A feature which characterizes the path is the negative or small positive $\Delta H^{\ddagger}$ values.

An implication of this work is that it may be possible to obtain experimental data which reveal details of the activation process not considered in the Marcus–Hush model for outer-sphere electron transfer. In fact, it may be possible by experimental means to identify a series of paths for outer-sphere electron transfer which differ in detail from the "normal" Marcus–Hush path. In addition to the path discussed here, Lavallee, *et al.*, have suggested that the oxidation of Np(III) by $Ru(NH_3)_6{}^{3+}$ and $Ru(NH_3)_5H_2O^{3+}$ may occur by an "unorthodox" transition state characterized by large negative $\Delta S^{\ddagger}$ values in which one of the oxygens bound to neptunium attacks an octahedral face of the ruthenium complexes.[14] Outer-sphere electron-transfer reactions involving Co(III)–Co(II) complexes may also occur by a distinct path; Rillema and Endicott have recently inferred that certain key factors which make major contributions to such reactions are not considered in current theoretical models of outer-sphere electron transfer.[15]

Mechanistic Details of the Non-Marcus Path. The full mechanistic details of the non-Marcus path discussed here are not clear. However, the oxidation of $Fe(H_2O)_6{}^{2+}$ by iron(III)-polypyridine complexes has been studied in detail by Sutin and coworkers. From their work certain facts are known which allow inferences to be drawn.

1. The pattern of activation parameters—negative or small positive $\Delta H^{\ddagger}$ values, large negative $\Delta S^{\ddagger}$ values—is paralleled by the thermodynamic parameters for the overall reactions: for $Fe(H_2O)_6{}^{2+} + Ru(bipy)_3{}^{3+} \rightarrow Fe(H_2O)_6{}^{3+} + Ru(bipy)_3{}^{2+}$, $\Delta H_{12}{}^{\circ} = -27$ kcal/mol and $\Delta S_{12}{}^{\circ} = -43$ eu;[16,17] and for $Fe(H_2O)_6{}^{2+} + Fe(bipy)_3{}^{3+} \rightarrow Fe(H_2O)_6{}^{3+} + Fe(bipy)_3{}^{2+}$, $\Delta H_{12}{}^{\circ} = -23$ kcal/mol and $\Delta S_{12}{}^{\circ} = -47$ eu.[16,17]

2. Ford-Smith and Sutin found no evidence for specific steric effects in the reactions of the 5,6- and 3,4,7,8-methyl-substituted iron–phenanthroline complexes with $Fe(H_2O)_6{}^{2+}$. The absence of specific steric effects led Ford-Smith and Sutin to suggest that in the activated complex for electron transfer, $Fe(H_2O)_6{}^{2+}$ is located in the space between phenanthroline groups rather than at the periphery of a phenanthroline group.[4]

3. In other solution reactions where negative $\Delta H^{\ddagger}$ (or E_a) values have been observed, mechanisms have been invoked in which enthalpically favorable preequilibria exist.[18-21] For the reactions studied here, an equilibrium involving ion-pair formation between the reacting ions must exist. Electron transfer presumably follows ion-pair formation, *e.g.*

$$Fe(H_2O)_6{}^{2+} + Fe(phen)_3{}^{3+} \rightleftharpoons Fe(H_2O)_6{}^{2+},Fe(phen)_3{}^{3+} \quad (K) \qquad (4)$$

$$Fe(H_2O)_6{}^{2+},Fe(phen)_3{}^{3+} \rightarrow Fe(H_2O)_6{}^{3+} + Fe(phen)_3{}^{2+} \quad (k) \qquad (5)$$

For a reaction involving unlike-charged ions, direct evidence has been obtained that ion-pair formation precedes electron transfer.[22] Hemmes has calculated that ion pairing between large cations can be thermodynamically favorable.[23] From attempts to observe ion pairing between $Co(H_2O)_6{}^{2+}$ and $Ru(bipy)_3{}^{3+}$ spectrophotometrically, it was concluded that $K < 0.5$.[1]

Ion pairing preceding electron transfer could make a negative contribution to the observed enthalpy of activation.[24] In media of high ionic strength, electrostatic effects are small and expected to make a minor contribution.[25] However, nonelectrostatic effects may be important. Such effects might include charge fluctuation forces[26] or the effect of solvent structure which has been suggested to enhance ion pairing when both ions are large.[27]

