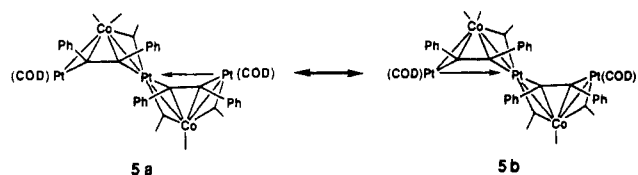


Figure 4. ORTEP drawing of $\text{Pt}_3\text{Co}_2(\text{CO})_6(\text{COD})_2(\mu_3\text{-PhC}_2\text{Ph})_2$ (**5**), showing 40% probability thermal ellipsoids.

trochemically.²¹ Compound **2** contains a total of 58 valence electrons, which is 2 less than the electron-precise value of 60 typically found for tetrahedral M_4 cluster complexes. This lower count has been observed in other platinum-containing M_4 cluster complexes^{22,23} and is probably due to the tendency of platinum to form stable complexes with 16-electron configurations.²⁴ Other 58-electron cluster complexes containing two platinum atoms that have been characterized have also been found to contain long Pt–Pt distances.^{6,23} Fusi et al. have reported that compound **6** exhibits a significant ability to catalyze the hydrogenation of terminal

alkynes, but no complexes that might shed light upon the mechanism of the process were characterized.¹² We have not yet investigated the ability of **2** to produce catalytic hydrogenation of alkynes; however, since **2** contains a COD ligand that should be easily displaced, we have investigated the reaction of **2** with internal alkynes in the hopes of preparing and characterizing some platinum–cobalt cluster complexes containing alkyne ligands.

The reaction of **2** with EtC_2Et yielded the new bis(alkyne) complex **4**, while the reaction of **2** with PhC_2Ph yielded the bis(alkyne)triplatinumdicobalt complex **5**. Compound **4** contains 62 valence electrons and is electron precise (i.e. all metal atoms obey the effective atomic number rule). However, compound **5** contains a total of 76 valence electrons, which is 2 less than the value of 78 that is expected for an electron-precise bow-tie cluster. As with **2**, the deficiency is probably related to the tendency of platinum to form stable structures with 16 electrons. By using this idea, we propose that the structure of **5** can be represented as an average of the two resonance structures **5a** and **5b**, in which



both the external platinum atoms formally have a 16-electron configuration and one of these then has no formal bond to the central atom Pt(2), which has 18 electrons. This idea would also explain the long Pt–Pt bond lengths found in **5**. The presence of three platinum atoms in **5** implies that **2** is undergoing fragmentation processes during its reaction with PhC_2Ph . Fragmentation processes could limit the potential to develop these compounds as catalysts.¹²

Acknowledgment. This research was supported by the National Science Foundation under Grant CHE-8919786.

Supplementary Material Available: For **1**, **2**, **4**, and **5**, tables of crystallographic data, hydrogen atom coordinates, and anisotropic thermal parameters and, for **5**, a table of coordinates of the carbon atoms of the phenyl rings (9 pages); tables of calculated and observed structure factors for all four structural analyses (72 pages). Ordering information is given on any current masthead page.

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Structure and Magnetic Properties of Bis(*N,N*-diisopropylthiocarbamato)copper(II)

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The complex bis(*N,N*-diisopropylthiocarbamato)copper(II), $\text{C}_{14}\text{H}_{28}\text{CuN}_2\text{S}_4$, crystallizes in the space group $P\bar{1}$ of the triclinic system with $Z = 2$. The unit cell has parameters $a = 11.559$ (3) Å, $b = 11.692$ (3) Å, $c = 7.629$ (2) Å, $\alpha = 96.35$ (2)°, $\beta = 96.35$ (2)°, and $\gamma = 88.78$ (2)°. The final weighted R factor is 0.048 based on 1625 [intensity $\geq 2.5\sigma(I)$] measured reflections. The two independent half-molecules in the unit cell are square planar with exactly planar CuS_4 units and nearly planar $>\text{NCS}_2$ moieties. The average of the four independent copper–sulfur distances is 2.283 Å, and the average of the four carbon–sulfur distances is 1.716 Å. The latter distance is indicative of considerable double-bond character. The shortest copper–copper intermolecular distance is 7.629 Å, and the shortest copper–sulfur intermolecular distance is 6.041 Å. There are significant intermolecular antiferromagnetic interactions transmitted over these long distances, as reflected by the reduction of the magnetic moment from about $1.8 \mu_B$ near 20 K to $1.5 \mu_B$ at 1.76 K. This observation provides additional documentation that sulfur bridges provide effective superexchange pathways for magnetic interactions between paramagnetic centers.

