Table I. Observed ^1H and ^{13}C NMR Shifts[a] of $[Cu(bpy)L_2]ClO_4$ in Acetone-d_6

L	H-6	H-5	H-4	H-3	C-2	C-3	C-4	C-5	C-6
bpy[b]	8.67	7.41	7.92	8.48	156.92	124.62	137.59	121.35	149.96
CO	9.13	7.89	8.35	8.67	152.65	127.89	141.47	123.31	151.66
$C_6H_{11}NC$	8.98	7.81	8.27	8.63	*c*	127.04	139.72	122.99	150.64
$P(C_4H_9)_3$	8.99	7.82	8.27	8.68	153.00	127.25	140.13	123.51	150.93
$P(OCH_3)_3$	9.06	7.86	8.33	8.70	152.92	127.63	140.71	123.51	151.31
$P(OC_4H_9)_3$	9.12	7.87	8.33	8.73	153.24	127.89	140.91	123.98	151.48
$P(OC_6H_5)_3$	7.65	7.43	8.02	8.16	157.53	126.99	139.95	123.40	150.42

[a] Shifts in ppm from Me_4Si at 25 (^1H) and 31 °C (^{13}C). Error limit ±0.01 (^1H) and ±0.03 ppm (^{13}C). [b] Signals of a metal-free bpy. [c] Signals of the C-2 nucleus were hardly detected due to low S/N ratio.

440 nm.[1] In ternary complexes, the absorption spectra of $[Cu(bpy)L_2]$, however, reveal a blue shift (<360 nm) of the MLCT band, exhibiting a strong contribution of L to π back-bonding of Cu(I) and bpy. This shows that the good π acceptor effectively suppresses the π back-bonding[6] between Cu(I) and bpy as a consequence of competing with bpy. NMR spectra also provide valuable information about metal–ligand binding in addition to the structure in solution. C-4 of bpy is located at the position para to a pyridine nitrogen. The shift of C-4 is available because it is attributable to the variation of the charge based on a through-bond interaction. Among the ternary complexes in Table I, the order in upfield shift of the C-4 resonance signal is CO < $P(OC_4H_9)_3$ < $P(OCH_3)_3$ < $P(C_4H_9)_3$ < $C_6H_{11}NC$. It is to be noted in Table I that the above order is in fairly good agreement with that obtained from the shift of H-4: the increase in shielding of C-4 just accompanies the increase in shielding of H-4. Good correlation between ^1H and ^{13}C chemical shifts has been also found in transition-metal cyclopentadienyl derivatives.[7] Cyclopentadienyl carbon resonance is more shielded as the shielding of the corresponding proton shift increases. The obtained order expressed with ligand L is regarded as the reverse order of π-acceptor capability of L in complexes $[Cu(bpy)L_2]ClO_4$: CO > $P(OC_4H_9)_3$ > $P(OCH_3)_3$ > $P(C_4H_9)_3$ > $C_6H_{11}NC$. This order agrees with that obtained from carbonyl stretching frequencies of the mixed-ligand Co and Mo complexes containing CO,[8] indicating that phosphines, phosphites, isocyanides, and CO act as good π acceptors and exert a trans-influence-like effect on another ligand in the mixed-ligand transition-metal complexes.

With the use of $M^{II}(phen)_3$ (M^{II} = Ru, Fe, Zn),[9] it has been demonstrated that the metal ion having strong π-back-bonding capability causes an upfield shift of the proton signals of phen. Analogously, the upfield shift of bpy protons of $[Cu(bpy)L_2]ClO_4$ is explained by increased π back-bonding in Cu–bpy and concurrently decreased π back-bonding in Cu–L. In this sense, the π back-bonding of Cu–bpy is controlled by the Cu–L bonding, which is well reflected by the ^1H and ^{13}C resonance shifts.

The C-6 and H-6 shifts are also associated with the variation of the charge in a through-bond interaction, giving an order similar to that obtained for C-4 and H-4. Shifts of C-2 and C-5, however, show a different trend. C-5 is para to the 2,2′-bond of bpy. C-2 and C-5 are affected by the variation of the 2,2′-bond[11] upon coordination.