The existence of important nonelectrostatic effects could also explain the poor agreement obtained using eq 3. Marcus has suggested that this result may be due to a failure of nonelectrostatic terms to cancel in the work done in bringing the reactants together.[28]

4. The reactions between $Fe(H_2O)_6{}^{2+}$ and the iron(III)-polypyridine complexes show strong specific anion effects.[4,29] Especially striking is the path for catalysis by SCN^- in 1.0 *M* $HClO_4$ at 25.0° in which $FeNCS^{2+}$ is formed quantitatively.[26] The specific anion effects for anions like SCN^- or $N_3{}^-$ may arise as a consequence of preequilibria involving complex ion formation, *e.g.*, $FeNCS^+$; however, with other anions, most notably $ClO_4{}^-$, energetically favorable ion pairing with the polypyridine complex may be an important part of the overall electron-transfer reaction.

Acknowledgment. Acknowledgment is made to the National Science Foundation through Grant GP17083 for support of this research.

Registry No. $Fe(H_2O)_6{}^{2+}$, 15365-81-8; $Fe(terpy)_2{}^{3+}$, 47779-99-7; $Fe(bipy)_3{}^{3+}$, 13479-48-6.

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Organoantimony Compounds. IV. Preparation, Characterization, and Vibrational Spectra of Trimethyl- and Triphenylantimony Diazides and Diisocyanates[1,2]

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In continuation of our investigation into the preparation, structure, and chemical properties of triorganoantimony(V) derivatives, we initiated a study[3] on triorganoantimony(V)

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Table I. Analytical Data and Melting Points

	Analysis, %						
	Calcd			Found			
Compd	C	H	N	C	H	N	Mp, °C
$Me_3Sb(N_3)_2$	14.36	3.62	33.50	14.23	3.73	33.48	91.5–92.5
$Ph_3Sb(N_3)_2$	49.46	3.46	19.23	49.93	3.70	18.91	103.5–104.5
$Me_3Sb(NCO)_2$	23.94	3.62	11.17	24.14	3.99	10.60	53–54
$Ph_3Sb(NCO)_2$	54.95	3.46	6.41	54.83	3.53	6.29	113–114

pseudohalides of the type R_3SbX_2. The first such derivative, $Me_3Sb(NCS)_2$, had been reported in 1907 by Hantzsch and and Hibbert.[4] The analogous phenyl derivative was prepared several years later by Challenger and coworkers,[5] who also reported the corresponding diisocyanate. $Me_3Sb(NCS)_2$ and $Ph_3Sb(NCS)_2$ have been characterized recently by Dehnick and coworkers.[6] The vibrational spectra of both compounds have also been reported.[2] Herein we report on the preparation, characterization, and vibrational spectra of the corresponding diazides and diisocyanates.

In contrast to the diisothiocyanates, which are unaffected by moisture, the diazides and diisocyanates are readily hydrolyzed to form the oxygen-bridged derivatives of the type $(R_3SbX)_2O$. Preceding this work, Schmidt[7] had reported on the preparation and characterization of $Me_3Sb(N_3)_2$. Some infrared data for $Ph_3Sb(N_3)_2$ had also been reported by Thayer,[8] although no information on its preparation and characterization had been given. Our results show that the previously reported $Ph_3Sb(N_3)_2$ was in fact a hydrolyzed product. The infrared spectrum for $Me_3Sb(N_3)_2$, reported by Schmidt, also shows bands which can be attributed to $[Me_3Sb(N_3)]_2O$.

Experimental Section

General Information. Trimethyl- and triphenylantimony dichlorides were prepared as reported previously.[2] Sodium azide and silver cyanate were obtained commercially. Sodium azide was dried at 200° for 24 hr. Benzene, petroleum ether, and diethyl ether were dried by treatment with sodium wire and subsequent distillation. Acetonitrile was treated with calcium hydride and subsequently distilled. Chloroform was refluxed over potassium carbonate and subsequently distilled. The solution of hydrazoic acid in dry benzene was prepared as described in the literature.[9]

The compounds were prepared under anhydrous conditions and were manipulated either in a nitrogen-filled drybox or in a conventional vacuum system. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Trimethyl- and Triphenylantimony Diazides. In a typical preparation trimethyl- or triphenylantimony dichloride (1.000 g) was dissolved in 40 ml of a 20% solution of hydrazoic acid in benzene and excess of sodium azide (1:4 mole ratio) was added. The mixture was stirred overnight in a stoppered flask and the solid was filtered off. The filtrate was concentrated under vacuum until the appearance of white crystals, which were filtered and recrystallized from a benzene solution containing hydrazoic acid.