Introduction

Exchange interactions between paramagnetic centers may occur over relatively long distances. These magnetic interactions may readily be seen if they are antiferromagnetic, since magnetic moments of substances that exhibit these interactions decrease

markedly from single-ion magnetic moments. Long-range interactions have been found frequently when the metal ions are bridged by sulfur ligands.^{1–4} In our program devoted to the

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Table I. Crystal Data for Bis(*N,N*-diisopropylidithiocarbamato)copper(II)

$C_{14}H_{28}CuN_2S_4$	MW = 416.2
$a = 11.559(3) \text{ \AA}$	$\alpha = 96.35(2)^\circ$
$b = 11.692(3) \text{ \AA}$	$\beta = 96.35(2)^\circ$
$c = 7.629(2) \text{ \AA}$	$\gamma = 88.78(2)^\circ$
$V = 1018.4 \text{ \AA}^3$	triclinic, $P\bar{1}^a$
$F(000) = 438 e$	$Z = 2$
$R = 0.041$	$R_w = 0.048$
$NO = 1625 > 2.5\sigma(I)$	$NV = 218$

^aThe triclinic cell can be transformed into a C-centered pseudo-monoclinic cell by the matrix (1 1 0, -1 1 0, 0 0 1) with cell-dimensions $a = 16.615(3) \text{ \AA}$, $b = 16.265(4) \text{ \AA}$, $c = 7.629(2) \text{ \AA}$, $\alpha = 90.05(2)^\circ$, $\beta = 98.91(2)^\circ$, and $\gamma = 89.34(2)^\circ$ and with $V = 2036.8(9) \text{ \AA}^3$.

identification of chemical and structural features that lead to long-range exchange interactions, we have been searching for examples whose intermolecular metal-bridging contacts are longer than the sum of the van der Waals' radii and yet which show evidence of exchange interactions. As shown by the structural and magnetic studies described herein, bis(*N,N*-diisopropylidithiocarbamato)copper(II) is an example of a compound with long intermolecular contacts and readily identifiable antiferromagnetic interactions.

Experimental Section

Synthesis. $CuCl_2 \cdot 2H_2O$ (1.26 g, 0.025 mol) was dissolved in 100 mL of water. Carbon disulfide (3.01 mL, 0.05 mol) was added, followed quickly by isopropylamine (5.06 g, 0.05 mol). An additional 50 mL of water was added, and the mixture was stirred overnight. Upon collection by filtration, it was evident that two substances had formed: one brown and the other gray. The mixture was washed with water, dried overnight in air, and dissolved in the minimum amount of benzene. Only the brown solid was soluble. The solution was filtered, placed in a series of small beakers, and ethanol was added to each, giving benzene/ethanol ratios of 60/40. Small black crystals grew overnight. These were collected, dried, and submitted for elemental analysis. Anal. Calcd for $C_{14}H_{28}CuN_2S_4$: C, 40.40; H, 6.78; N, 6.73. Found: C, 40.65; H, 6.93; N, 6.77.

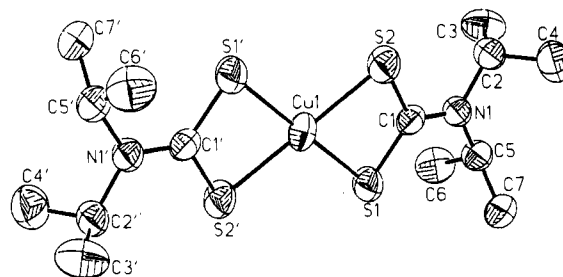
Magnetic Measurements. Magnetic susceptibility data from 1.76 to 20 K were collected by using a Princeton Applied Research Model 155 Foner vibrating-sample magnetometer and procedures that have been described earlier.⁵ The magnetometer was calibrated with $HgCo(NC-S)_4$.^{6,7} Samples of the standard and the compound under study were contained in precision-milled Lucite sample holders. Approximately 150 mg of each was used. A correction for the diamagnetism of the constituent atoms was estimated from Pascal's constants.^{8,9}