Finally, we refer to the ^1H chemical shift of $[Cu(bpy)(P(OC_6H_5)_3)_2]ClO_4$. The signal of H-6 shifts upfield (7.65 ppm), while that of the other ternary complexes in Table I falls within the range 8.98–9.13 ppm. H-6 of $[Fe^{II}(bpy)_3]Cl_2$ shows a considerable upfield shift[10] (~1 ppm), which is caused by the magnetic anisotropy of an aromatic ring of a neighboring ligand due to octahedral geometry (through-space interaction), and the signal of H-6 appears near that of H-5. In the case of $[Cu(bpy)_2]ClO_4$,[4] the upfield shift of H-6, whose degree is much smaller than that in $[Fe(bpy)_3]Cl_2$, is also associated with the similar magnetic anisotropy of a neighboring ligand even in tetrahedral geometry. On this basis, H-6 of $[Cu(bpy)L_2]ClO_4$ may also undergo a through-space interaction with a neighboring ligand L having aromatic groups. The anomalous upfield shift of H-6 of $[Cu(bpy)(P(OC_6H_5)_3)_2]ClO_4$ exhibits that the phenyl group of the coordinated $P(OC_6H_5)_3$ is located in the vicinity of the coordinated bpy, and hence, it can exert a magnetic anisotropy effect upon bpy protons. The other protons of bpy may similarly undergo this effect of coordinated $P(OC_6H_5)_3$. Except for the case of $P(OC_6H_5)_3$, the appearance of the H-6 signal near the H-3 signal is characteristic of the ternary Cu(I) complexes in acetone.

In conclusion, the new ternary Cu(I) complexes were selectively prepared in solution by monitoring their ^1H and ^{13}C NMR spectra. The second ligand L delicately controls the π back-bonding between Cu(I) and bpy, whose features are readily revealed by the ^1H and ^{13}C NMR signals of H-4 and C-4, respectively. These findings regarding the shifts serve as a very useful guide for the investigation of mixed-ligand Cu(I) complexes in solution.

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Registry No. $[Cu(bpy)(P(C_4H_9)_3)_2]ClO_4$, 82661-29-8; $[Cu(bpy)(P(OCH_3)_3)_2]ClO_4$, 82661-31-2; $[Cu(bpy)(P(OC_4H_9)_3)_2]ClO_4$, 82665-09-6; $[Cu(bpy)(P(OC_6H_5)_3)_2]ClO_4$, 82661-33-4; $[Cu(bpy)(CNC_6H_{11})_2]ClO_4$, 82661-35-6; $[Cu(bpy)(CO)_2]ClO_4$, 82661-37-8; $[Cu(CH_3CN)_4]ClO_4$, 14057-91-1; ^{13}C, 14762-74-4.

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ESR Investigation of the Adduct between [1,2-Bis(diphenylphosphino)ethane]bis(3,5-dimethylpyrazolato-*N*)platinum(II) and Copper(II) Sulfate: Evidence of Magnetic Exchange Interaction between Copper(II) Ions Bridged by Sulfato Groups

Franco Cariati,[1a] Giovanni Micera,[1a] Andrea Scozzafava,[1a] Giovanni Minghetti,*[1a] and Guido Banditelli[1b]

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The reaction of the complexes $(L–L)M(pz)_2$ ((L–L) = $(Ph_2PCH_2)_2$, M = Pt; (L–L) = 2,2′-bipyridyl, M = Pt, Pd;