Trimethyl- and Triphenylantimony Diisocyanates. Stoichiometric amounts of trimethyl- and triphenylantimony dichloride and silver cyanate were stirred in anhydrous ether for 24 hr. The precipitated silver chloride was filtered off and the filtrate was concentrated under vacuum to give a white crystalline solid which was recrystallized from a mixture of anhydrous chloroform and petroleum ether (bp 30–60°).

Physical Measurements. Infrared spectra (4000–200 cm^{-1}) were recorded on a Beckman IR-12 double-beam spectrophotometer. Solid samples were prepared as mulls in Nujol or halocarbon oil and the spectra were obtained using KRS-5 and polyethylene windows. Solution spectra were obtained using sealed sodium chloride or polyethylene cells. Raman spectra were recorded on a Cary 82 Raman spectrometer using the 5145 Å exciting line of an argon ion laser. Spectra were measured on powdered samples sealed in melting point tubes or on benzene solutions placed in a quartz capillary. ^1H nmr spectra were obtained on a Varian A-60 nmr spectrometer at ambient temperatures using TMS as internal standard. The molecular weights were determined in benzene using a Hitachi Perkin-Elmer 115 vapor osmometer. The electrical conductivities were measured in acetonitrile at 25° with a Beckman RC-18A conductivity bridge. Melting points were determined with a Gallenkamp melting point apparatus and are uncorrected.

Table II. Molecular Weight[a] and Conductance[b] Data

	Mol wt		Λ_e, ohm^{-1} cm^2 $equiv^{-1}$			
Compd	Calcd	Found	2×10^{-3} *M*	1×10^{-3} *M*	5×10^{-4} *M*	2.5×10^{-4} *M*
$Me_3Sb(N_3)_2$	250.91	252	0.36	0.41	0.66	1.05
$Ph_3Sb(N_3)_2$	437.11	434	0.98	1.25	1.72	2.38
$Me_3Sb(NCO)_2$	250.89	253	0.80	0.98	1.04	1.12
$Ph_3Sb(NCO)_2$	437.09	429	0.79	1.34	2.40	3.68

[a] In benzene. [b] In anhydrous acetonitrile at 25°.

Results and Discussion

The analytical data and melting points for the compounds reported herein are recorded in Table I. All of the four compounds are soluble in polar organic solvents. They are also sparingly soluble in benzene and petroleum ether. Molecular weight data, which are recorded in Table II, show that all of the four compounds behave as monomeric molecular species in benzene. The molecular nature of these compounds was further confirmed by electrical conductance measurements, in acetonitrile solution. The observed conductances are also recorded in Table II. The melting point of triphenylantimony diazide had been reported[8] previously to be 138°, which is considerably higher than that observed in this work. During several attempts to prepare this compound we obtained products containing varying amounts of $[Ph_3Sb(N_3)]_2O$ and their melting points ranged from 112 to 155°. Thus, there can be little doubt that the previously reported $Ph_3Sb(N_3)]_2$ was in fact a hydrolyzed product containing substantial amounts of $[Ph_3Sb(N_3)]_2O$.

The proton nmr spectra of trimethylantimony diazide as well as the diisocyanate in $CDCl_3$ showed a sharp single peak at 1.97 ppm with a "line width" of less than 2 Hz. The spectra of the corresponding phenyl compounds consisted of a quartet (8.26 ppm for the diazide and 8.25 ppm for the diisocyanate) and a triplet (7.60 ppm for the diazide and 7.70 ppm for the diisocyanate). The integrated intensities for the quartets and triplets were in the ratio 2:3. Therefore, the quartet can be assigned to the hydrogens in the ortho positions of the phenyl rings and the triplet to the hydrogens in the meta and para positions. Thus the ^1H nmr spectra for the methyl as well as the phenyl compounds are consistent with the presence of three equatorial methyl or phenyl groups. However, due to the possibility of a rapid intramolecular exchange process other structures cannot be ruled out.