X-ray Crystallography. A tabular crystal measuring approximately $(0.55 \times 0.18 \times 0.4 \text{ mm})$ was mounted on a thin glass fiber along the long crystal direction and was used for all measurements, which were carried out at room temperature, by using Mo $K\alpha$ radiation on a Nicolet R3m/u diffractometer equipped with a pulse height analyzer and a graphite monochromator. The cell constants were obtained by a least-squares refinement of the setting angles of 25 reflections with 2θ values between 20 and 30° . The intensity data were collected for all reflections of the type hkl , $h\bar{k}l$, $hk\bar{l}$, and $h\bar{k}\bar{l}$ between 3 and 45° in 2θ by the $\omega/2\theta$ scan technique at scan speeds between 4 and $29.3^\circ/\text{min}$. Stationary-background measurements were made at the beginning and end of a scan, each for half the scan time. One standard reflection (101) was measured after every 30 measurements, which showed no significant variation in intensity. Out of the 2801 reflections measured, 1625 reflections with intensities $> 2.5\sigma(I)$ were used in the structure refinement. The data were

Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($\text{\AA}^2 \times 10^3$)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U^a</i>
Cu1	5000	0	5000	56 (1)
Cu2	0	5000	0	54 (1)
S1	5150 (2)	1234 (2)	2922 (2)	65 (1)
S2	6616 (2)	1040 (2)	6131 (2)	63 (1)
S3	4 (2)	3065 (1)	212 (3)	68 (1)
S4	1502 (2)	4326 (1)	-1546 (3)	63 (1)
C1	6279 (5)	1827 (5)	4359 (7)	47 (2)
N1	6831 (4)	2777 (4)	4157 (6)	47 (2)
C2	7779 (5)	3232 (5)	5519 (8)	55 (3)
C3	7465 (7)	4396 (6)	6366 (10)	89 (4)
C4	8925 (6)	3222 (7)	4756 (10)	83 (3)
C5	6545 (5)	3448 (5)	2635 (8)	56 (3)
C6	5351 (6)	4010 (6)	2602 (10)	78 (3)
C7	6775 (6)	2803 (6)	883 (8)	68 (3)
C8	1138 (5)	2991 (5)	-1060 (7)	49 (2)
N2	1649 (4)	2014 (4)	-1629 (6)	45 (2)
C9	2603 (5)	1939 (5)	-2804 (9)	58 (3)
C10	3704 (6)	2511 (7)	-1920 (11)	93 (4)
C11	2198 (7)	2253 (6)	-4642 (9)	80 (3)
C12	1272 (6)	910 (5)	-1068 (8)	60 (3)
C13	755 (7)	114 (4)	-2627 (10)	92 (4)
C14	2255 (8)	379 (7)	62 (11)	106 (4)

^aEquivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

**Figure 1.** View of one of the independent molecular units of bis(*N,N*-diisopropylidithiocarbamato)copper(II) that shows the numbering of the atoms and thermal ellipsoids at the 40% probability level.

corrected for background and Lorentz and polarization effects but not for absorption. The linear absorption coefficient, μ , is 15.0 cm^{-1} .

The structure was solved by the heavy-atom and difference Fourier techniques and refined by the blocked-cascade least-squares refinement to the conventional residuals *R* and R_w of 0.041 and 0.048, respectively, where

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$R_w = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\sum |F_o|^2} \right]^{1/2}$$

The quantity minimized was $\sum w(|F_o| - |F_c|)^2$ where $|F_o|$ and $|F_c|$ are observed and calculated structure amplitudes and $w = 1/[\sigma^2(F_o) + 0.0008F_o^2]$. The anomalous dispersion corrections, $\Delta f'$ and $\Delta f''$, for copper were included in the calculations of F_c . Non-hydrogen atoms were refined with anisotropic temperature factors. Hydrogen atoms were placed in calculated positions at 0.96 \AA from the attached carbon atom and refined in the riding mode with an isotropic temperature factor that was 1.2 times the equivalent isotropic temperature factor of the attached carbon atom. A secondary extinction correction was applied near the end of the refinement; the value of the extinction coefficient was $3(1) \times 10^{-5}$. The goodness of fit parameter was 1.0. The final difference Fourier was featureless, the largest difference peak being $0.3 e/\text{\AA}^3$. A summary of crystal data is presented in Table I.

