

exchange the NMR environments of both alkynes by flipping first one alkyne and then the other.^{1e,6}

Possible chelate-based rearrangements could also equilibrate both ends of the alkynes. Rearrangement of the octahedral ground-state structure to a trigonal-prismatic intermediate (cf. Mo(CO)₂(dte)₂¹⁵) would generate a C_{2v} molecular entity with all alkyne units equivalent by symmetry. Alternatively dechelation of a bound sulfur and rearrangement of the five-coordinate species through a C_{2v} geometry could effect the observed exchange (cf. W(O)(RC₂R)(dte)₂).⁴ Although neither of these rearrangements can be rigorously excluded, reference to earlier studies of Mo(RC₂R)₂(dte)₂ fluxionality suggests that alkyne rotation is the most reasonable choice for the dynamic process under consideration. Note that either sulfur dechelation or a trigonal-prismatic intermediate structure would be expected to average not only the alkyne termini but also the dithiocarbamate substituents. For the pyrrole case, rotation around the C-N bond at low temperatures conceals any further chelate-based rearrangement with a higher energy barrier. However, for alkyl-substituted dithiocarbamates the different alkyl groups retained their chemical shift integrity even when the alkynes were rapidly averaging on the NMR time scale, thus ruling out dechelation or metal-based global geometric rearrangements for the al-

kyldithiocarbamate complexes. The similarity of the barriers for averaging of the alkyne environments of the pyrrole-*N*-carbodithioate complexes discussed here and for Mo-(EtC₂Et)₂(S₂CNEt₂)₂ (15.1 kcal/mol) suggests that an analogous process is occurring in each of these complexes. For this reason we feel alkyne rotation is the most likely mechanism for the high-temperature exchange process observed in Mo-(RC₂R)₂(pdte)₂ (R = Me, H).

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Registry No. Mo(PhC₂Ph)₂(pdte)₂, 87101-84-6; Mo(PhC₂H)₂(pdte)₂, 87101-85-7; Mo(PhC₂Me)₂(pdte)₂, 87101-86-8; Mo-(MeC₂Me)₂(pdte)₂, 87101-90-4; Mo(EtC₂Et)₂(pdte)₂, 87101-87-9; Mo(*n*-BuC₂H)₂(pdte)₂, 87101-88-0; Mo(HC₂H)₂(pdte)₂, 87101-89-1.

Supplementary Material Available: Atomic coordinates used for least-squares analysis (Table VI), weighted least-squares planes and associated deviations (Table VII), dihedral angles between planes (Table VIII), thermal parameters (Table IX), complete bond angles (Table X), and structure factors (Table XI) (20 pages). Ordering information is given on any current masthead page.

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Synthesis, Characterization, and Spectroscopic Studies of Some Metal Derivatives of Hemiporphyrzine

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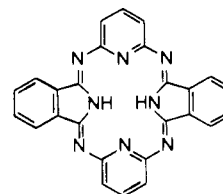
A systematic investigation of the coordination chemistry of the divalent tetraaza macrocycle hemiporphyrzine has been undertaken. Metal derivatives with Co(II), Ni(II), Cu(II), and Zn(II) have been isolated in the form of anhydrous species, water adducts, and complexes of analytical composition M(hp)(HX)_n (HX = HCl, HBr; *n* = 1, 2). On the basis of their chemical and spectroscopic properties the last compounds are formulated as true adduct derivatives of the M(hp) complexes stabilized by proton interaction with the peripheral nitrogens of the ligand. Upon axial coordination the low-spin Co(hp) undergoes a transition to the high-spin form, whereas Cu(hp) gives low-symmetry derivatives which, in some cases, can be described as tetragonally compressed compounds, with a predominant d_{z²} ground state. In spite of its apparent similarity to porphyrin-like ligands, hemiporphyrzine is a rather peculiar macrocycle with coordination properties strongly influenced by the weakness and low symmetry of its ligand field.

Introduction

Hemiporphyrzine (hpH₂, Chart I), first synthesized by Linstead some 30 years ago,¹ is a highly conjugated tetraaza macrocyclic ligand with a number of features in common with the much more popular porphyrins (pH₂) and phthalocyanins (pcH₂). Important differences are its low aromatic character,² due to the presence of a delocalization pathway of 20 π electrons, and the strong inequivalence of the two pairs of inner nitrogens.

A few metal derivatives of hpH₂ have been reported, but information on their properties is sparse and sometimes misleading. The crystal and molecular structures of the free ligand³ and its Ni(II)⁴ and Ge(IV)^{3,5} derivatives have been reported. More recently electrochemical and magnetic data were published for the Mn(II), Co(II), Ni(II), and Cu(II) complexes.⁶⁻⁸ In striking disagreement with the behavior of

Chart I



the related p and pc complexes typical high-spin magnetic moments were found for Co(hp) and Mn(hp), 4.67 and 5.80 μ_B , respectively. On this basis the authors concluded that hpH₂ is not a suitable porphyrin analogue.

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Table I. Analytical Data and Some Physical Properties for M(hp) Complexes