Infrared and Raman Spectra. The observed infrared and

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Raman frequencies due to the internal vibrations of the azide and the cyanate groups are listed in Table III. These frequencies are similar to those for the corresponding triphenylbismuth derivatives[10,11] which have also been studied recently in this laboratory. Like the triphenylbismuth diazide, the spectra for the triorganoantimony diazides also showed a band at *ca.* 1320 cm^{-1}. A similar band has been reported for a number of organoarsenic azides[12] and it has been assigned as the first overtone of the δ_{NNN} mode. The cyanate frequencies for both the methyl and phenyl derivatives occur in the same range as reported for N-bonded isocyanate complexes.[13]

The infrared and Raman frequencies due to the skeletal vibrations for the methyl compounds are listed in Table IV. For both the diazide and the diisocyanate the skeletal frequencies are similar to those for the corresponding dihalides[2] and can be interpreted in terms of a D_{3h} skeletal symmetry. However, it is interesting to note that in the case of the diazide and diisocyanate the symmetric and antisymmetric $Sb\text{-}N_3$ or Sb-NCO stretching frequencies are almost identical. For D_{3h} skeletal symmetry the antisymmetric Sb-N stretching frequency is expected to be only infrared active and the symmetric Sb-N stretching mode is expected to be only Raman active. The infrared spectra of the diazide and the diisocyanate, in benzene solutions, showed a single band of medium strong intensity at 353 and 325 cm^{-1}, respectively. The Raman spectrum of the diazide, in benzene, also showed a polarized band of medium intensity at 355 cm^{-1}. Although the Raman spectrum of the diisocyanate could not be obtained in solution, in the solid state a Raman band of medium intensity was observed at 320 cm^{-1}. In this region, no other infrared or Raman band was observed for this compound. However, the Raman and infrared spectra of the diazide, in the solid state, showed an additional band at *ca.* 330 cm^{-1}. Since this band is not observed in solution, it can be attributed to a lower symmetry of the diazide in the solid state.

For both compounds only the antisymmetric Sb-C stretching frequency was observed in the infrared spectra, and both the symmetric and the antisymmetric Sb-C stretching frequencies were observed in the Raman spectra. In the case of the diazide the assignment for the symmetric Sb-C stretching frequency was confirmed by polarization measurements in solution. The infrared and Raman data for both the compounds are, thus, in accord with a trigonal planar SbC_3 skeleton.

The infrared spectrum of $Me_3Sb(N_3)_2$ reported by Schmidt[7] contained bands at 768, 590, and 522 cm^{-1}. These bands were not observed in the present work. However, the infrared spectra of the hydrolyzed samples of $Me_3Sb(N_3)_2$ showed bands at *ca.* 765, 582, and 530 cm^{-1}. The latter three bands were also observed in the spectrum of $[Me_2Sb(N_3)]_2O$. Furthermore, the $\nu_a(N_3)$ frequency for $Me_3Sb(N_3)_2$, in the solid state, has been reported to be at 2050 cm^{-1}. We observed this frequency at 2080 cm^{-1} for $Me_3Sb(N_3)_2$ and at 2040 cm^{-1} for $[Me_3Sb(N_3)]_2O$. It is therefore evident that the infrared spectrum reported by Schmidt was, in part, due to the hydrolyzed $Me_3Sb(N_3)_2$.

Table III. Infrared and Raman Frequencies[a] (cm^{-1}) Due to the Pseudohalide Groups

Compd		ν_a	ν_s	δ
$Me_3Sb(N_3)_2$	Ir	2080 vs (2064)	1285 m	685 m
	R	2080 w	1290 w	656 w
$Ph_3Sb(N_3)_2$	Ir	2080 vs (2072)	1268 m	648 mw
	R	2080 vw	1270 w	650 w
$Me_3Sb(NCO)_2$	Ir	2200 vs (2200)	1365 w	620 s
	R		1364 w	
$Ph_3Sb(NCO)_2$	Ir	2210 vs (2208)		633 m
	R		1370 m	638 vw

[a] In the solid state except the values in parentheses which were obtained in chloroform solutions. Description of abbreviations: Ir, infrared; R, Raman; ν_a, pseudoantisymmetric stretching; ν_s, pseudosymmetric stretching; δ, bending; m, medium; s, strong; v, very; w, weak.

