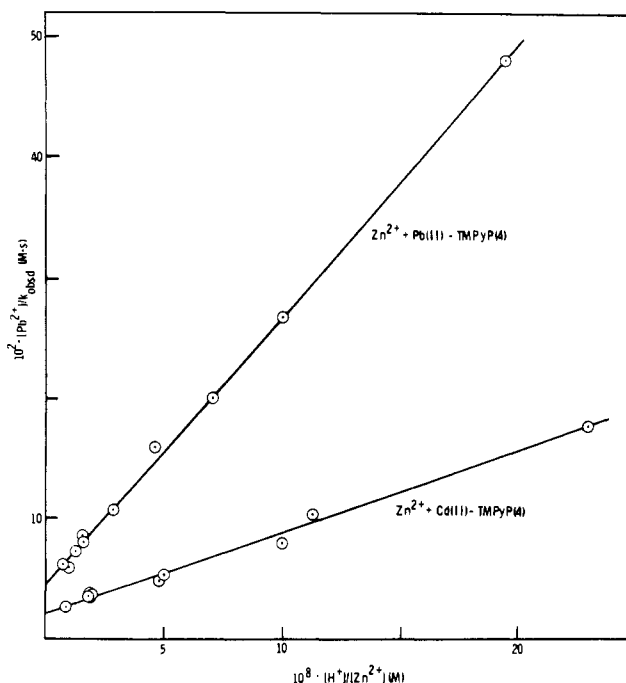


Figure 2. Exchange-reaction plots (see eq 7). For the Zn²⁺/Cd^{II}-TMPyP(4) reaction, the ordinate should be $[\text{Cd}^{2+}]/k_{\text{obsd}}$.

range. There is a general correlation of k_f with the water-exchange rates of the metal ions, consistent with a dissociative interchange mechanism.²¹⁻²⁵

Both labile cadmium and lead porphyrins follow the same kinetic mechanism for their replacements by Zn²⁺, Co²⁺, and Mn²⁺. The activated complex contains a deprotonated (P²⁻) porphyrin and both the replacing and replaced metal ions. The same has been found for the Zn²⁺/Cd^{II}-P and Zn²⁺/Hg^{II}-P reactions in nonaqueous media⁸ and the Cu²⁺/Zn^{II}-P reactions in water.^{10,13} It has not yet been shown whether the two metal ions in the activated complex are on the same side of the porphyrin plane, competing for the same orbitals, or on opposite sides of the plane, as shown in crystal structures on dirhenium and dirhodium porphyrins.¹

In the M²⁺/Pb^{II}-TMPyP(4) reactions, Zn²⁺ and Co²⁺ exchange about 300 times faster than they incorporate into the free-base porphyrin itself, while for M²⁺/Cd^{II}-TMPyP(4), they react about 1000 times faster. This is in agreement with qualitative work on Mn²⁺/M^{II}-P reactions in water²⁶ and quantitative data on Zn²⁺/M^{II}-P reactions in pyridine.⁸ For the same rate law, the catalysis is in the order Hg²⁺ > Cd²⁺ > Pb²⁺. In fact, Hg²⁺ catalyzes the Zn²⁺/Pb^{II}-P reactions in pyridine,⁸ through the formation of Hg^{II}-P. This catalysis has been ascribed to deformation of the porphyrin nucleus^{21,24,27} and higher labilities of the metal ion being replaced as contrasted to those of the free-base-porphyrin protons.²⁵ The data in Table II indicate that factors that enhance the M²⁺/H₂-P reactions also favor the M²⁺/M^{II}-P exchange reactions. For example, Zn²⁺ incorporates into H₂-TMPyP(4) about 50 times faster than does Co²⁺, and Zn²⁺ reacts with Pb^{II}-TMPyP(4) about 50 times faster than does Co²⁺. Similar results are found for Cd^{II}-TMPyP(4).

The tetrakis(*N*-methyl-2-pyridyl)porphyrin is presumably a mixture of the four atropisomers that arise from steric interactions between the ortho *N*-methylpyridyl groups and the pyrrole β-hydrogen atoms. The (4,0) isomer, with the four

(20) Fleischer, E. B.; Krishnamurthy, M. *J. Coord. Chem.* **1972**, *2*, 89.

(21) Adeyemo, A.; Shamim, A.; Hambright, P.; Williams, R. F. X. *Indian J. Chem., Sect. A* **1982**, *21A*, 763.

(22) Turay, J.; Hambright, P. *Inorg. Chem.* **1980**, *19*, 562.

(23) Hambright, P.; Chock, P. B. *J. Am. Chem. Soc.* **1974**, *96*, 3123.

(24) Bain-Ackerman, M. J.; Lavallee, D. K. *Inorg. Chem.* **1979**, *18*, 3358.

