Table IV. Variable-Temperature Molar Magnetic Susceptibility per Dimer, χ_m, and Effective Moment, μ_{eff}/Cu(II), for $[CuCl_2(dmgH)]_2$ (Fitting Parameters: $J = +0.31$ cm^{-1}, $g = 2.00$, $\Theta = -0.82$ K, $N\alpha = 60 \times 10^{-6}$ cm^3 mol^{-1}, Curie Constant $C_{Cl} = 0.797$)

	$10^{-3}\chi_m$, cm^3 mol^{-1}		μ_{eff}/Cu(II),[a] μ_B	
temp, K	exptl	theor	exptl	theor
4.2	156.25	155.23	1.62	1.61
4.8	138.39	138.10	1.63	1.63
5.7	116.83	118.50	1.63	1.64
6.9	99.46	99.66	1.66	1.66
8.0	86.12	87.00	1.66	1.67
9.4	75.03	74.89	1.68	1.68
10.6	66.82	66.91	1.68	1.68
12.5	57.33	57.26	1.69	1.69
15.0	48.01	48.13	1.70	1.70
16.2	44.80	44.71	1.70	1.70
17.6	40.94	41.28	1.70	1.70
19.7	37.25	37.03	1.71	1.71
21.8	33.87	33.58	1.72	1.71
23.8	31.14	30.84	1.72	1.71
25.7	29.05	28.62	1.73	1.71
27.6	26.80	26.70	1.72	1.71
29.8	25.20	24.78	1.73	1.72
31.9	23.43	23.18	1.73	1.72
34.1	22.15	21.72	1.74	1.72
36.2	20.86	20.48	1.74	1.72
38.3	19.57	19.38	1.73	1.72
40.4	18.92	18.40	1.75	1.72
45.4	16.67	16.41	1.74	1.72
50.4	15.07	14.81	1.74	1.72
55.3	13.65	13.51	1.73	1.72
60.3	12.43	12.41	1.73	1.73
65.3	11.53	11.48	1.73	1.73
70.1	10.79	10.70	1.73	1.73
80.2	9.41	9.37	1.73	1.73
100.2	7.62	7.53	1.74	1.73
120.2	6.34	6.29	1.74	1.73
150.3	5.21	5.05	1.76	1.73
179.9	4.37	4.23	1.76	1.73
220.4	3.53	3.47	1.75	1.73
259.8	3.05	2.95	1.76	1.73
298.9	2.70	2.57	1.78	1.73

[a] Calculated from the expression $\mu_{eff} = 2.83(T(\chi_m - N\alpha)/2)^{1/2}$.

tions.[23] For a quantitative evaluation of these effects, however, EPR measurements on single crystals are required.

It is to be noted, finally, that the systematic role of the bridging halogen in the superexchange effect, even in the case of the isomorphous dimers dealt with here, can be assessed most unambiguously *only if* the bridging angle remains virtually the same for any set of dimers under study. The importance of the present work, nonetheless, is rather fundamental, as the research progressing along these lines has already initiated the synthesis of new copper(II) bromide and copper(II) chloride adducts with a number of 1,2-benzoquinone dioxime ligands.[24] So far, the dimeric nature of these new compounds has been most reasonably inferred from the matching results of magnetic and spectroscopic investigations. The novelty of scientific interest in these systems resides in the observation that the electrophilic character of the benzoquinonoid ligands affects the intradimer exchange interaction as well. This observation has led to the anticipation that it might well become possible to induce desirable spin orderings in paramagnetic cluster compounds by systematically modulating the electrophilicity of this type of ligands through proper chemical modifications (ligand-induced nephelauxetic effect[24,25]).

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We thank Dr. E. J. Laskowski for his invaluable assistance with EPR and susceptibility measurements. We owe many thanks to Professors R. H. Holm and H. Taube for the use of their equipments and to Professor K. O. Hodgson and J. M. Berg for their help with X-ray diffractions. M.M.B. acknowledges useful conversations with Professors R. Hoffmann of Cornell and Z. G. Soos of Princeton.

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Registry No. $[CuBr_2(dmgH)]_2$, 69043-81-8; $[CuCl_2(dmgH)]_2$, 41553-44-0.

Supplementary Material Available: A listing of variable-temperature diamagnetic susceptibilities of $Ni(dmg)_2$ measured in the range 4.2–300 K (1 page). Ordering information is given on any current masthead page.