All crystallographic calculations were performed on a Data General Desktop microEclipse computer with the program package SHELXTL,¹⁰ taking the X-ray atomic scattering factors and anomalous dispersion corrections from ref 11.

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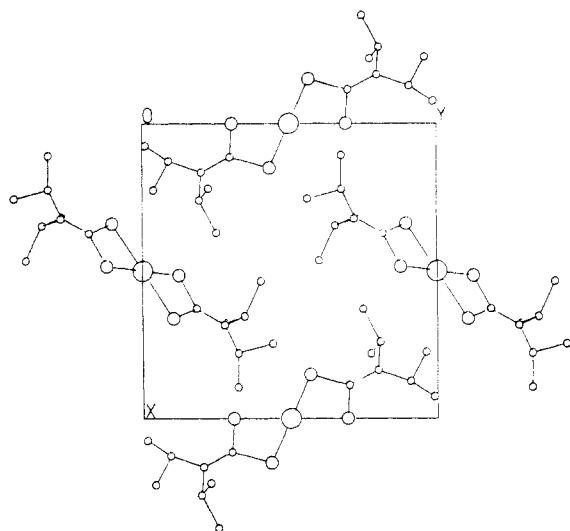


Figure 2. Packing diagram for the crystal structure of bis(*N,N*-diisopropylthiocarbamato)copper(II) which reveals that there are no discrete dimers in structure and that there are no close copper-sulfur contacts.

Table III. Selected Bond Distances and Angles in Bis(*N,N*-diisopropylthiocarbamato)copper(II)

Bond Lengths (Å)			
Cu1-S1	2.280 (2)	C1-S1	1.715 (5)
Cu1-S2	2.284 (2)	C1-S2	1.723 (6)
Cu2-S3	2.286 (2)	C8-S3	1.711 (7)
Cu2-S4	2.283 (2)	C8-S4	1.715 (6)
C1-N1	1.324 (7)		
C8-N2	1.327 (7)		
Bond Angles (deg)			
S1-Cu1-S2	77.2 (1)	S3-Cu2-S4	76.7 (1)
S1-Cu1-S2' ^a	102.8 (1)	S3-Cu2-S4' ^a	103.3 (1)
Cu1-S1-C1	85.4 (2)	Cu2-S3-C8	85.8 (2)
Cu1-S2-C1	85.1 (2)	Cu2-S4-C8	85.9 (2)
S1-C1-S3	111.8 (3)	S3-C8-S4	111.6 (3)

^a Primed atoms are related to the corresponding unprimed atoms by inversion through a center of symmetry.

Results and Discussion

Crystal and Molecular Structure. The fractional atomic coordinates for the non-hydrogen atoms are given in Table II, and those for the hydrogen atoms are deposited as supplementary material. Views of the independent molecular units that show the numbering scheme for the non-hydrogen atoms are given in Figures 1 and S1 (supplementary material), and a packing diagram is given in Figure 2. A table of anisotropic temperature factors for non-hydrogen atoms and a table of structure factors are deposited as supplementary material.

The copper atoms are situated at inversion centers, which makes the CuS₄ moiety exactly planar with the following deviations, in angstroms, from planarity: moiety 1 N1 (-0.0010), C1 (0.0024), S1 (-0.0007), S2 (-0.0007); moiety 2 N2 (-0.0038), C8 (0.0091), S3 (-0.0026), S4 (-0.0027). The copper atom Cu1 is off the plane of moiety 1 by 0.27 Å, and the copper atom Cu2 is off the plane of moiety 2 by 0.09 Å.

The four independent Cu-S bonds have an average bond distance of 2.283 Å, and the four carbon-sulfur bonds have an average distance of 1.716 Å. The ligand "bite" angle S-C-S has a mean value of 111.7°. The N-C and C-S bond distances reported for individual bonds in Table III are consistent with considerable double-bond character in these bonds.