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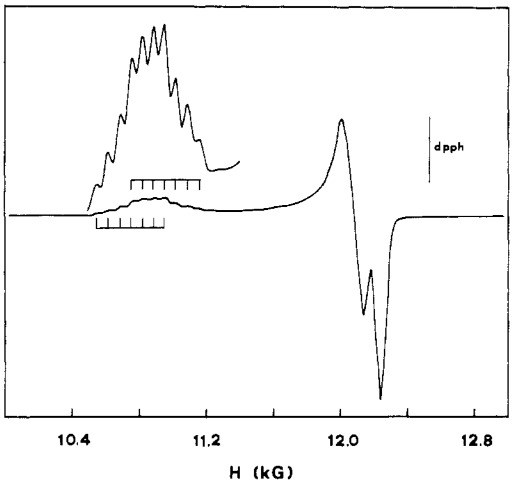
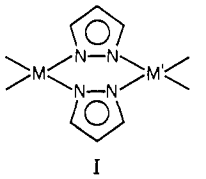


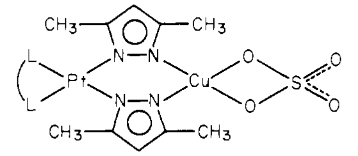
Figure 1. Q-Band (34.93 GHz) ESR spectrum of polycrystalline (dpe)Pt(3,5-$Me_2pz)_2CuSO_4$ at room temperature.

pzH = pyrazole or 3,5-dimethylpyrazole) with Lewis acids, to give 1:1 or 1:2 adducts, has been recently described by some of us.[2] In most cases the 1:1 adducts have been fully characterized as heterodinuclear species where the different metals join the pyrazolato anions (see I). In the case of an adduct with copper(II) sulfate, namely, (dpe)Pt(3,5-$Me_2pz)_2CuSO_4$, it was impossible to distinguish between **1** and **2**.



I

M = Pt, Pd; M′ = Zn, Cd, H



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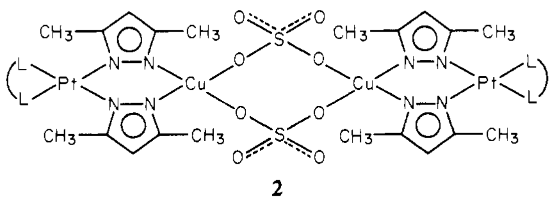

2

(L-L) = $PPh_2(CH_2)_2PPh_2$

The IR spectrum (Nujol) was consistent with the presence of a C_{2v} symmetry sulfate, but the distinction between a bridging and a chelating anion is not straightforward: on the other hand, the molecular weight determination was prevented by insufficient solubility in suitable solvents.

In order to ascertain the nature of this adduct, we undertook an ESR investigation, and the results are reported in this note. Evidence has been reached for a dimeric complex, at least in the solid state, with a long-range interaction between the copper nuclei; a pseudotetrahedral or a five-coordinated chromophore is suggested.

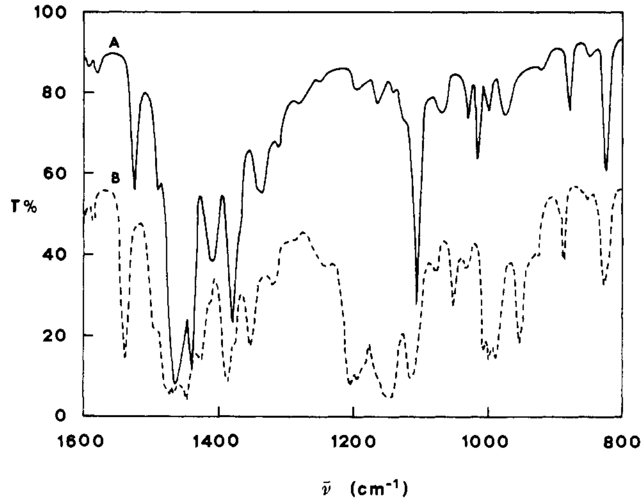

Figure 2. IR spectra (Nujol): A (—), (dpe)Pt(3,5-$Me_2pz)_2$; B (···), (dpe)Pt(3,5-$Me_2pz)_2CuSO_4$.