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Evidence for the Existence of the Phthalocyanine Dianion: The Demetalation of Dilithium Phthalocyanine

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There are several reports in the literature that provide evidence for the existence of the metal-free phthalocyanine dianion in solution.[2-5] Whalley[4] measured the spectrum of H_2Pc dissolved in pyridine and observed a single, MPc-like band in the 650-nm region rather than the typical spectrum observed for H_2Pc in aromatic solvents.[5] Analysis of the IR spectrum of metal-free tetraazaporphyrin isolated from a pyridine solution provided evidence for the presence of pyridinium ions.[4] Ledson and Twigg[6] concluded that the metal-like spectrum of H_2Pc in a variety of solvents observed following the addition of base resulted from the metalation of the ring by alkali metal ions. More recently, we have observed that H_2Pc reacts with a variety of ligands in dimethyl sulfoxide (Me_2SO) and *N*,*N*-dimethylacetamide (DMA).[2,7] In each of these experiments, the spectrum of the product exhibited the single MPc-like Q band associated with a D_{4h} symmetry for the ring.[5] The question remains, however, as to whether these species retain the two protons and, therefore, can still be described as H_2Pc. In our analysis of the temperature dependence of the H_2Pc spectrum in Me_2SO and DMA,[2,7] we concluded that the H_2Pc was not completely deprotonated by these weakly coordinating solvents, rather two protonated solvent molecules assumed an axial coordination that resulted in the required D_{4h} symmetry for the ring π system.

We report here additional data to support this finding. Dilithium phthalocyanine (Li_2Pc) is demetalated by distilled water to form a D_{4h}, metal-free species in the weakly coor-

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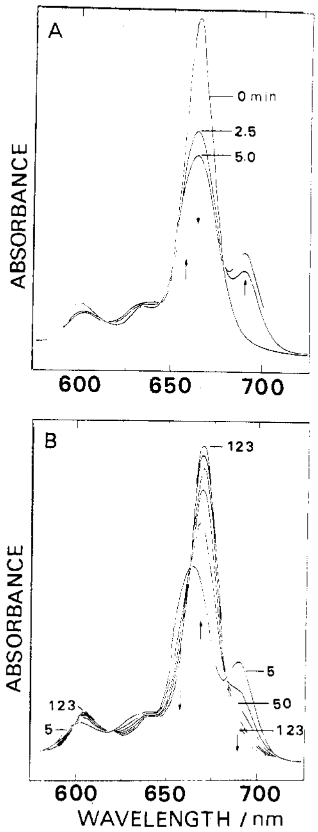

Figure 1. The demetalation of Li_2Pc in DMA following the addition of dilute acid to the cuvette. (a) Spectra recorded during the first 5 min (0.0, 2.5, 5.0 min); the trace at $t = 0.0$ is the initial spectrum with no acid added. The arrows indicate the increase in absorbance at 655 and 685 nm and the reduction at 658 nm. (b) Spectra recorded starting at 5.0 min, the arrows now show the new band forming at 664 nm and the decrease of the 655 and 685 nm bands.

dinating solvents DMA and Me_2SO. The "normal" D_{2h} H_2Pc (with the two protons located in the plane of the ring[8]) is clearly observed in the absorption spectrum during the reaction.

The series of spectra shown in Figure 1 are obtained when 0.1 mL of distilled water (pH ~6) is added to 2.5 mL of Li_2Pc in DMA or Me_2SO. The absorbance at 658 nm of this solution was 0.9 in a 1-cm cuvette. Immediately upon the addition of the water, the main peak at 658 nm collapses while new bands at ca. 655 nm (sh) and 685 nm appear. The absorbance of these bands diminishes quite rapidly (after 5 min) as a single, new band appears at 664 nm. Within 2 h this species, characterized by $\lambda_{max} = 664$ nm, is the only one present. The complete absorption spectra of the new species and that of the initial Li_2Pc in DMA are shown in Figure 2. Spectra recorded for the same species in Me_2SO are red shifted by 2 nm.

Comparison between the spectrum of the final reaction product and the spectra of species made by adding strongly coordinating basic ligands to H_2Pc[2,4,7] indicates that the Li_2Pc has indeed been demetalated. We suggest that solvent molecules, either DMA or Me_2SO, are protonated and can then act as axial ligands above and below the plane of the phthalocyanine ring. If this demetalated species ($\lambda_{max} = 664$ nm) is heated to about 100 °C, the spectrum recorded is similar to that of a heated solution of metal-free phthalocyanine[2,7] in the same solvent: a typical D_{2h} spectrum, with Q bands at 658 and 685 nm (in DMA), is now observed.

While characterization of the initial species as Li_2Pc and the reaction product as H_2Pc is relatively straightforward, the identity of the intermediate observed after 5.0 min in Figure 1 is less clear. Addition of more concentrated acid (HCl, pH 5) to Li_2Pc solutions in either DMA or Me_2SO results in the formation of an unstable species (precipitation occurs within 10 min) with a spectrum shown in Figure 3. There are two, well-resolved bands at 653 and 685 nm and a shoulder at ca. 670 nm.