compd	color ^a	anal. data, found (calcd)				μ_{eff}, μ_B
		% C	% N	% H	% X ^b	
Co(hp)	maroon	62.6 (62.78)	22.5 (22.57)	2.8 (2.82)		2.40
Ni(hp)	green	63.0 (62.81)	22.8 (22.55)	2.9 (2.82)		diamag
Cu(hp)	green	62.1 (62.21)	22.4 (22.33)	2.9 (2.79)		1.96
Co(hp)H ₂ O	brown-green	60.3 (60.59)	21.6 (21.75)	3.3 (3.11)		4.50
Ni(hp)(H ₂ O) ₂	green	58.4 (58.57)	21.1 (21.02)	3.4 (3.38)		3.10
Zn(hp)(H ₂ O)	green	59.8 (59.83)	21.4 (21.4)	3.4 (3.07)		$\chi_M = 1.23 \times 10^{-4}$ cgsu
Co(hp)(HCl) ₂	brown-red	55.1 (54.76)	19.2 (19.65)	3.0 (2.83)	12.0 (12.43)	4.60
Ni(hp)(HCl) ₂	red	54.4 (54.78)	19.6 (19.66)	3.0 (2.83)	11.0 (12.44)	3.00
Ni(hp)(HBr) ₂	red	46.4 (46.46)	16.8 (16.75)	2.8 (2.39)	23.6 (24.25)	
Cu(hp)(HCl) ₂	red	53.9 (54.30)	19.0 (19.50)	3.0 (2.78)	11.5 (12.35)	1.80
Zn(hp)(HCl)	brown-red	57.5 (57.78)	20.5 (20.74)	3.0 (2.78)	6.3 (6.57)	$\chi_M = 1.24 \times 10^{-4}$ cgsu
Zn(hp)(HCl) ₂	red	52.8 (54.13)	19.1 (19.43)	3.1 (2.78)	10.4 (12.31)	
Zn(hp)(HBr)	brown-red	53.3 (53.4)	19.1 (19.18)	2.8 (2.57)	14.2 (13.7)	

^a The color refers to ground materials. ^b All the HX derivatives are used and analyzed as crude products. In spite of some less satisfactory analytical results the reported formulation is firmly established also on the basis of X-ray and IR spectra.

Recently we have undertaken a systematic investigation of the hpH₂ derivatives with the first transition series metals, our main interest being the reactivity of these complexes with small molecules such as CO, O₂, NH₃, etc. Preliminary results indicated that different compounds can be obtained depending on preparative details and that the chemical formulation of some of the compounds already reported, such as the Co(II) complex, was incorrect.

These findings stimulated a more complete characterization, and we now report the synthesis and some general properties of the Co(II), Ni(II), Cu(II), and Zn(II) derivatives of hpH₂.

Experimental Section

Reagents. All materials and solvents were of reagent grade and were used as supplied. The free hemiporphyrine ligand was prepared as previously reported⁹ and used as such or after vacuum sublimation (~420 °C, 10⁻² torr).¹⁰ ⁶³Cu was supplied by Oak Ridge National Laboratory, Oak Ridge, TN, in the form of ⁶³CuO.

Preparation of Metal Complexes. The metal complexes were prepared by reacting hpH₂ with metallic acetates or halides in dimethylformamide (DMF) heated to reflux. A metal-to-ligand ratio larger than unity was always used to obtain final yields between 80 and 100%. In the case of copper, a much larger excess of the metal ion was necessary (M/hpH₂ > 2). Depending on the metal ion, anhydrous (Ni²⁺, Cu²⁺) or hydrated (Co²⁺, Zn²⁺) derivatives were obtained with the acetate reaction, whereas the halide reaction invariably gave products of analytical composition M(hp)(HX), M = Zn²⁺, or M(hp)(HX)₂, M = Ni²⁺, Co²⁺, Cu²⁺. Typical preparations are as follows.

Co(hp)H₂O. hpH₂ (400 mg, 0.9 mmol) and Co(CH₃COO)₂·4H₂O (300 mg, 1.2 mmol) were gently refluxed in DMF (6 mL) for 3 h. After the mixture cooled, the brown precipitate was filtered, washed with DMF and methanol, and vacuum-dried. The complexes were usually purified by vacuum sublimation (~420 °C, 10⁻² torr). In this way Zn(hp) and Co(hp) are obtained as anhydrous or partially anhydrous complexes. Upon air exposure the Zn complex readily

reconverts to the monohydrate, and simple treatment with solvents like DMF or nitrobenzene yields a complete conversion of Co(hp) to Co(hp)H₂O.

Co(hp)(HCl)₂. A suspension of hpH₂ (400 mg, 0.9 mmol) in 12 mL of DMF was stirred at room temperature for about 30 min. CoCl₂·6H₂O (280 mg, 1.2 mmol) was added, and the suspension was heated to reflux. After 1 h the reddish precipitate was filtered, washed with DMF and CH₃OH, and vacuum-dried.

Longer reaction times (up to 8 h) do not modify the composition of the final product. Since vacuum sublimation led to an almost complete loss of HX, the crude complexes were normally used.

Co(hp), Ni(hp)(H₂O), and Zn(hp)(HCl)₂ could not be obtained directly and were prepared as follows.

Co(hp). Repeated vacuum sublimation of Co(hp)H₂O yielded reasonably pure samples of Co(hp), but better results were obtained by heating a few hundred milligrams of the monohydrate at 250 °C for 5–6 h under a stream of rigorously dehydrated nitrogen.

Ni(hp)(H₂O)₂. This compound could be obtained by refluxing Ni(hp)(HCl)₂ in DMF for about 2 h. Alternatively, crystallization of Ni(hp) from pyridine yielded an air-unstable bis(pyridine) derivative which slowly converted to the dihydrate (8 weeks). Exposure of Ni(hp)(py)₂ to water vapors can shorten this time to about 3 days.

Zn(hp)(HCl)₂. A suspension of Zn(hp)HCl or Zn(hp)H₂O in DMF containing a slight excess of 0.1 M HCl was stirred for a few minutes at room temperature. The heterogeneous reaction gave a red solid, which was filtered, washed with DMF, and vacuum-dried. Similarly all the above complexes can be converted to the corresponding M(hp)(HCl)₂ species.

Analytical data and some physical properties of all the complexes isolated are reported in Table I.

Physical Measurements. Thermogravimetric analyses were carried out under anhydrous N₂ on a Du Pont 950 thermal analyzer. IR spectra and optical reflectance spectra were recorded respectively on a Perkin-Elmer 580B and on a Beckman DK2A spectrophotometers. EPR spectra were recorded with a Varian E 9 spectrometer equipped with a 35-GHz microwave bridge. An Oxford continuous-flow cryostat (ESR 9) was used to measure liquid-helium spectra at the X-band frequency. Field and frequency were measured with a Bruker BNM20 gauss meter and with a 6246A Systrom-Donner counter. Doped samples were obtained by cosublimation or direct preparation from metal salts. Magnetic susceptibilities were measured by the Gouy method. Diamagnetic corrections were obtained from the magnetic susceptibility of the Zn(II) complexes. X-ray powder spectra were measured with a Debye camera using Cu K α filtered radiation.

