light. The results of six experiments, when the apparent Φ is plotted vs. fraction of complex photolyzed and extrapolated to zero fraction, yield Φ of 0.35 ± 0.03. As this value is for H^+ uptake, the real quantum yield for disappearance of *trans*-$Cr(en)_2F_2^+$ is equal to or slightly greater than this value depending on how much of the F^- is titrated at a pH of 2.4. This value is lower than reported previously,[10] presumably because of incorrect correction for thermal aquation and H^+-induced processes.

Conclusions. The photoaquation of *trans*-$Cr(en)_2F_2^+$ leads to three products, with **1** the dominant material formed. This material retains the net stereochemistry of the starting material but is still subject to mechanistic stereochemical inversion.[12]

Our results appear to disagree[20] with those of Manfrin et al.;[16] we have only one explanation of this disagreement. In the course of our studies on this system we noted that a solution of *trans*-$Cr(en)_2F_2^+$ has a relatively strong temperature dependence to its absorbance at 520 nm. This amounts to about a 2% change in absorbance between 10 and 20 °C; thus the small spectral differences between photolyzed and unphotolyzed solutions must be made on solutions at the same temperature (as we have done in what is reported herein).

We have examined this phenomenon in sufficient detail to understand its origin in general terms if not in detail. The temperature dependence (for constant absorbance) is more pronounced in the concentrated solutions (short path length) than in dilute ones (long path length). This is, we believe, because ion pairs are the source of the temperature-sensitive absorbancies, and the more concentrated solution causes the greatest number of ion pairs. Photolysis on solutions as concentrated as those used by Manfrin et al. will be subjected to this temperature-dependent absorbancy. However, whatever the cause of difficulty in the absorbance–pH experiments, it is clear that their values of $\Delta\bar{A}$/mol of H^+ consumed are greater than what we find; we are confident of our results because they are verified by ion-exchange separations.

Acknowledgment. We thank Don Dubois for his work on the temperature-sensitive absorbance changes.

Registry No. **1**, 34398-37-3; **2**, 73650-10-9; **3**, 34431-44-2; *trans*-$Cr(en)_2F_2^+$, 24407-74-7.

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[20] From the reported values of Φ_{H+} and Φ_F of Manfrin et al.[16] and their statement that ϵ of "$Cr(en)_2H_2OH^{2+}$" would have to be 200 M^{-1} cm^{-1} at 520 nm, we calculate that they believe the apparent extinction coefficient of the H^+-consuming products of photolysis of *trans*-$Cr(en)_2F_2^+$ is 53 M^{-1} cm^{-1}.

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Superexchange in Copper(II) Dimers. 1. Synthesis, Characterization, and Magnetic Behavior of the Novel Di-μ-bromo-bis[bromo(dimethylglyoxime)copper(II)], $[CuBr_2(dmgH)]_2$

Michel Mêgnamisi-Bêlombê*[1] and Mark A. Novotny

Received May 14, 1979

The study of magnetic superexchange[2-4] interactions in dimeric copper(II) complexes has recently received increased scientific attention from inorganic chemists.[5-9] This rapidly growing interest has been motivated mainly by the urgent search for a sufficiently sound theory on which to base the explanation of the two types of expected intradimer spin orderings, notably the *ferromagnetic* or triplet ground state with the spins oriented parallel and the *antiferromagnetic* or singlet ground state with the spins oriented antiparallel to each other. So far, correlations of experimental results aimed at assessing sign and magnitude of the superexchange effect in such dimers have been based, unfortunately, essentially on the oversimplified theory of molecular field approximation or Heisenberg–Dirac–Van Vleck (HDVV) model.[10] The tenuous character of this theory, therefore, calls for at least a supplementation by systematic correlations of empirical observations.