(25) Lavallee, D. K. *Coord. Chem. Rev.*, in press.

(26) Tabata, M.; Tanaka, M. *Inorg. Chim. Acta* **1980**, *40*, 71.

(27) Shah, B.; Shears, B.; Hambright, P. *Inorg. Chem.* **1971**, *10*, 1818.

groups pointing in the same direction, should statistically be in 12.5% abundance, the (3,1) in 50%, the trans (2,2) in 12.5%, and the cis (2,2) in 25%. Thermal equilibration studies on various picket-fence porphyrin derivatives²⁸ show a number of cases where less of the (4,0) and more of the trans (2,2) derivative occur than expected statistically. Similarly, for a given porphyrin, Ni²⁺, diacid, and free-base adducts interconvert ((4,0) → (3,1)) faster than do Zn²⁺, Pd²⁺, or Cu²⁺ derivatives, and the (4,0) free base shows atropisomerization of the resulting nickel complex under rather gentle nickel incorporation conditions. We do not know if H₂-TMPyP(2) interconverts upon equilibration with Pb²⁺, as might be expected for a deformed Pb^{II}-P derivative. Equilibrium constants and rates of metal ion reactions with individual picket-fence porphyrin isomers have been studied. For copper²⁹ and zinc³⁰ kinetic work, the rate span is less than a factor of 6 among the four isomers and within a factor of 10 for equilibrium constants³⁰ of cadmium complexation in aqueous solution with water-soluble picket-fence porphyrins. The Pb²⁺/H₂-TMPyP(2) reaction data presented are thus average values for the isomer distribution present.

For individuals with lead intoxication, large amounts of zinc protoporphyrin are found in the erythrocytes, presumably bound to the heme site of globin.¹⁵ Pb²⁺, Hg²⁺, Mn²⁺, and Zn²⁺ inhibit ferrochelatase,³¹⁻³³ the enzyme that incorporates Fe²⁺ into protoporphyrin IX. This enzyme can use Zn²⁺ and Co²⁺ as substrates in the absence of Fe²⁺, and both Mn²⁺ and Zn²⁺ are competitive inhibitors^{31,32} for Fe²⁺. It has been speculated¹⁵ that both enzymatic zinc chelatase activity³² (which has a pH profile similar to those of Zn²⁺/H₂-P reactions³⁴) and nonenzymatic zinc chelation routes may be involved in the Zn-Proto formation in lead intoxication. On the basis of the present Zn²⁺/Pb^{II}-P results, a lead-catalyzed route may also be operative. This notion, however, is tempered by the fact that in severe iron deficiency anemia, Zn-Proto is also formed, while for humans with inherited erythropoietic porphyria (a ferrochelatase deficiency), the unmetallated protoporphyrin IX is mainly produced.¹⁵

Acknowledgment. This work was supported by Howard University NIH Biomedical Research Grant 5-SO-6-RR-08016-9.

Registry No. H₂TMPyP(2), 59728-89-1; H₂TMPyP(4), 38673-65-3; H₂TAP, 69458-19-1; Pb, 7439-92-1; Zn, 7440-66-6; Co, 7440-48-4.

- (28) Freitag, R. A.; Whitten, D. G. *J. Phys. Chem.* **1983**, *87*, 3918.
 (29) Turay, J.; Hambright, P. *Inorg. Chim. Acta* **1981**, *53*, L147.
 (30) Valiotti, A.; Adeyemo, A.; Williams, R. F. X.; Ricks, L.; North, J.; Hambright, P. *J. Inorg. Nucl. Chem.* **1981**, *43*, 2653.
 (31) Dailey, H. A.; Fleming, J. E. *J. Biol. Chem.* **1983**, *258*, 11453.
 (32) Camadro, J.-M.; Labbe, P. *Biochim. Biophys. Acta* **1982**, *707*, 280.
 (33) Dailey, H. A.; Lascelles, J. *Arch. Biochem. Biophys.* **1974**, *160*, 523.
 (34) Shamim, A.; Hambright, P. *Inorg. Chem.* **1983**, *22*, 694.

Contribution from the Section of Chemistry,
Karl Marx University, DDR-7010 Leipzig, GDR

Single-Crystal EPR Spectra of (n-Bu₄N)₂[⁶³Cu(dmit)₂]

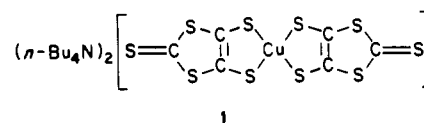
Joachim Stach, Reinhard Kirmse,* Wolfgang Dietzsch,
Ruth-Maria Olk, and Eberhard Hoyer