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(10) Upon simple suspension in solvents like DMF, the red anhydrous ligand easily converts to the yellow monohydrate. The high thermal stability (up to 170 °C) and the lowering of the NH stretching frequency (200 cm⁻¹) indicate fairly strong interaction between the macrocycle and the water molecule.

Table II. Electronic Absorption Spectral Data for Solid M(hp) Complexes in the Region 6000–16 000 cm^{-1}

compd	d-d bands, cm^{-1} (nm)
Co(hp)	9350 (1070)
Ni(hp)	
Cu(hp)	12 050 (830)
Co(hp)H ₂ O	10 750 (930)
Ni(hp)(H ₂ O) ₂	9090 (1100), 10 530 (950)
Co(hp)(HCl) ₂	10 000 (1000)
Ni(hp)(HCl) ₂	8475 (1180)
Cu(hp)(HCl) ₂	10 000 (1000), 12 900 (775)

Elemental analyses were performed by the Servizio Microanalisi-Area della Ricerca di Roma and by A. Bernhardt-Analytische Laboratorien, Elbach, West Germany.

Results

M(hp) Species. The reaction of hpH₂ with an excess of the appropriate metallic acetate, in refluxing DMF, gives two anhydrous nonisomorphous complexes, Ni(hp) and Cu(hp), and two isomorphous monohydrates, Co(hp)H₂O and Zn(hp)H₂O. Co(hp) and Zn(hp) were obtained by heating the corresponding hydrates for a few hours at ca. 250 °C under a stream of anhydrous nitrogen. The former is an air-stable compound whereas the latter readily reconverts to Zn(hp)H₂O upon air exposure. Among the four anhydrous complexes isolated only Co(hp) and Ni(hp) are isomorphous and show superimposable IR spectra (Figure 4).

The optical and magnetic properties of the M(hp) compounds are summarized in Tables I and II. Co(hp) is a low-spin compound with a room-temperature magnetic moment of 2.40 μ_B , suggesting that the reported value of 4.67 μ_B ⁸ was obtained by measuring the monohydrate derivative.

Polycrystalline EPR spectra were obtained, at the X- and Q-band frequencies, by diluting Cu(hp) and Co(hp) in the diamagnetic Ni(II) and Zn(II) derivatives and in the free ligand. With the exception of the system Co/Ni(hp) the host and guest compounds were not isomorphous and the geometry of the host was found to have a strong effect on the electronic properties of the doping impurity. In the case of the Co(II) ion a transition from the low- to the high-spin state was observed.

Measurements on the pure paramagnetic compounds were prevented by the low solubility of these complexes in nondonor solvents.

M(hp)L_n Species (L = H₂O, HCl, HBr; n = 1, 2). In addition to the above-mentioned Co(hp)H₂O and Zn(hp)H₂O, Ni(hp)(H₂O)₂ could be prepared by exchange of the other adducts (see Experimental Section), whereas H₂O derivatives of the much less reactive Cu(hp) could not be obtained as pure compounds.

Co(hp)H₂O, Ni(hp)(H₂O)₂, and Zn(hp)H₂O are air-stable, sparingly soluble complexes that crystallize unchanged from high-boiling polar solvents such as DMF. Thermogravimetric analysis indicated that Ni(hp)(H₂O)₂ loses its coordinated water in a single step at ca. 100 °C whereas Co(hp)H₂O and Zn(hp)H₂O are stable up to 220–240 °C. This much higher thermal stability is paralleled by a lower OH stretching frequency (3100 cm^{-1} vs. 3250 cm^{-1} in Ni(hp)(H₂O)₂) and by the finding that Co(hp)H₂O can sublime unchanged, thus pointing to an unusually strong interaction between these complexes and the water molecule.

The metal chlorides of Co(II), Ni(II), Cu(II), and Zn(II) all react with hpH₂ in hot DMF solution to give stable products of analytical composition M(hp)(HCl)₂, M = Co, Ni, Cu, or Zn. Analogous HBr derivatives can be obtained by using the nickel(II) and zinc(II) bromides, whereas the iodides mainly give the anhydrous or hydrated compounds. Prolonged reaction times (up to 8 h) do not modify the composition of the final products, whereas almost pure samples

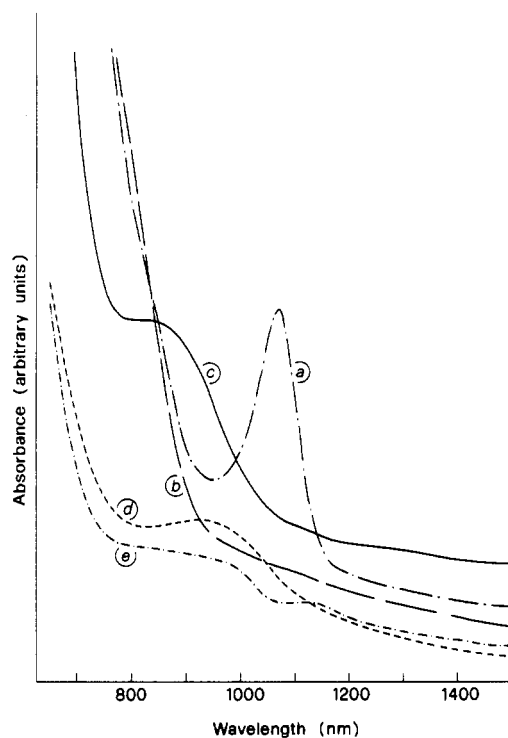


Figure 1. Electronic reflectance spectra of (a) Co(hp), (b) Ni(hp), (c) Cu(hp), (d) Co(hp)H₂O, and (e) Ni(hp)(H₂O)₂.

of Zn(hp)(HCl)₂ are obtained by stopping the reaction after ca. 30 min. This latter compounds, as well as all the other bis adducts, was also prepared by simple reaction of HCl with Zn(hp)HCl or Zn(hp)H₂O suspended in cold DMF (see Experimental Section).