Results and Discussion

The polycrystalline powder ESR spectra of the pure complex were recorded at either X- or Q-band frequency. The Q-band spectrum at room temperature (Figure 1) shows ten hyperfine lines in the low-field absorption region, the separation among the peaks being ca. 7 mT. No significant difference is observed in the spectra down to 4 K. The presence of ten lines can be explained by assuming partial overlap of two sets of seven hyperfine components of the parallel absorptions, arising from the interaction between two copper(II) ions in a dimeric system. The intensity ratio of the ten lines fits well the values expected if the two sets of components overlap through the four inner lines of the signal. A detailed analysis of the spectrum, in the usual manner, yielded the ESR parameters $g_\parallel = 2.320$, $g_{\perp_1} = 2.080$, $g_{\perp_2} = 2.056$, $A_\parallel = 227.8$ MHz, and $D_\parallel = 299.8$ MHz. If the magnetic interaction is assumed to be of dipolar nature, a Cu–Cu distance close to 7.0 Å can be calculated from the equation $R = (0.65g_\parallel^2/D_\parallel)^{1/3}$.[3] Such a value seems to be reasonable in a system where two copper(II) ions are linked through a sulfato group. The large distance between the two magnetically interacting centers would involve a very small value of J, the singlet–triplet energy separation. Indeed, the magnetic moment at room temperature does not show any deviation from the spin-only value.

Evidence of a dimeric system is given also by the X-band spectrum, even if only eight hyperfine components are detected, owing to the partial overlap with the signal of the normal region.

As previously mentioned, the IR spectrum (Nujol) (Figure 2) is consistent with the presence of a C_{2v} symmetry sulfate, the required four bands being found at 1200 (s), 1140 (s), and 1110 (s) cm^{-1} (arising from $\nu_3(F_2)$ stretching vibration of T_d symmetry) and at 1000 (m) cm^{-1} (tentative assignment, from $\nu_1(A_1)$), respectively.[4]

The electronic spectrum of the complex (solid state) exhibits a d–d transition around 13 500 cm^{-1}, a value which, taken with the ESR data, suggests a pseudotetrahedral or a five-coordinated chromophore.[5] In any case no evidence of association through the dimers is given by the ESR spectra. Indeed the well-resolved parallel components in the spectra of the undoped

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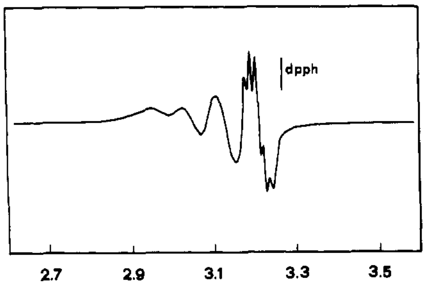
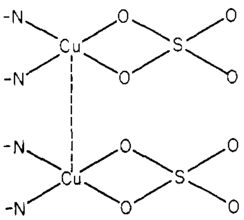


Figure 3. X-Band (9.15 GHz) ESR spectrum of (dpe)Pt(3,5-$Me_2pz)_2CuSO_4$ in CH_2Cl_2 at room temperature.

powdered samples indicate a large Cu–Cu distance among the dimeric unities.

The ESR data are consistent either with a structure of type **2** or with a system where a pair of neighboring molecules of type **1** are interacting, e.g., as in **3** or **4**.



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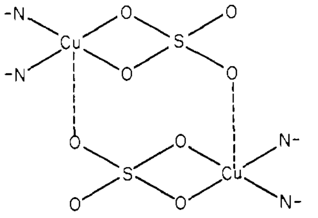

4

When the complex is dissolved in dichloromethane, a glassy ESR spectrum is obtained, typical of a magnetically diluted copper(II) complex with axial symmetry ($g_{\parallel} = 2.304$, $g_{\perp} = 2.051$, $A_{\parallel} = 482.7$ MHz). The room-temperature ESR spectrum (Figure 3) displays, in addition, five well-resolved shf lines, indicating the presence of two nitrogen atoms in the chromophore. The electronic spectrum shows a noticeable shift of the maximum to 17 240 cm^{-1}, suggesting a more planar geometry at the copper ion.