Table IV. Infrared and Raman Spectra[a] (600–100 cm^{-1}) of Trimethylantimony Diazide and Diisocyanate

$Me_3Sb(N_3)_2$		$Me_3Sb(NCO)_2$		
Ir	R	Ir	R	Assignment
576 m	576 m[b]	588 m	588 m	ν_a(Sb–C)
	529 s, p[b]		542 vs	ν_s(Sb–C)
353 ms[b]	355 m, p[b]	325 ms[b]	320 m	ν(Sb–N)
	220 m		201 m	$\delta_\perp$(Sb–C)
	150 m		149 m	$\delta_\parallel$(Sb–C)
	100 vs		100 vs	Lattice mode?

[a] In the solid state unless stated otherwise. Description of abbreviations: Ir, infrared; R, Raman; m, medium; p, polarized; s, strong; v, very; ν_a, antisymmetric stretch; ν_s, symmetric stretch; $\delta_\perp$, out-of-plane bending; $\delta_\parallel$, in-plane bending. [b] In benzene.

Table V. Infrared and Raman Spectra[a] (600–100 cm^{-1}) of Triphenylantimony Diazide and Diisocyanate

$Ph_3Sb(N_3)_2$		$Ph_3Sb(NCO)_2$		
Ir	R	Ir	R	Assignment
458 s	455 vw	458 s	455 vw	y mode
355 s[b]	360 ms, p[b]	335 m[b]	338 m	ν(Sb–N)
298 s[b]	290 w[b]	298 s[b]	290 w	t mode [ν_a(Sb–C)]
265 m[b]	265 w	265 m[b]	268 w	u mode
230 w	230 s, p[b]		228 s	t mode [ν_s(Sb–C)]
	205 w		210 w	x mode
	160 w		170 m	

[a] In the solid state unless stated otherwise. Description of abbreviations: Ir, infrared; R, Raman; ν, stretching; ν_a, antisymmetric stretching; ν_s, symmetric stretching; m, medium; p, polarized; s, strong; v, very; w, weak. [b] In benzene.

The infrared and Raman data, for triphenylantimony diazide and diisocyanate, in the low-frequency regions, are recorded in Table V. As can be seen from the data in Table V the Sb-N stretching frequencies for the phenyl compounds are very close to those for the methyl compounds. Like the methyl compounds, the symmetric and the antisymmetric Sb-N stretching frequencies for the phenyl compounds are also found to be almost identical.

As expected, the infrared and Raman frequencies due to the Ph_3Sb group for the diazide as well as the diisocyanate are very similar to those for the triphenylantimony dihalides. The assignments for the vibrational frequencies for the latter compounds have been made previously, by comparison with those for triphenylantimony.[14] On this basis the strong Raman band at *ca.* 220 cm^{-1} was assigned to the x mode and the weak Raman band at *ca.* 290 cm^{-1} and the medium Raman band at *ca.* 260 cm^{-1} were assigned to the t modes, which are essentially metal-phenyl stretching vibrations. However, from the Raman polarization measurements[15]

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(15) Raman spectrum of $Ph_3Sb(NCO)_2$ could not be obtained in solution due to its insufficient solubility in benzene.

on benzene solutions of the dihalides and the diazide, it was found in the present work that the 220-230-cm^{-1} band is very strongly polarized but the 260-cm^{-1} band is depolarized. Therefore the 220-230-cm^{-1} band should be assigned to the symmetric $Sb-C_6H_5$ stretching vibration. Accordingly, the strong Raman band at *ca.* 230 cm^{-1} is assigned to the symmetric $Sb-C_6H_5$ stretching frequency and the 290-cm^{-1} band, which appears strong in the infrared but is weak in Raman, is assigned to the antisymmetric $Sb-C_6H_5$ stretching frequency. Thus the vibrational spectra for triphenylantimony diazide and the diisocyanate are also in accord with a trigonal-bipyramidal skeleton.

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Registry No. $Me_3Sb(N_3)_2$, 51019-36-4; $Ph_3Sb(N_3)_2$, 51019-33-1; $Me_3Sb(NCO)_2$, 51019-34-2; $Ph_3Sb(NCO)_2$, 51019-35-3.