Co(hp)(HCl)₂, Ni(hp)(HCl)₂, and Cu(hp)(HCl)₂ form an isomorphous series, although different crystal modifications of the Co(II) and Ni(II) compounds could be obtained by slightly changing the reported preparative procedure. All the bis adducts, including Zn(hp)(HX)₂, exhibit almost superimposable IR spectra. The sample spectra in Figure 4c,d show the essential features of the common M(hp) core, with some additional absorptions. Particularly significant are the bands in the region 3300–2700 cm^{-1} , which we assign to the vibrations of the N–H bonds formed by the proton–ligand interaction discussed below.

The M(hp)(HX)_n species are indefinitely stable at room temperature and do not show any loss up to ca. 300 °C. At this temperature Ni(hp)(HCl)₂ and Cu(hp)(HCl)₂ lose both the HCl molecules, whereas the Zn(II) and Co(II) analogues first give the corresponding monoadducts at 280 and 350 °C, respectively. Co(hp)HCl, obtained in this way, gave IR and X-ray powder spectra identical with those of Zn(hp)HCl. However, satisfactory elemental analyses could not be obtained and the compound was not characterized further. Upon vacuum sublimation all the HX derivatives are recovered as anhydrous species apart from Co(hp)(HCl)₂, which gives a mixture of Co(hp), Co(hp)HCl, and Co(hp)(HCl)₂.

This high solid-state stability is not paralleled in solution. All the M(hp)(HCl)_n species easily dissociate upon dissolution in hot DMF or cold pyridine, unless an excess of HCl is present. The anhydrous or solvated species are recovered from these solutions, and similarly, suspensions of M(hp)(HCl)_n in cold DMF instantaneously give the unchlorinated compounds, upon treatment with a DMF solution of thallium acetate. Since the metalation reaction of hpH₂, as well as of other related macrocycles,¹¹ is not a simple process which easily

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Table III. EPR Spectral Data for Co(hp) Complexes (Hyperfine Components $\times 10^{-4} \text{ cm}^{-1}$)

compd ^a	g_1	g_2	g_3	A_1^{Co}	A_2^{Co}	A_3^{Co}
Co/Ni(hp)	3.560	1.831	1.725	249.5	<i>b</i>	31.5
Co/Zn(hp)H ₂ O	6.77	2.375	1.55	229	≤ 15	65
Co/Zn(hp)HCl	7.00	2.314	1.52	267	≤ 13	68.5
Co/Zn(hp)(HCl) ₂	6.66	2.723	1.65	224	≤ 21	76

^a A nominal cobalt concentration of about 5% was used. The spectrum of Co/Ni(hp) was recorded at 35.0 GHz at 110 K. All the other spectra were measured at 9.3 GHz at ca. 10 K.

^b Resolution of this A_1^{Co} component must await completion of a single-crystal study.

Table IV. 35-GHz EPR Spectral Data for ⁶³Cu(hp) Complexes (Hyperfine Components $\times 10^{-4} \text{ cm}^{-1}$)

compd ^a	g_1	g_2	g_3	A_1^{Cu}	A_2^{Cu}	A_3^{Cu}
⁶³ Cu/Ni(hp)	2.177	2.054	2.027	135.5		
⁶³ Cu/Zn(hp)	2.208	2.07	2.07	105.7	24	24
⁶³ Cu/Zn(hp)H ₂ O	2.231	2.093	2.033	104	54	93
⁶³ Cu/Zn(hp)HCl	2.240	2.110	2.031	87	45	106
⁶³ Cu/Zn(hp)(HCl) ₂	2.255	2.141	2.028	88	32	106

^a A nominal copper concentration of about 2% was used. All the spectra were measured at room temperature.

proceeds in the cold, these properties strongly support the formulation of the above compounds as true adducts of the M(hp) complexes.

The optical and magnetic properties of all the H₂O and HX derivatives are given in Tables I and II.

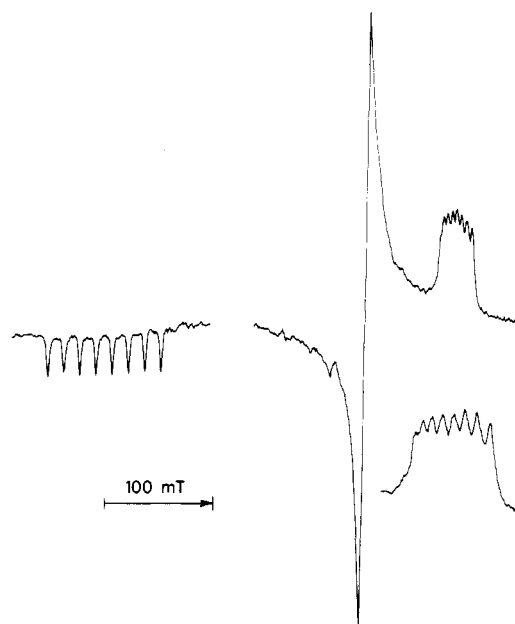
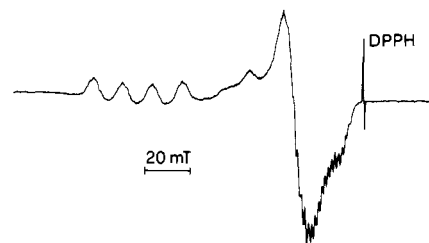
The EPR spectra (Tables III and IV) were recorded by diluting the Cu(II) and Co(II) ions into the three available matrixes, i.e. Zn(hp)H₂O, Zn(hp)HCl, and Zn(hp)(HCl)₂. Only the systems Co/Zn(hp)H₂O and Co/Zn(hp)HCl correspond to isomorphous substitutions, whereas in all other cases the host and guest compounds were not isomorphous (Co/Zn(hp)(HCl)₂ and Cu/Zn(hp)(HCl)₂) or the pure paramagnetic compounds could not be isolated (Cu(hp)H₂O and Cu(hp)HCl). The Cu(II) spectra were recorded at room temperature at the Q-band frequency and did not show significant variations down to liquid-nitrogen temperature. The Co(II) adducts are all high-spin species, and their spectra were recorded at ca. 10 K at the X-band frequency.