Received February 17, 1984

Isotrithione-3,4-dithiolate (dmit; from the notation dimercaptioisotrithione used primarily) represents a new type of sulfur-rich dithiolene ligand forming covalent complexes with various metal ions.¹⁻³ Metal bis complexes of dithiolene

ligands are known to show interesting electric and magnetic properties in dependence on the cations. Some of these compounds are of special interest for the preparation of linear-chain materials.⁴⁻⁶ The EPR spectra—especially the single-crystal spectra—of the corresponding paramagnetic transition-metal complexes are characterized by very small line widths, allowing the detection of small ligand hyperfine interactions as shown for the Ni(III), Pd(III), and Pt(III) dmit complexes n-Bu₄N-[Ni(dmit)₂], n-Bu₄N-[Pd(dmit)₂], and n-Bu₄N-[Pt(dmit)₂].⁷ The investigation of superhyperfine interactions (shfs) due to the interactions of the unpaired electron with ligand nuclei is useful for the characterization of the nature of the metal-ligand bonds because complete shfs data provide direct information about the molecular orbital of the unpaired electron and give a more detailed picture of the spin-density distribution in covalent complexes.

In this paper we report a detailed analysis of the ³³S superhyperfine interactions (³³S: natural abundance 0.74%, I = 3/2) observed in the single-crystal EPR spectra of tetra-n-butylammonium bis(isotrithione-3,4-dithiolato)cuprate(II), (n-Bu₄N)₂[Cu(dmit)₂] (1), diamagnetically diluted by the corresponding Ni(II) chelate.



The experimental parameters will be compared with those obtained by Maki et al.⁸ and Plumlee et al.⁹ for (n-Bu₄N)₂[Cu(mnt)₂] (mnt = cis-1,2-dicyanoethenedithiolate). Up to now ³³S hfs data have been detected only for a small number of complexes having a CuS₄ coordination sphere.¹⁰⁻¹³

Experimental Section

The ligand and the Cu(II) and Ni(II) complexes were prepared as described earlier by Steimecke et al.¹⁻³ For the preparation of (n-Bu₄N)₂[⁶³Cu(dmit)₂], ⁶³Cu-enriched CuCl₂·2H₂O (97.8% ⁶³Cu, 2.2% ⁶⁵Cu) was used. Suitable single crystals containing about 0.5 mol % (n-Bu₄N)₂[⁶³Cu(dmit)₂] in the corresponding Ni(II) complex could be grown by slow solvent evaporation from acetone/ethanol (20/1) solutions.

The EPR spectra were recorded on a Varian E-112 spectrometer in the X band at room temperature.

Results and Discussion

The structure of the host complex is known.¹⁴ (n-Bu₄N)₂[Ni(dmit)₂] crystallizes in the monoclinic space group P2₁/c, with two molecules per unit cell. The complex anion is nearly planar; Ni occupies an inversion center. As expected according to the structure of the Ni complex, the single-crystal

- (1) Steimecke, G.; Kirmse, R.; Hoyer, E. *Z. Chem.* **1975**, *15*, 28.
 (2) Steimecke, G. Ph.D. Thesis, Karl Marx University, Leipzig, 1977.
 (3) Steimecke, G.; Sieler, J.; Kirmse, R.; Hoyer, E. *Phosphorus Sulfur* **1979**, *7*, 49.
 (4) Siedle, A. R. *Ext. Linear Chain Compd.* **1982**, *2*, 469.
 (5) Alcacer, L.; Novais, H. *Ext. Linear Chain Compd.* **1983**, *3*, 319.
 (6) Kobayashi, A.; Sasaki, Y. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2650.
 (7) Kirmse, R.; Stach, J.; Dietzsch, W.; Steimecke, G.; Hoyer, E. *Inorg. Chem.* **1980**, *19*, 2679.
 (8) Maki, A. H.; Edelstein, N.; Davison, A.; Holm, R. H. *J. Am. Chem. Soc.* **1964**, *86*, 4580.
 (9) Plumlee, K. W.; Hoffman, B. M.; Ibers, J. A.; Soos, Z. G. *J. Chem. Phys.* **1975**, *63*, 1926.
 (10) Kirmse, R.; Stach, J.; Dietzsch, W.; Hoyer, E. *Inorg. Chim. Acta* **1978**, *26*, L53.
 (11) Attanasio, D.; Keijzers, C. P.; Van den Berg, J. P.; De Boer, E. *Mol. Phys.* **1976**, *31*, 501.
 (12) Kirmse, R.; Solovev, B. V. *J. Inorg. Nucl. Chem.* **1977**, *39*, 41.
 (13) Stach, J.; Kirmse, R.; Dietzsch, W. *Inorg. Chim. Acta* **1979**, *36*, L395.
 (14) Sjölin, L.; Lindqvist, O.; Sieler, J.; Steimecke, G.; Hoyer, E. *Acta Chem. Scand., Ser. A* **1979**, *A33*, 445.