Magnetic Properties. Magnetic susceptibility data were collected in the temperature range 1.76–20 K, and the data are shown as μ_{eff} versus temperature in Figure 3. The data may be fit by using the Curie-Weiss law, yielding parameters $C = 0.415$ and $\theta = -0.737^\circ$. There is significant deviation from the Curie-Weiss law at the lowest temperatures of the measurements. Prior to the structural determination reported herein, the data were fitted by

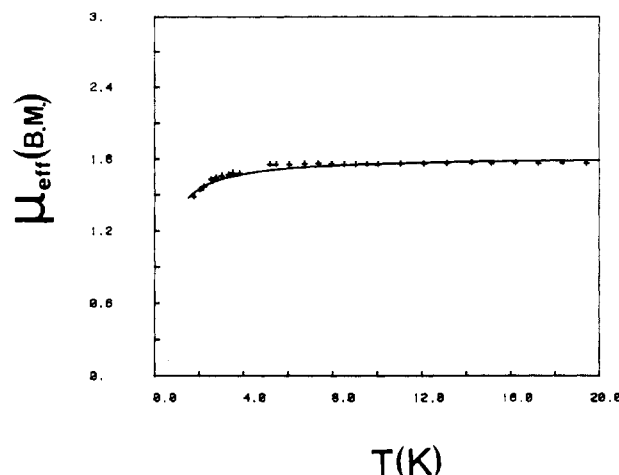


Figure 3. Temperature dependence of the magnetic moment of bis(*N,N*-diisopropylthiocarbamato)copper(II). Experimental data are shown as +s, and the solid line was generated as described in the text.

the dimer equation for a pair of exchange-coupled $S = 1/2$ ions, and a satisfactory fit was obtained. However, the subsequent structural determination showed that dimers did not exist, and since the magnetic parameters obtained from the fitting calculations are not meaningful, they will not be given here. We will now utilize available magnetic models, suggested by the structural determination, to approximate the magnitude of the antiferromagnetic exchange coupling in bis(*N,N*-diisopropylthiocarbamato)copper(II).

A number of magnetic models exist for regular spin lattices; these include the chain model, various two-dimensional models, the simple cubic three-dimensional model, the face-centered cubic model, the body-centered cubic model, and others. All of the models that were examined in this work gave a small antiferromagnetic exchange coupling constant and a g value in good agreement with the g value determined from EPR measurements on a powdered sample at 77 K. We choose to discuss only the results from the body-centered cubic model and the chain model, since these had the lowest least-squares agreement factors.

By using the exchange Hamiltonian

$$\mathcal{H} = -2J_i S_i \cdot S_j$$

Rushbrooke and Wood¹² have expressed the magnetic susceptibility of a body-centered lattice in terms of the expansion

$$\chi = (Ng^2\mu_B^2/3kT)[S(S+1)][\sum a^n (J/kT)^n]$$

with coefficients a_1, a_2, \dots, a_6 for both antiferromagnetic and ferromagnetic cases. In addition, Rushbrooke and Wood found that, above the critical temperatures, the theoretical curves for magnetic susceptibilities were rather insensitive to the precise lattice structures. Although the structure of bis(*N,N*-diisopropylthiocarbamato)copper(II) only crudely approximates a body-centered system, the findings of Rushbrooke and Wood lend some validity to the approach used here.

A least-squares fit of the magnetic susceptibility equation to the data by using a nonlinear Simplex fitting routine yielded $J = -0.12 \text{ cm}^{-1}$ and $g = 2.10$. Both parameters were allowed to vary freely in the fitting process. The solid line shown in Figure 4 was generated with these best-fit parameters.

An inspection of the structure reveals aspects of nearly isolated chains running along the c axis, these having intermolecular copper-copper separations of 7.629 Å along the "chains" and intermolecular copper-copper separations greater than 11 Å between the chains. This observation stimulated the attempt to fit the experimental data with the Heisenberg chain theory and the results of Bonner and Fisher.¹³ The best-fit parameters were $J = -0.39 \text{ cm}^{-1}$ and $g = 2.11$.

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The important conclusion from these fitting exercises is that long copper-sulfur intermolecular contacts can lead to significant exchange coupling interactions. Other long copper-sulfur intermolecular contacts that give rise to large exchange coupling constants include $[\text{Cu}(\text{TCH})\text{Cl}_2]\text{Cl}_2$ (TCH = 1H^+ -thiocarbonylhydrazidium), which has a long copper-sulfur bond in the Cu_2S_2 unit of 3.310 \AA ¹⁴ and $J = -12.4 \text{ cm}^{-1}$,¹⁵ $[\text{Cu}(\text{dmdtc})_2]_\infty$ (dmdtc = dimethyldithiocarbamate), with the long Cu-S bonding being 3.159 \AA ¹⁶ and $J = -1.2 \text{ cm}^{-1}$,¹⁷ and a series of dithiaalkane alternating-chain compounds of the general formula $[\text{Cu}(\text{dithiaalkane})\text{Cl}_2]_\infty$.¹⁸ Also germane to this discussion is the observation of a J value of -8.5 cm^{-1} in $[\text{Ni}(\text{DDDT})_2]^-$ (DDDT = 5,6-dihydro-1,4-dithiin-2,3-dithiolate), in which the shortest