Discussion

M(hp) Species. Ni(hp) crystallizes in the monoclinic space group *C2/c* with *Z* = 4. Its crystal structure determination dates back to 1953⁴ and is affected by rather large experimental errors.³ The hemiporphyrine anion appears to be nonplanar, with the isoindole and pyridine rings tilted by about 25° out of the equatorial plane in opposite directions. In spite of this the four inner nitrogens are almost coplanar with the central metal. The Ni(II) ion is in a low-symmetry environment mainly due to the strong inequivalence of the isoindole and pyridine nitrogens. The two bond distances are 190 and 198.5 pm, respectively. No significant intermolecular interactions are present.

Ni(hp) is diamagnetic, and its d-d spectrum is completely masked by ligand and charge-transfer absorptions which extend down to 13 500 cm⁻¹.

The low-spin, isomorphous Co complex shows a rather intense absorption band at 9350 cm⁻¹, which is typical of planar Co(II) complexes¹² and can be assigned to the $|yz\rangle$ or $|z^2\rangle \rightarrow |x^2 - y^2\rangle$ transition.¹³ At the Q-band frequency polycrystalline Co/Ni(hp) yields a rhombic EPR spectrum (Table III; Figure 2) with $g_1 = 3.560 \gg g_2 \approx g_3 = 1.831, 1.725$, whereas the

**Figure 2.** Q-band EPR powder spectrum of Co/Ni(hp) at 105 K.**Figure 3.** Room-temperature Q-band EPR powder spectrum of ⁶³Cu/Ni(hp).

usual porphyrin-type spectrum, $|z^2\rangle$ ground state, is axial and has a reversed relationship between the principal *g* values ($g_{\perp} \approx 3.0 \gg g_{\parallel} < 2.0$).¹⁴ In the absence of rotation data the orientation of the magnetic axes is not known and a reliable assignment of the ground state is not possible.¹⁵ The close similarity of our spectrum with that of low-symmetry Schiff base type complexes¹⁶ would favor a $|yz\rangle$ ground state, but the first doublet excited state is very close in energy (ca. 1500 cm⁻¹). Single-crystal measurements on Co/Ni(hp) are in progress and should clarify this point.

The transition of Co(hp) from low- to high-spin configuration upon dilution into the nonisomorphous Zn(hp) and hpH₂ indicates that very low-lying quartet states are present in this complex. The crystal and molecular structure of Zn(hp) is not known, but in the case of hpH₂ two aza nitrogens from other ligand molecules lay above and below the molecular plane at ca. 330 pm along the axial direction.³ Deviations from planar geometry, which are probably present also in Zn(hp), strongly affect the electronic properties of the Co(II) ground state. The energy of the excited quartet states is lowered, and if they are close enough, a change in the ground-state spin multiplicity can occur.¹⁷

Cu(hp) shows a broad low-energy d-d band (12 050 cm⁻¹), suggesting that a tetrahedral, *D*_{2d}, distortion is present in the pure compound.¹⁸ However, the rhombic EPR spectrum

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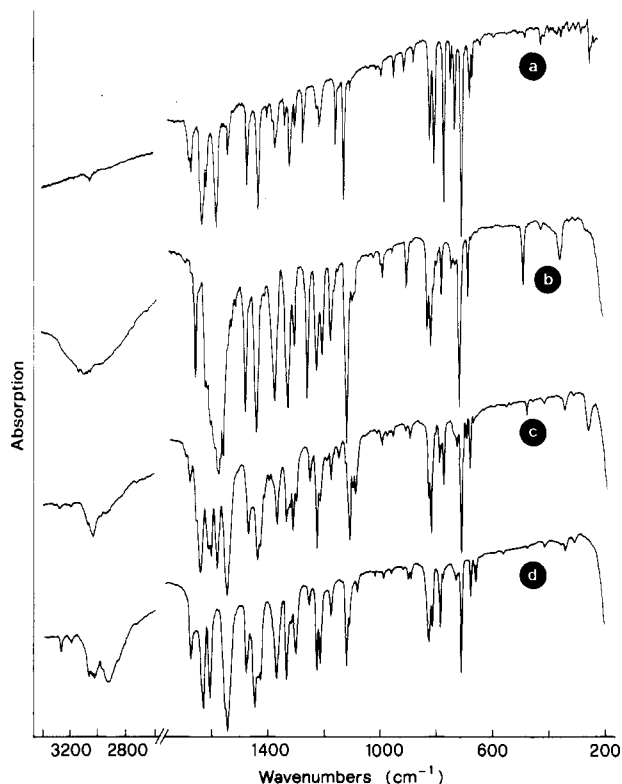


Figure 4. Infrared spectra of (a) Co(hp), (b) Co(hp)H₂O, (c) Co(hp)HCl, and (d) Co(hp)(HCl)₂ in the region 4000–200 cm⁻¹. Spectrum a was obtained by subliming the sample directly on CsI disks. The others were recorded as Nujol and hexachlorobutadiene mulls.

obtained upon dilution into the nonisomorphous Ni(II) host (Figure 3; Table IV) is not in line with this result. The expected reduction of the A_1 value (135.5×10^{-4} cm⁻¹ as compared to 219×10^{-4} cm⁻¹ for CuPc¹⁹) is not paralleled by a simultaneous increase in g_1 . The measured g values are similar to those of related macrocyclic complexes,¹⁴ pointing to an essentially planar stereochemistry. Therefore, the small A_1 value is better interpreted in terms of a strong deviation from tetragonal symmetry, which allows mixing of the $|z^2\rangle$ orbital into the $|x^2 - y^2\rangle$ ground state. The two orbitals give contributions to A_1 that are opposite in sign, qualitatively accounting for the low experimental value.²⁰

Clear nitrogen hyperfine structure was detected on the three g features of the spectrum. Because of the presence of inequivalent nitrogens more than $2nI + 1 = 9$ lines are expected from the splitting of each copper line. Although this is the case, low resolution and dissymmetries in the pattern prevented a precise determination of the couplings to be made.