Table I. Crystal Data of $[CuBr_2(dmgH)]_2$ and $[CuCl_2(dmgH)]_2$ (Triclinic $P\bar{1}$)

	$[CuBr_2(dmgH)]_2$, $[(C_4H_8O_2N_2)$-$CuBr_2]_2$	$[CuCl_2(dmgH)]_2$, $[(C_4H_8O_2N_2)$-$CuCl_2]_2$
mol wt	678.96	501.14
a, Å	7.786	7.702 (7.697)[a]
b, Å	8.577	8.161 (8.194)
c, Å	8.262	8.111 (8.120)
α, deg	108.26	108.06 (108.14)
β, deg	68.98	69.14 (69.16)
γ, deg	78.86	78.60 (78.69)
V, Å^3	458.63	424.92 (425.84)
Z, dimers/unit cell	1	1 (1)
d_{calcd}, g/cm^3	2.46	(1.96)
d_{obsd}, g/cm^3	2.45[b]	(1.95)

[a] Values in parentheses are from ref 12. [b] Density determined by flotation methods in $CBr_4/CBrCl_3$.

In the special category of dimeric halo-bridged adducts of copper(II) halides with α,β-dione dioxime ligands, some $CuCl_2$ adducts with a number of glyoxime derivatives have been prepared earlier,[11] but only one member of this category, di-μ-chloro-bis[chloro(dimethylglyoxime)copper(II)] or di-μ-chloro-bis[chloro(2,3-butanedione dioxime)copper(II)], $[CuCl_2(dmgH)]_2$, has been structurally well characterized[12] so far and its magnetic behavior briefly examined.[7,13] Analogous adducts of $CuBr_2$, however, have not been reported hitherto.

In this work, we have synthesized the first member of a $CuBr_2$ addition complex with an α,β-dione dioxime ligand,

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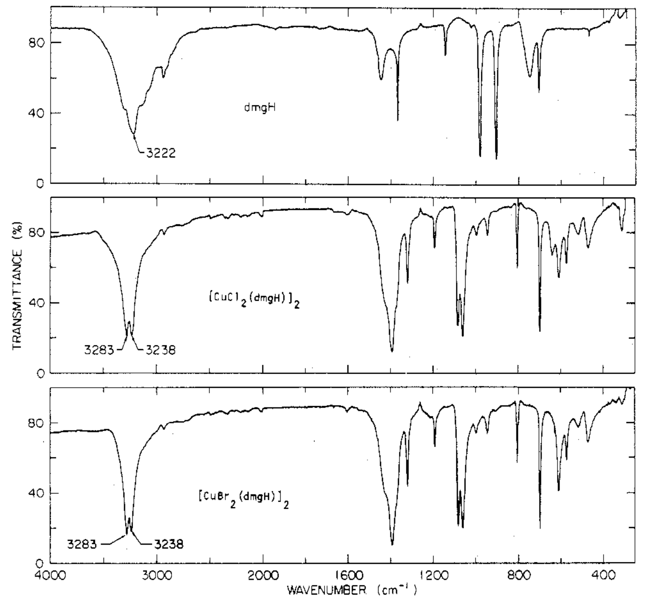

Figure 1. Infrared spectra of dmgH, $[CuCl_2(dmgH)]_2$, and $[CuBr_2(dmgH)]_2$ recorded at room temperature.

namely, di-μ-bromo-bis[bromo(dimethylglyoxime)copper(II)], $[CuBr_2(dmgH)]_2$, or di-μ-bromo-bis[bromo(2,3-butanedione dioxime)copper(II)]. The macroscopic shape of the dark green crystals strikingly resembles the shape of the blue-green crystals of the previously characterized chloro analogue.[12] For a check on the microscopic structural similarity of both compounds, their unit cells were determined by single-crystal X-ray diffraction according to the manner described in the literature.[14] The two unit cells, indeed, were found to be *isostructural*; i.e., they crystallize in the same space group but differ substantially in their volumes (Table I). While this manuscript was progressing, the structure of $[CuBr_2(dmgH)]_2$ was fully determined.[15] It confirms nicely our preliminary findings and demonstrates unequivocally the *isomorphous* character of the two dimer types which differ basically by the nature of their halogen ligands. Clearly, $[CuBr_2(dmgH)]_2$ and $[CuCl_2(dmgH)]_2$ provide a good opportunity to check the systematic variation of the superexchange effect as a function of the halide ions involved in the bridges. For this purpose, we have subjected the two compounds to magnetic and spectroscopic examinations as reported below.