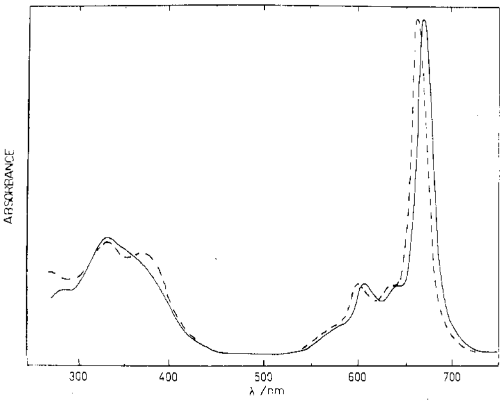

Figure 2. The spectra of the initial Li_2Pc in DMA (---) and the species formed by the addition of dilute acid to the Li_2Pc (—).

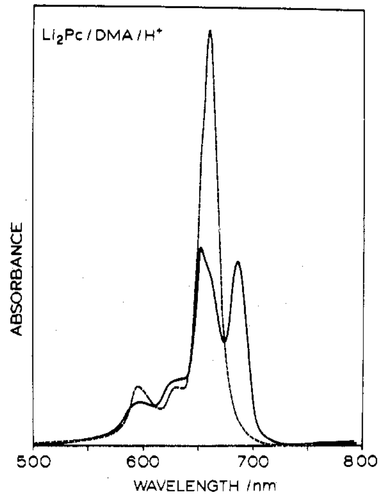

Figure 3. (---) The Q-band region of Li_2Pc in DMA. (—) The spectrum recorded after the addition of pH 5 acid.

Although the Q_x and Q_y band centers observed in the spectrum of H_2Pc in aromatic solvents are somewhat different, for example, at 660 and 698 nm[5] in dichlorobenzene, the band separation and half-widths are much the same in the two types of solvent. In addition, the complicated overlap of transitions in the Q_{vib} region (at about 625 nm) of H_2Pc in aromatic solvents[5] appears to be reproduced in spectra recorded with DMA or Me_2SO, Figure 1 (at 5 min), and, especially, Figure 3. Each of these features is supporting evidence that complete protonation to H_2Pc occurs when dilute acid is added to Li_2Pc in DMA or Me_2SO leaving a D_{2h} H_2Pc in solution.

We would expect that LiHPc would be formed as an intermediate during this demetalation reaction. The preparation of this species has been reported by Linstead et al.[9] although no spectral data were reported. If the D_{2h} arrangement is adopted at this point, then it seems reasonable that the Q bands may well have the same energy as the D_{2h} H_2Pc itself. However, if the D_{4h} arrangement is maintained until after both lithium ions have been displaced, then we would expect a D_{4h} spectrum similar to that of the mixed metal phthalocyanines,

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for example, AgLiPc or CuLiPc.[10]

Dimerization is very common in the chemistries of both phthalocyanines and porphyrins; however, it seems unlikely that at the low concentrations used (ca. 10^{-5} M) in these coordinating solvents (DMA and Me_2SO) and with the very narrow bandwidths observed throughout the sequence of spectra in Figure 1, that the dimer concentration is at all significant. Ring-to-ring dimerization of phthalocyanines appears to result in rather broad bands; see, for example, the comparison between the spectra of H_2Pc in chloronaphthalene and H_2Pc as a sublimed film in ref 11. Tetrasulfanated phthalocyanine solutions are found to be monomeric in Me_2SO[12,13] even though dimerization occurs readily in other solvents at much lower concentrations.

Porphyrins (P) readily form the D_{4h} species H_4P^{2+} in acidic media, with, in general, noncoordinating solvents.[14] For example, trifluoroacetic acid is commonly used to produce H_4P^{2+} complexes in solvents such as benzene.[15] Solvents with a high dielectric constant, such as *N*,*N*-dimethylformamide and Me_2SO, have been shown to reduce the tendency of H_4P^{2+} formation.

Addition of 0.1 mL of concentrated trifluoroacetic acid to a 2.5 mL solution of Li_2Pc in DMA or Me_2SO results in the formation of H_2Pc (characterized by the twin Q bands). No other species could be detected in the absorption spectrum.

This finding further supports our conclusion that the final species formed by the demetalation of Li_2Pc by distilled water, Figure 2, is the D_{4h} H_2Pc rather than the cationic H_4Pc^{2+} complex. The geometry of this H_2Pc species is, then, similar to that of Li_2Pc and Na_2Pc for which typical MPc spectra are observed.