M(hp)L_n Species (L = H₂O, HCl, HBr; n = 1, 2). All the hemiporphyrzine complexes are fairly strongly reactive toward axial ligation, and in many cases, 1/1 or 1/2 adducts are obtained directly from the preparation. This is true even in these cases where the presence of a fully occupied $|z^2\rangle$ orbital, d^8-d^{10} configurations, would anticipate fairly stable four-coordinated complexes. Apparently this axial reactivity is larger than in the related porphyrin complexes and, more importantly, is less dependent on the nature of the metal ion. The existence of a stable Ni(hp)(H₂O)₂ complex is a convincing example of this behavior.

The reaction between hpH₂ and metal halides yields M(hp)(HX)_n species which we formulate as true adduct deriv-

atives of the M(hp) complexes on the basis of their chemical and spectroscopic properties (see below). Alternative formulations such as free ligand adducts of the metal halides or, more generally, intermediates in the metalation process such as the so-called "sitting-atop" porphyrin complexes cannot be reconciled with these properties.²¹

Although similar adducts with different complexes are not unknown,^{22,23} this seems to be the first characterization of an extensive series of such compounds in the solid state. The best known example in the literature, i.e. FePcHCl,^{22,24} is considerably complicated by the possible existence of iron in different oxidation states. However, there is general agreement that these complexes are strongly stabilized if extensive proton ligand interaction is possible.

In the case of the PcH₂ ligand and its complexes, protonation, or interaction with Lewis acids, of the peripheral aza nitrogens has been clearly demonstrated.^{25,27}

Similar interactions are present in the M(hp)(HX)_n complexes and imply that partial dissociation of the HX molecule has occurred on coordination. We believe that the relative ease with which the M(hp) complexes coordinate protic molecules is probably due to the combined effect of a fairly weak in-plane ligand field and the possibility of such proton-ligand interaction. Its presence is clearly demonstrated by the already mentioned IR bands which occur in the N-H stretching region. Closely similar absorptions were found in the analogous phthalocyaninato compounds²⁸ and assigned to proton interaction with both the outer and the inner nitrogens of the ligand. However, the interactions with the inner pyrrolic nitrogens was found to affect strongly the π -systems and the symmetry of the ligand and, hence, the general appearance of the spectrum. We have already pointed out that coordination of the HX molecules does not influence the basic trend of the spectra, thus suggesting that the acid protons mainly interact with the outer nitrogens.

The similarity of the spectra obtained when HBr is substituted for HCl supports partial dissociation of the acid molecules upon coordination.

A similar proton-ligand interaction is probably present in the H₂O-containing complexes, where the N-H absorptions are more difficult to locate.

The bisadduct compounds, i.e. Ni(hp)(H₂O)₂ and the three isomorphous M(hp)(HCl)₂ complexes, M = Co, Ni, Cu, exhibit magnetic and optical properties that are entirely consistent with a six-coordinated, grossly tetragonal geometry.

Ni(hp)(H₂O)₂ has a room-temperature magnetic moment of $3.10 \mu_B$. Its optical spectrum shows two weak absorptions at 9090 and 10350 cm⁻¹ (Figure 1), which are assigned as the lowest energy octahedral transition split by the tetragonal field.²⁹ No splitting is apparent on the first octahedral band of Ni(hp)(HCl)₂ at 8475 cm⁻¹, suggesting that a considerably lower tetragonal distortion is present in this case.

Co(hp)(HCl)₂, as well as the other Co(II) adduct Co(hp)H₂O, is a high-spin compound with $\mu_{\text{eff}} = 4.60 \mu_B$. Once again this confirms that very low-lying excited quartet states are present in Co(hp). Previous examples of this behavior are

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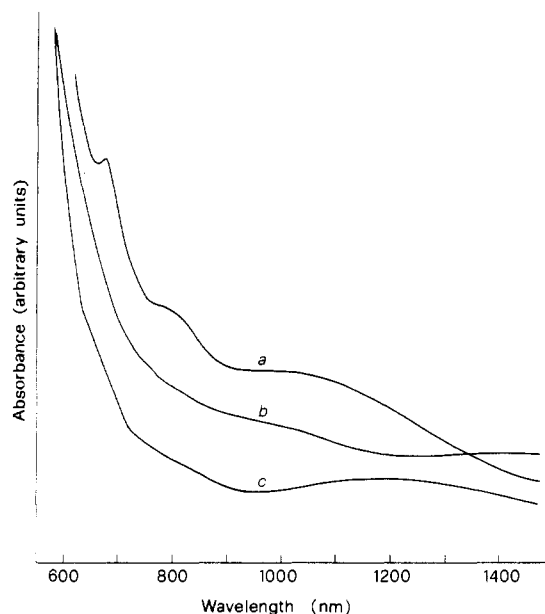


Figure 5. Electronic reflectance spectra of (a) $\text{Cu}(\text{hp})(\text{HCl})_2$, (b) $\text{Co}(\text{hp})(\text{HCl})_2$, and (c) $\text{Ni}(\text{hp})(\text{HCl})_2$.