Ni-Ni distance is 8.152 \AA ,³ and the recent report of a J value of -23.8 cm^{-1} in the sulfur-bridged iron dimer $\{\text{K}_2[\text{Fe}(\text{dithiooxalato})_2\text{NO}]\}_2$, where the long Fe-S contact in the Fe_2S_2 exchange-coupled unit is 3.823 \AA .⁴

Antiferromagnetic exchange coupling interactions are reasonably easily detected, even if they are small, since the observed magnetic moments depart from the spin-only moment toward lower values. If the interactions are ferromagnetic, they are significantly more difficult to detect, especially in the presence of zero-field splittings and, for clusters, in the presence of anti-ferromagnetic intermolecular interactions.

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Supplementary Material Available: A figure showing the labeling of the non-hydrogen atoms in the second independent molecule in the unit cell and tables of hydrogen atom coordinates, anisotropic thermal parameters, bond lengths, and bond angles (5 pages); a listing of calculated and observed structure factors (16 pages). Ordering information is given on any current masthead page.

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Ferro- and Antiferromagnetic Coupling between Metal Ions and Pyridine-Substituted Nitronyl Nitroxides

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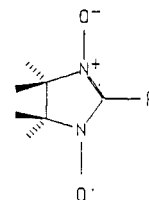
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The synthesis and crystal structure of two novel adducts of manganese(II) and nitronyl nitroxide radicals of formula $\text{Mn}(\text{hfac})_2(\text{NITpPy})_2$ (I) and $\text{MnCl}_2(\text{NITpPy})_4$ (II), where hfac = hexafluoroacetylacetonate and NITpPy = 2-(4-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazolyl-1-oxyl 3-oxide, are reported. Compound I crystallizes in the monoclinic space group $P2_1/n$ with $a = 14.037$ (2) \AA , $b = 6.500$ (7) \AA , $c = 22.180$ (5) \AA , $\beta = 99.39$ (1)°, and $Z = 2$. Compound II crystallizes in the triclinic space group $P\bar{1}$ with $a = 7.205$ (4) \AA , $b = 13.613$ (2) \AA , $c = 13.630$ (4) \AA , $\alpha = 89.74$ (2)°, $\beta = 78.69$ (4)°, $\gamma = 86.88$ (4)°, and $Z = 1$. In both cases the complex is mononuclear with the manganese ion octahedrally coordinated and bound to the nitronyl nitroxide radicals through the nitrogen atom of the pyridine ring. The magnetic susceptibility of both compounds suggests that the manganese ion and the radicals are ferromagnetically coupled with a coupling constant of about 1 cm^{-1} . The nickel(II) analogues, $\text{Ni}(\text{hfac})_2(\text{NITpPy})_2$ (III) and $\text{NiCl}_2(\text{NITpPy})_4$ (IV), were also synthesized, and IV was found to be isomorphous with II. The magnetic behavior of the nickel derivatives suggests that the metal ion is antiferromagnetically coupled to the radical through the pyridine ring with a coupling constant of about 10 cm^{-1} . The mechanism of exchange was analyzed in terms of orbital pathways involving the π^* molecular orbital of the NITpPy radical containing the unpaired electron, the pyridine nitrogen lone pair, and the metal orbitals.

Introduction

We are currently attempting to synthesize molecular based ferromagnets²⁻⁵ by using metal ions directly bound to stable organic radicals as building blocks.⁶ The radicals we have used so far are the *o*-semiquinones^{7,8} and the nitronyl nitroxides,⁶ NITR

(NITR = 2-R-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazolyl-1-oxyl 3-oxide), whose general formula is sketched as follows:



As far as the elementary interactions are concerned, the conditions under which either ferro- or antiferromagnetic coupling is established between the metal ions and the radicals are now

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