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Electronic Studies of Copper(II) Complexes of Amino Acids. IV. The Copper–Carnosine System, a Magnetically Dilute Copper Dimer

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Great interest has developed in the last several years in the study of coordination compounds of amino acids and peptides.[1-3] The general purpose in this field has been to try to elucidate the special physical properties of the larger protein and enzyme metal complexes, a problem which at this time still remains unresolved. Several very interesting aspects have been brought forward by investigators such as Gray,[4] Vallee and Williams,[5] and Malmstrom and Vannagard.[6] In particular, Villa and Hatfield[7,8] have demonstrated the possibility of spin interactions in dimeric Cu(II) compounds of amino acids such as the tyrosinato system. In this paper, the magnetic, epr, and spectral properties of the copper(II)-β-alanyl-L-histidine (carnosine) complex will be presented and discussed. The interest in this compound was prompted by its structure,[9] shown in Figure 1, where it can be seen that two carnosine molecules bridge between two copper ions forming a strict dimeric structure. The Cu(II) is pentacoordinated by an amino, a peptide, and an imidazole (3) nitrogen, by a carboxyl oxygen, and by a water molecule. There exist possibilities of spin interaction *via* the bridging ligands or through space, as well as interdimer interactions.

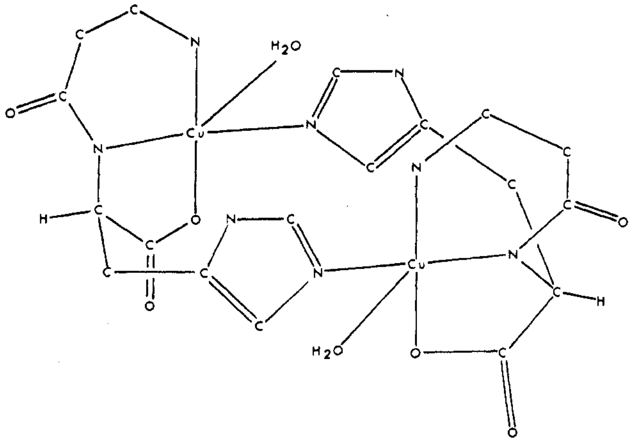

Figure 1. Structure of the (carnosine)copper dimer.

Experimental Section

The compound, (β-alanyl-L-histidinato)copper(II) dihydrate, was prepared according to Freeman[9] by dissolving 2 mmol of carnosine with excess freshly prepared $Cu(OH)_2$ in about 10 ml of H_2O, filtering off the excess hydroxide, and adjusting the final pH to 10 with 10% NaOH. Dark blue crystals formed within 1 hr. *Anal.* Calcd for $Cu(C_9H_{16}N_4O_5)$: C, 33.38; H, 4.98; N, 17.30. Found: C, 33.12; H, 4.78; N, 17.32. The magnetic measurements were made as previously described[10] in a Faraday susceptibility setup down to 77°K and in a vibrating-sample magnetometer from 77 to 4°K. The epr measurements were carried out in Varian Associates E-3 and EM-500 spectrometers at the X band. The visible–near-infrared spectra were obtained as Nujol mulls between glass plates in a DK-2A spectrophotometer. Analyses were commercially done by Galbraith, Inc.

Results

The epr spectrum of the copper–carnosine compound is shown in Figure 2, which can be described with an $S = {}^1/_2$ spin Hamiltonian. Under close scrutiny it can be observed that the spectrum is not symmetrical and can be interpreted as being composed of a $g_{\parallel} = 2.20$ and $g_{\perp} = 2.08$. The solid spectrum of the pure material at 77°K corroborates this interpretation. A solid solution spectrum at 77°K of the mother liquor (from the preparation of the compound) gave a completely symmetrical spectrum with $g_{av} = 2.11$, again indicating the presence of an $S = {}^1/_2$ species.

The magnetic susceptibility for this compound was measured from room temperature to 4°K and is shown in Figure 3. The X's are the experimental points while the lines are the theoretical χ and $1/\chi$ expected from a Curie law with $\mu = 1.80$ BM. It is evident from the figure that the fit of the data to the Curie law is excellent and that the temperature axis intercept is 0.

The solid-state electronic spectrum consisted of one broad band at 14,000 cm^{-1} which can be assigned to the $E \leftarrow B_1$ transition.

Discussion

Two different types of magnetic interactions have been postulated in copper(II) compounds: (1) through-space interactions, such as in the $[Cu(ac)_2]_2$ dimer, and (2) interactions *via* the bridging ligands, such as in the copper–tyrosine compounds. The Cu–Cu distance in the first type of compounds is less than 3 Å while in the second

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