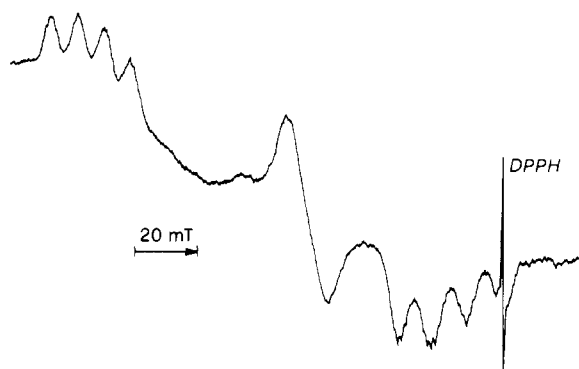


Figure 6. Room-temperature Q-band EPR powder spectrum of $^{63}\text{Cu}/\text{Zn}(\text{hp})\text{HCl}$.

limited to some five-coordinated derivatives of CoPc with substituted pyridines,³⁰ whereas all the other macrocyclic $\text{Co}(\text{II})$ complexes retain their low-spin configuration on going from four to higher coordination numbers. Only the first expected absorption is detected for $\text{Co}(\text{hp})(\text{HCl})_2$, at ca. $10\,000\text{ cm}^{-1}$, whereas the d-d spectrum of the copper analogue is partially resolved in two main absorptions at $10\,000$ and $12\,900\text{ cm}^{-1}$.

Both with water and with hydrochloric acid $\text{Co}(\text{hp})$ and $\text{Zn}(\text{hp})$ form 1/1 adducts instead of, or in addition to, the already discussed 1/2 compounds. In the region not masked by ligand or CT transitions the high-spin $\text{Co}(\text{hp})\text{H}_2\text{O}$ shows a single low-intensity band at ca. $10\,750\text{ cm}^{-1}$, suggesting that a six-coordinated tetragonal structure is present also in this 1/1 adduct. Analytically pure samples of $\text{Co}(\text{hp})\text{HCl}$, isomorphous with the $\text{Zn}(\text{II})$ analogue, could not be obtained, and its optical spectrum is not reported. However, dilution of $\text{Co}(\text{II})$ into $\text{Zn}(\text{hp})\text{H}_2\text{O}$ and $\text{Zn}(\text{hp})\text{HCl}$ or $\text{Zn}(\text{hp})(\text{HCl})_2$ gave almost superimposable EPR spectra, (Table III; Figure 7), confirming that a six-coordinated tetragonal geometry is present in both the $\text{Co}(\text{II})$ and the $\text{Zn}(\text{II})$ 1/1 adducts. The raising of the coordination number from 5 to 6 can be due to dimerization of the molecules with strong intermolecular interactions or to the formation of infinite chains with the water or hydrochloric acid groups acting as bridging ligands.

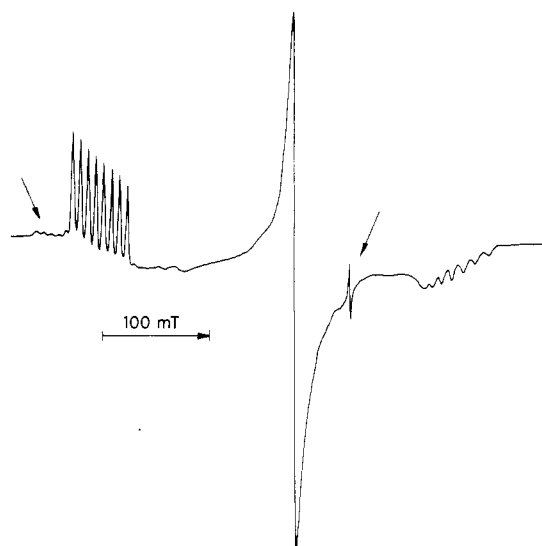


Figure 7. X-Band EPR powder spectrum of $\text{Co}/\text{Zn}(\text{hp})\text{H}_2\text{O}$ at 10 K. Arrows indicate a radical absorption and the weak lines attributed to Co-Co pairs.

The $\text{Co}(\text{II})$ ion diluted into the $\text{Zn}(\text{hp})$ adducts behaves as an effective spin $1/2$, showing that these low-symmetry complexes give rise to a zero-field splitting that is definitely higher than the microwave energy ($\sim 0.3\text{ cm}^{-1}$). It is well-known that direct information concerning the detailed stereochemistry around the metal ion is difficult to extract from these spectra.³¹ However, the measured parameters are in line with those of other six-coordinated high-spin $\text{Co}(\text{II})$ complexes reported so far.^{32,33} Other weak lines are clearly observed in the region near $g = 12$ ($A \approx 6.8\text{ mT}$) (Figure 7) and interpreted as cobalt-cobalt pair spectra.^{34,35}

The EPR spectra of the $\text{Cu}(\text{II})$ adducts were obtained by diluting $\text{Cu}(\text{hp})$ into the three diamagnetic hosts $\text{Zn}(\text{hp})\text{H}_2\text{O}$, $\text{Zn}(\text{hp})\text{HCl}$, and $\text{Zn}(\text{hp})(\text{HCl})_2$. We recall that the pure copper compounds could not be isolated in the first two cases whereas $\text{Cu}(\text{hp})(\text{HCl})_2$ and $\text{Zn}(\text{hp})(\text{HCl})_2$ are not isomorphous. The three systems give strictly similar EPR spectra (Table IV), confirming that the coordination geometry around the $\text{Zn}(\text{II})$ ion is essentially the same in both the 1/1 and the 1/2 adducts. The sample spectrum presented in Figure 6 is peculiar in that it shows an unusually rhombic g tensor ($g_1 - g_2 \approx g_2 - g_3$) with one g value close to g_e and a strongly reduced anisotropy of the metal hyperfine. These features are typical of a very low-symmetry environment with extensive mixing of different d orbitals into the ground state. Labeling the experimental principal values 1, 2, 3 as x, y, z and taking as ground state the linear combination $a|z^2\rangle + b|x^2 - y^2\rangle$, we evaluated the mixing coefficients following a previously reported procedure.²⁰

$\text{Cu}/\text{Zn}(\text{hp})(\text{HCl})_2$, with $b = 0.285$, has a predominant $|z^2\rangle$ ground state. The $|x^2 - y^2\rangle$ admixture is much larger in $\text{Cu}/\text{Zn}(\text{hp})\text{H}_2\text{O}$, which gives $b = 0.462$. Recalling that $a|z^2\rangle + b|x^2 - y^2\rangle$ reduces to $|z^2 - y^2\rangle$ when $b = 0.5$, the ground state of $\text{Cu}/\text{Zn}(\text{hp})\text{H}_2\text{O}$ is better described as a predominant $|x^2 - y^2\rangle$ orbital after interchanging the x and z axes. An intermediate situation occurs in $\text{Cu}/\text{Zn}(\text{hp})\text{HCl}$.