Experimental Section

Compound Preparation. 1. $CuBr_2(dmgH)$ was prepared at room temperature[16] by using analytical grade chemicals (Baker Analyzed Reagents). A 1-g (8.6-mmol) sample of dmgH (dimethylglyoxime) was dissolved in 150 mL of acetone. While being stirred vigorously, the filtered solution was treated with 1.20 g (5.4 mmol) of finely powdered anhydrous $CuBr_2$ which was added portionwise. Toward the end of the addition, green cyrstals precipitated. Stirring was pursued for another 45–60 min to ensure completeness of the reaction. Most of the solvent was removed by slow evaporation at ambient temperature. The crystals were filtered off, washed with two 25-mL portions of ice-cold dry ether/acetone (2:1), dried in air at room temperature, and then left overnight at about 60 °C. The yield was 1.38 g (76%) of $CuBr_2(dmgH)$ or $C_4H_8O_2N_2CuBr_2$, which decomposes above 200 °C. Anal. Calcd for $C_4H_8O_2N_2CuBr_2$: C, 14.15; H, 2.38; N, 8.25; Br, 47.08; Cu, 18.72. Found: C, 14.22; H, 2.40; N, 8.27; Br, 46.79; Cu, 18.70.

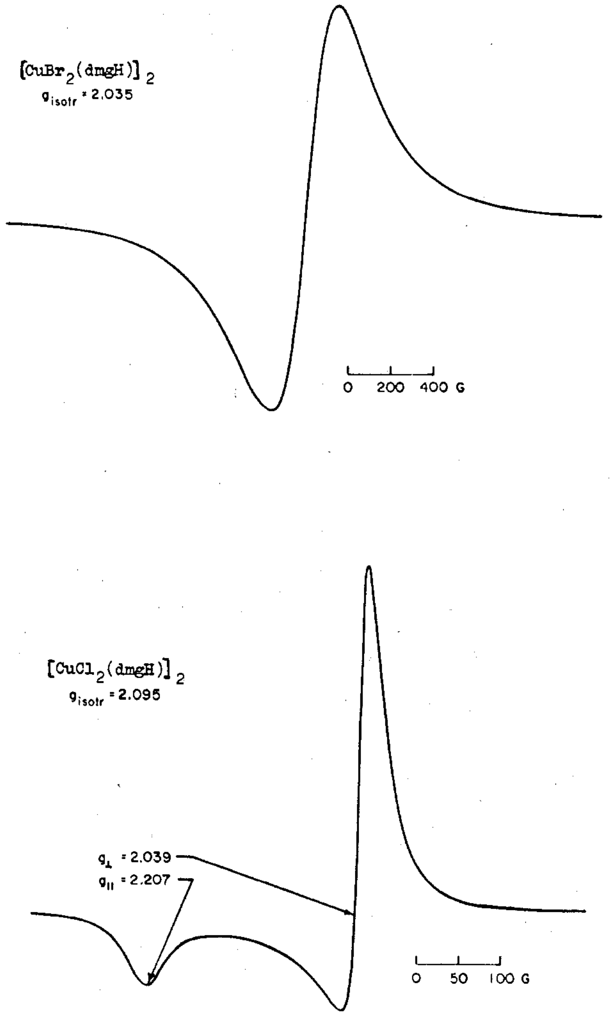

Figure 2. Room-temperature X-band EPR spectra of polycrystalline $[CuBr_2(dmgH)]_2$ and $[CuCl_2(dmgH)]_2$.

2. $CuCl_2(dmgH)$ was either obtained similarly or obtained as described in the literature.[11,12] The blue-green crystals (86% yield) gave an excellent microanalysis.

Large single crystals (up to 20 mg each) of $CuBr_2(dmgH)$ and $CuCl_2(dmgH)$ were grown by the slow evaporation of saturated acetone solutions. The two compounds dissolve readily in water (light-brown solution) and moderately in acetone (green solution) at room temperature. In the heat, the solutions obviously undergo a redox decomposition indicated by the formation of bromoacetone (tears!) in the case of $CuBr_2(dmgH)$.

Infrared and Electron Paramagnetic Resonance (EPR) Spectra. The infrared spectra of dmgH, $CuCl_2(dmgH)$,[12] and $CuBr_2(dmgH)$ (Figure 1) were recorded at room temperature with a Perkin-Elmer 621 grating infrared spectrophotometer by using the potassium bromide (KBr) pellet method.