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Registry No. Li_2Pc, 25510-41-2; H_2Pc, 574-93-6.

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Polydentate Ligands Containing Phosphorus. 4. Group 6 Metal Carbonyl Derivatives of *N*-(Diphenylphosphino)methyl Derivatives of Ethylenediamine[1]

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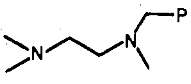
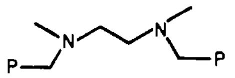
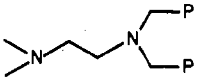
Neutral polydentate ligands can exhibit a wide variety of coordination behaviors, which can influence stereochemistry and other properties of the resulting complexes. Over the years numerous groups have investigated polydentate ligands of group 5 donor atoms.[3-6] Some time ago we[7] synthesized some previously unreported *N*-(diphenylphosphino)methyl derivatives of ethylenediamine by a well-established synthetic route.[8,9] This paper reports on some of the complexes of the group 6 metal carbonyls with these ligands: $Ph_2PCH_2N(CH_3)CH_2CH_2N(CH_3)_2$, L_I, *N*-[(diphenylphosphino)methyl]-*N*,*N*′,*N*′-trimethylethylenediamine; $Ph_2PCH_2N(CH_3)CH_2CH_2N(CH_3)CH_2PPh_2$, L_{IIs}, *N*,*N*′-bis[(diphenylphosphino)methyl]-*N*,*N*′-dimethylethylenediamine; $(Ph_2PCH_2)_2NCH_2CH_2N(CH_3)_2$, L_{IIu}, *N*,*N*-bis[(diphenylphosphino)methyl]-*N*′,*N*′-dimethylethylenediamine; and $(Ph_2PCH_2)_2NCH_2CH_2N(CH_2PPh_2)_2$, L_{IV}, *N*,*N*,*N*′,*N*′-tetrakis[(diphenylphosphino)methyl]ethylenediamine.



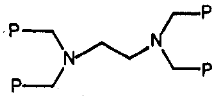
L_I



L_{IIs}



L_{IIu}



L_{IV}

With these ligands, numerous types of coordination behavior can be displayed. For example, the symmetrical bis(phosphine) ligand, L_{IIs}, could conceivably be a mono-, di-, tri-, or tetradentate ligand. If monodentate, then there is a possibility of ambidentate behavior, i.e., N- or P-coordination. If bidentate, then there is the possibility of N,N- (5-membered chelate ring), N,P- (4- or 7-membered chelate ring), or P,P- (9-membered chelate ring) coordination. Further possibilities would result from tri- and tetradentate behavior. In addition, one molecule of ligand might bind to more than one metal center, leading to bridging and possibly to oligomeric coordination compounds. Each of the ligands in this study can display this complex behavior, including the possibility of hexadentate coordination in L_{IV}.

Results and Discussion

In this investigation we have used only soft metals which have a stronger tendency to bind with the soft phosphine donor atoms rather than with the harder amine nitrogen. The following compounds have been synthesized and characterized: $L_ICr(CO)_5$, $L_IMo(CO)_5$, $L_IW(CO)_5$, $L_{IIu}Cr(CO)_4$, $L_{IIu}Mo(CO)_4$, $L_{IIu}W(CO)_4$, $L_{IIu}[W(CO)_5]_2$, $L_{IIs}Cr(CO)_4$, $L_{IIs}Mo(CO)_4$, $L_{IIs}W(CO)_4$, $L_{IIs}[Cr(CO)_5]_2$, $L_{IIs}[Mo(CO)_5]_2$, $L_{IIs}[W(CO)_5]_2$, $L_{IV}[Cr(CO)_4]_2$, $L_{IV}[Mo(CO)_4]_2$, $L_{IV}[W(CO)_4]_2$, $L_{IV}Cr(CO)_4$, $L_{IV}Mo(CO)_4$, $L_{IV}[Cr(CO)_4][Mo(CO)_4]$, and $L_{IV}[W(CO)_5]_4$. The gentle methods of synthesis and specifically chosen stoichiometries of the reactants have resulted in these fairly simple coordination compounds in which only phosphorus is directly coordinated to the transition metal. Generally, this conclusion has been reached by examination of the ^{31}P NMR spectra of the compounds, although occasionally the ^1H NMR spectra also aided in the structural assignments or corroborated the ^{31}P results. The ^{31}P NMR data are given in Table I.

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(1) (a) Part 3: Grim, S. O.; Satek, L. C.; Mitchell, J. D. *Z. Naturforsch.*, in press. (b) Taken in part from the Ph.D. Dissertation of D. P. Shah, University of Maryland, 1976.
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