These unexpected results are the direct consequence of the strong dissymmetry of the in-plane ligand field in $\text{Cu}(\text{hp})$. The

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physical meaning is that, upon axial coordination, the direction of the unique axis can switch from the normal to the macrocyclic plane to the direction of the strongest metal-ligand bond, i.e. to the metal-isindole nitrogen direction. Simultaneously the electronic structure changes from rhombically elongated to rhombically compressed.

Conclusive support for this picture should come from single-crystal studies, through location of the highest and lowest *g* values along the above-mentioned directions. Unfortunately, we were not able, up to now, to obtain suitable single crystals from any of the copper-doped zinc adducts.

Conclusions

The information provided above indicates that hpH_2 , in spite of its apparent similarity with porphyrin-like ligands, is a rather peculiar macrocycle with a coordination chemistry strongly influenced by its low aromaticity, by the inequivalence of the coordinating nitrogens, and by the weakness of its ligand field.

Compared to other macrocycle species, the $M(hp)$ complexes appear to be low-symmetry compounds with substantial admixture of different *d* orbitals into the ground state. They easily coordinate axial ligands, and in the case of protic molecules, the adducts are strongly stabilized by proton-ligand

interaction with partial dissociation of the coordinated molecules. Both the 1/1 and the 1/2 adducts isolated behave as six-coordinated compounds, apparently through intermolecular association. Furthermore, the coordination of axial ligands strongly affects the electronic structure of the $M(hp)$ complexes, as shown by the ground-state changes that occur for the two quasi-degenerate Co(II) and Cu(II) compounds. Upon axial coordination Co(hp) goes from low- to high-spin configuration and Cu(hp) may change from a rhombically elongated to a rhombically compressed electronic structure.

Besides the preparation of crystals suitable for X-ray analysis current work is now aimed at the characterization of hpH_2 complexes with different metal ions and at the study of their reactivity with small molecules.

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Registry No. Co(hp), 21600-72-6; Ni(hp), 21600-71-5; Cu(hp), 17857-08-8; Co(hp) H_2O , 86822-42-6; Ni(hp)(H_2O) $_2$, 86822-43-7; Zn(hp)(H_2O), 86822-44-8; Co(hp)(HCl) $_2$, 86822-45-9; Ni(hp)(HCl) $_2$, 86822-46-0; Ni(hp)(HBr) $_2$, 86822-47-1; Cu(hp)(HCl) $_2$, 86822-48-2; Zn(hp)(HCl), 86834-25-5; Zn(hp)(HCl) $_2$, 86834-26-6; Zn(hp)(HBr), 86822-49-3.

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Marcasites and Arsenopyrites: Structure, Bonding, and Electrical Properties

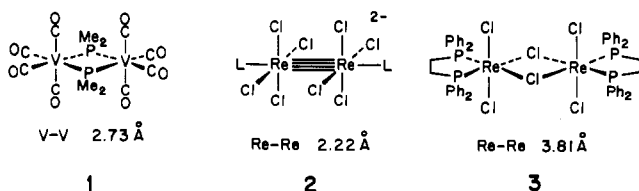
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The structure of marcasite is discussed in terms of infinite chains of trans-edge-sharing octahedra. Distortion of these chains along their axes is considered. In d^6 marcasite, filled-shell repulsion of the ligand backbone keeps the metal atoms apart. In contrast, a uniform shortening of the chain axis for electron count d^4 is seen to result in partial ligand-ligand bond formation ($P-P = 2.7 \text{ \AA}$ in FeP_2) as well as the expected metal-metal bonding. The contraction from d^6 geometry is shown to occur due to the emptying of a $P-P \sigma^*$ orbital early along the reaction coordinate. $M-M$, $L-L$, and $M-L$ interactions all work together to produce a band gap for the d^4 -contracted chain. Arsenopyrite is the result of a pairing distortion (d^5). It is a semiconductor, for the same reason as d^1 $NbCl_4$ is. The optimal electron count at which pairing occurs is related to the nature of the ligand in marcasite, rutile, $NbCl_4$, and model intermediates.

Given a ratio of elements subjected to a certain temperature and pressure, what will come out of a flask? That, incredibly enough, is the question posed by solid-state chemists. Clearly the theoretician can come nowhere near an answer, but it is possible he or she could answer questions of preference for one of a few closely related structures. What do we mean by closely related? It seems reasonable to look for analogies from the comparatively well-understood world of molecules.

Recently, Shaik, Hoffmann, Fisel, and Summerville¹ studied compounds 1-3. Each of these M_2L_{10} compounds has the



same octahedral coordination around the metal and the same

Table I. Distortions as a Function of Electron Count in Some Edge-Sharing Octahedral Structures

structure type	electron count		
	uniform expansion	pairing distortion	uniform contraction
$NbCl_4$ ^{2,13}	d^4	d^1 ($d^{2?}$)	
rutile (MO_2) ¹⁴	d^4, d^5	d^1, d^2, d^3	
marcasite (ML_2) ^{21d} ($L = P-Bi, S-Te$)	d^6	d^5	d^2, d^4

electron count, d^4 . But, what a difference in $M-M$ distance results from changing the ligand in these three compounds.

An obvious extension of the M_2L_{10} edge-sharing compounds to infinity is chain 4 in which octahedra share only trans edges. Three well-known structures, $NbCl_4$, rutile, and marcasite, contain such chains. As in the case of the molecules, contractions perpendicular to the shared edges can occur, leading to shorter $M-M$ distances.

Now, however, this contraction can have any periodicity within the infinite chain. Table I lists data for these compounds, for electron counts d^6 and below, and for the extreme periodicities consisting of the uniform contraction 5 and the

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