The EPR spectra (Figure 2) of powder samples were taken under a nitrogen atmosphere at ambient temperature by using an X-band instrument (Varian Associates E-12) calibrated with Pitch (0.1% in KCl).

Static Magnetic Susceptibility Measurements. With use of a SQUID-type susceptometer operating at about 2 kG, the magnetic moments of high-purity powder samples of $CuBr_2(dmgH)$ and $CuCl_2(dmgH)$ were determined at 36 closely spaced temperature points in the range 4.2–300 K. Details of the experimental setting and instrument calibration have been reported recently.[17]

The molar susceptibility of $Ni(dmg)_2$[18] determined at the 36 selected temperatures was used, together with Pascal's constants[19] for 2H +

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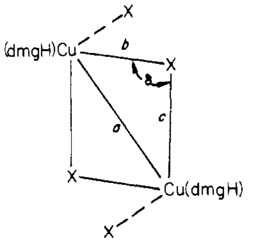
Table II. Characteristic Data for the CuXCuX Core in the $[CuX_2(dmgH)]_2$ Dimers ($X = Cl^-, Br^-$; dmgH = Dimethylglyoxime)



X^-	δ, deg	*a*, Å	*b*, Å	*c*, Å	ref
Br^-	85.59	3.599	2.387	2.883	15
Cl^-	88.0	3.445	2.240	2.700	12

4Cl$^-$ or 2H + 4Br$^-$, as the total diamagnetic correction for the $[CuCl_2(dmgH)]_2$ and $[CuBr_2(dmgH)]_2$ dimers, respectively.

Least-Squares Fit. The fitting of the experimental susceptibility data, χ_m, to the isotropic singlet–triplet equation (1) was done with

$$\chi_m = \frac{2Ng^2\mu^2}{3k(T-\Theta)}\left[1 + \frac{1}{3}\exp\left(-\frac{2J}{kT}\right)\right]^{-1} + N\alpha \qquad (1)$$

respect to the three variable parameters g, J, and Θ, by using an iterative computer program.[20] The Van Vleck temperature-independent paramagnetic constant, $N\alpha$,[21] was taken as 60×10^{-6} cm^3/mol.

If the temperature-dependent magnetic susceptibility, χ, is roughly expressed by $\chi = C/(T-\Theta)$ (Curie–Weiss Law), an uncertainty in χ is related to an uncertainty in C and Θ by (2).

$$\Delta\chi = \Delta C/(T-\Theta) + C(\Delta\Theta)/(T-\Theta)^2 \qquad (2)$$

If Θ is known, the uncertainty in C is $\Delta C = (T-\Theta)\Delta\chi$. This expression shows that the error bar in χ at higher temperature leads to a bigger error bar in C (which contains g and J) for the temperature range considered. Thus, the least-squares fit was weighted by the factor $(T-\Theta)^{-1}$ to discount the high-temperature data.

Results and Discussion

The X-ray structural results show that the crystalline lattice of the present materials consists of discrete $[CuX_2(dmgH)]_2$ dimers in which the monomers lying roughly in two parallel planes are doubly bridged by two halogen atoms and are related by a center of symmetry situated midway between the Cu sites.[12,15] For the understanding of magnetic exchanges between the paramagnetic centers of a dimer, the quadrangle defined by the core CuXCuX (Table II) is the most relevant structural element. According to the so-called 90° angle rule,[5-7,22] the exchange coupling in the particular case of a d^9 dimer is likely to be ferromagnetic if the bridging angle, δ, is nearly 90° and antiferromagnetic if δ diverges considerably from 90°.

The derived figures for the intradimer exchange parameters, J, obtained in the present study are consistent with this rule. In $[CuCl_2(dmgH)]_2$, δ (=88°)[12] is fairly close to 90°, and hence $J_{Cl} = +0.31$ cm^{-1} indicates a weak ferromagnetic exchange coupling (triplet ground state). It should be noted here that our value for J_{Cl} departs considerably from the value of +3.15 cm^{-1} reported in the literature.[7,13] In $[CuBr_2(dmgH)]_2$, on the other hand, δ (=85.59°)[15] is substantially smaller than 90°, and hence $J_{Br} = -1.51$ cm^{-1} definitely indicates an antiferromagnetic exchange coupling (singlet ground state). The latter result suggests in particular that the empirical correlations of Hatfield[7] (which predict positive J values for $\delta \lesssim 97°$) may not hold for bridging angles much smaller than 90°.