Thus it seems that, upon dissolution, not only the magnetic exchange is lost but also the chromophore attains a different geometry. This observation is more consistent with the hypothesis that, in the solid state, a structure of type **2** or **4** is present, the sulfato bridge inducing a pseudotetrahedral distortion or a pentacoordination at the copper atom. Faced type **1** molecules (e.g., **3**), on the contrary, would likely interact axially; in this case the copper(II) ions, at a distance of ca. 7 Å, would be in a planar configuration even in the solid state, so that, upon dissolution, only minor changes in the electronic spectrum should be expected.

In conclusion the spectroscopic data point to the existence, in the solid state, of a structure where the copper atoms are bridged by sulfato groups.

Experimental Section

The synthesis of the complex has been described previously.[2]

Spectroscopic Measurements. ESR spectra were recorded down to 4 K in either X or Q band ($\simeq$9.1 and 34.9 GHz, respectively) on a Varian E9 spectrometer. Electronic spectra were obtained by using a Beckman Acta M IV spectrophotometer equipped with an integrating sphere for solid samples. IR spectra (4000–400 cm^{-1}) were obtained as Nujol mulls on a Perkin-Elmer 683 spectrophotometer.

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Registry No. 2, 82482-63-1.

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Characterization of the Gas-Phase Components in Equilibrium with the Ionic Compound Ammonium Trimethylsilyl Sulfite: A New Silanol Source

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Received February 24, 1982

In previous work we proposed a reaction scheme for the oxygen atom transfer reaction between sulfur dioxide and hexamethyldisilazane.[2] One of the products of this reaction is $NH_4(CH_3)_3SiOSO_2$ (**1**), a new ionic solid with an extraordinarily high volatility. Consistent with the proposed mechanism, this product was postulated to be in equilibrium with NH_3, SO_2, and $(CH_3)_3SiOH$, the gas-phase components from which it is formed in the reaction.[2]

There are several examples of ammonium salts that are in equilibrium with two or more molecular species in the gas phase.[3] Most have very small equilibrium constants and consequently low vapor pressures for this type of dissociative process, e.g., NH_4Cl and NH_4NO_3.[3] Ammonium sulfites and bisulfites, however, are characterized by considerably higher volatility and dissociate into three molecular components, NH_3, SO_2, and H_2O.[4,5] Equilibria of this type are rather rare, offering a challenging dynamical problem with respect to how they can occur at all. Since initial work in this laboratory with the new salt, **1**, indirectly indicated that a facile equilibrium existed with three molecular components[2] and the heat of sublimation of **1** was measured to be only 15 kcal/mol,[2a] we felt it important to seek direct evidence for the molecular species postulated to be in equilibrium with the solid. Additional motivation for this study derived from the earlier mechanistic suggestion that one of the molecular components was silanol.[2] Thus, the new sulfite was considered to be a candidate for a solid-state source of this reactive silyl alcohol.

The solid sulfite, $NH_4(CH_3)_3SiOSO_2$, was prepared with the method described previously[2b] by condensing dry SO_2 over a frozen, dried, and degassed sample of $((CH_3)_3Si)_2NH$. Upon warming, the reaction proceeds rapidly, giving the white solid product and the liquid coproducts $(CH_3)_3SiNSO$ and $((CH_3)_3Si)_2O$. Separation of products to yield the sulfite was carried out by using vacuum and Schlenk techniques as described earlier. Fourier transform infrared spectra of the vapor above the solid were obtained on a Nicolet 7199A spectrometer. Infrared spectra of solid films of the sulfite were collected on a Beckman IR-20 instrument. Mass spectral data were obtained with a Varian 112S mass spectrometer by using electron impact ionization at 60 V.

To verify the existence of the postulated equilibrium, we have measured the Fourier transform infrared spectrum of the vapor phase over **1**. The solid was introduced into a small well in a gas IR cell with a 10-cm path length, which was then evacuated, leaving solid **1** and its vapor-phase components. Figure 1A is an FT IR spectrum of the vapor in this cell. By inspection the spectrum was found to contain absorptions from several distinct substances: unassigned materials, NH_3 (lit.[6] 935 and 970 cm^{-1}), SO_2 (lit.[6] 1340 and 1380 cm^{-1}), and

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