Table III. Variable-Temperature Molar Magnetic Susceptibility per Dimer, χ_m, and Effective Moment, μ_{eff}/Cu(II), for $[CuBr_2(dmgH)]_2$ (Fitting Parameters: $J = -1.51$ cm^{-1}, $g = 1.97$, $\Theta = -1.49$ K, $N\alpha = 60 \times 10^{-6}$ cm^3 mol^{-1}, Curie Constant $C_{Br} = 0.762$)

	$10^{-3}\chi_m$, cm^3 mol^{-1}		μ_{eff}/Cu(II),[a] μ_B	
temp, K	exptl	theor	exptl	theor
4.2	87.91	87.91	1.21	1.21
4.8	84.64	84.56	1.27	1.27
5.7	78.59	78.76	1.34	1.34
6.9	71.49	71.21	1.40	1.40
8.0	64.77	65.05	1.44	1.44
9.4	58.23	58.34	1.48	1.48
10.6	53.27	53.50	1.50	1.51
12.5	47.31	47.19	1.54	1.53
15.0	40.96	40.77	1.57	1.56
16.2	38.77	38.26	1.58	1.57
17.6	35.99	35.68	1.59	1.58
19.7	32.20	32.40	1.59	1.60
21.8	29.81	29.67	1.61	1.61
23.8	27.43	27.45	1.61	1.61
25.7	25.23	25.64	1.61	1.62
27.6	24.05	24.04	1.63	1.63
29.8	21.45	22.43	1.60	1.63
31.9	21.27	21.08	1.64	1.64
34.1	20.08	19.82	1.65	1.64
36.2	19.28	18.76	1.67	1.65
38.3	18.07	17.80	1.66	1.65
40.4	17.07	16.94	1.66	1.65
45.4	14.88	15.19	1.64	1.66
50.4	14.09	13.77	1.68	1.66
55.3	12.49	12.61	1.66	1.67
60.3	11.50	11.61	1.66	1.67
65.3	10.51	10.76	1.65	1.67
70.1	9.72	10.06	1.65	1.67
80.2	8.93	8.84	1.69	1.68
100.2	6.95	7.13	1.66	1.68
120.2	5.75	5.98	1.65	1.69
150.3	4.55	4.81	1.64	1.69
179.9	3.97	4.04	1.68	1.69
220.4	3.27	3.32	1.68	1.69
259.8	3.01	2.83	1.75	1.70
298.9	2.60	2.47	1.74	1.70

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

The overall static magnetic behaviors of the two systems as displayed in Tables III and IV are very similar for the temperature range measured. No maximum susceptibility, χ_m, is seen above 4.2 K, consistent with the small J values observed.

The virtually identical infrared spectra of the two dimers along with the spectrum of the "free ligand" (dmgH) are shown in Figure 1. The doublet splitting of the O–H stretching absorption band at 3283 and 3238 cm^{-1} for the dimeric complexes reflects intimately the X-ray structural results which show that in the solid only one H atom of the two OH groups on each dmgH ligand participates in an *interdimer* O–H–O bridge.[12,15] In other words, the doublet splitting arises because in the dimeric lattice the two OH groups of each 2,3-butanedione dioxime occupy slightly different crystallographic positions. The spectrum of the "free ligand", by contrast, shows no obvious evidence for such a splitting.

Whereas the EPR spectrum of the chloro-bridged dimer exhibits a clear resolution of the **g** tensor into a parallel and a perpendicular component, the lack of such a resolution in the spectrum of the bromo-bridged dimer (Figure 2) may be reasonably attributed to a stronger exchange broadening induced by the bromide ligands—as reflected in the relatively large peak-to-peak line width of $\Delta H = 340$ G—but it may be as well interpreted in terms of a much stronger admixture of the bromide valence orbitals into the copper(II) wave func-

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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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