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Experimental and Quantum-Chemical Investigation of the Magnetic Exchange Mechanism in a Series of (μ-Terephthalato)bis[(polyamine)copper(II)] Complexes

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Weak antiferromagnetic exchange interactions are seen for four Cu(II) dimers of the general formula $[Cu_2(\mu\text{-TPHA})(\text{polyamine})_n]X_2$ (where TPHA is the terephthalate dianion, polyamine is dien, trien ($n = 2$), bpy, or *o*-phen ($n = 4$) ligands and X = ClO_4^- or PF_6^-) and a weak ferromagnetic one for the $[Cu_2(\mu\text{-TPHA})(bpy)_4](ClO_4)_2\cdot 2H_2O$, as evidenced by variable-temperature (4.2–290 K) magnetic susceptibility data. Exchange parameters, J, are found to be −1.83, −2.20, −0.45, −0.50, and +1.10 cm^{-1}, respectively, by least-squares fitting to the spin Hamiltonian $\hat{H} = -2J\cdot\hat{S}_1\cdot\hat{S}_2$. There is a monotonic decrease in the exchange interaction as the local geometry around each magnetic center varies from octahedral to distorted square-based pyramidal or trigonal bipyramidal. Insight concerning the effect of structural parameters on the magnitude of the magnetic exchange interactions was gained through EHMO calculations performed on model compounds exhibiting a wide range of stereochemistries on the two magnetic centers. Accordingly, the most suitable orbital pathways, mainly of σ-type, propagating the magnetic exchange interaction were verified. The magnetic exchange interaction mechanism was predicted to be both inter- and intramolecular in nature. Furthermore, the antiferromagnetic exchange interactions were found to be dependent on both the stereochemistry around the two magnetic centers and the bonding mode of the terephthalate dianion. Estimates of the J parameters experimentally derived were in close agreement with corresponding trend theoretically calculated. The possibility of the terephthalato ligand to be used as an appropriate bridging unit in designing magnetic systems with expected magnetic properties is discussed.

Introduction

The superexchange interaction between magnetic ion pairs in a variety of magnetic systems has attracted considerable interest in the last few years.[1] Attempts have been made to design magnetic systems with an intradimer separation between the two magnetic centers in the range[2,3] 10–11 Å. This distance, according to the relation proposed by Coffman and Buettner,[4] corresponds to the smallest $|J|$ value of about 0.1 cm^{-1}, detectable by the usual magnetic techniques. The terephthalato dianion and its thio analogues, being potential ambident ligands, seem to be appropriate bridging units to design such magnetic systems.

Recently,[2,3] few binuclear d^1–d^1 and d^9–d^9 magnetic systems, with the terephthalato dianion as an intervening ligand, have been isolated, and their magnetic properties were investigated thoroughly. In both cases very weak antiferromagnetic interactions were observed and attributed to different magnetic exchange mechanisms. Hendrickson et al.[3] proposed an intramolecular interaction in the d^1–d^1 (μ-terephthalato)bis(η^5-bicyclopentadienyl)dititanium(III) magnetic system. On the contrary, Kahn and co-workers[2] suggested that the magnetic interaction in the d^9–d^9 (μ-terephthalato)bis(*N*,*N*,*N*′,*N*″,*N*″-pentaalkyldiethylenetriamine)dicopper(II) magnetic systems could be intermolecular in nature. Moreover, we recently have communicated[7] on a novel (μ-terephthalato)copper(II) dimer with unexpected strong antiferromagnetic interaction, which according to theoretical investigations was attributed to intermolecular exchange interactions. The leading factors responsible for the different magnetic behavior of the binuclear μ-terephthalato magnetic systems, along with the mechanistic aspects of their magnetic exchange interactions, are not well understood so far. For this reason our recent research interest[5-7] has been focused on the investigation of the factors affecting the long-distance magnetic interactions. This is accomplished through a theoretical approach and experimental data. Within this framework the results concerning the synthesis, characterization, and magnetic properties of five new binuclear (μ-terephthalato)copper(II) complexes are presented. These new complexes are $[Cu_2(\mu\text{-TPHA})(dien)_2](ClO_4)_2$ (**1**), $[Cu_2(\mu\text{-TPHA})(trien)_2](ClO_4)_2$ (**2**), $[Cu_2(\mu\text{-TPHA})(bpy)_4](PF_6)_2\cdot 2H_2O$ (**3**), $[Cu_2(\mu\text{-TPHA})(phen)_4](ClO_4)_2\cdot 2H_2O$ (**4**), and $[Cu_2(\mu\text{-TPHA})(bpy)_4](ClO_4)_2\cdot 2H_2O$ (**5**), where TPHA is the intervening terephthalato ligand and dien, trien, bpy, and phen are the abbreviations for the terminal diethylenetriamine, triethylenetetramine, 2,2′-bipyridine, and 1,10-phenanthroline ligands, respectively.

The experimental results, along with the results of EHMO calculations performed on model compounds, enabled us to elucidate the following points: (i) the possibility that the terephthalato bridging unit, either in its bis(monodentate) or bis(bidentate) coordination mode, is able to support superexchange interactions in d^9–d^9 magnetic systems; (ii) the effect of the magnetic center's ground state on the singlet–triplet energy gap; (iii) the leading factors responsible for the different magnetic behavior of the d^9–d^9 μ-terephthalato dimers and the orbital mechanism of the magnetic exchange interactions in each case.

Finally, a comparison between estimates of the J parameters, experimentally derived, with the corresponding trend, theoretically calculated, was attempted, too.

Experimental and Theoretical Section

Synthesis. All copper(II) binuclear complexes, except complex **3**, were prepared in a similar way using the following general procedure.[7,2]

A solution of 0.336 g (1 mmol) of piperidinium terephthalate and 1 or 2 mmol of the corresponding polyamine in methanol (60 mL) was added slowly under continuous magnetic stirring at room temperature to a methanolic solution (40 mL) of 0.74 g (2 mmol) of $Cu(ClO_4)_2\cdot 6H_2O$. The light or dark blue microcrystalline material derived was filtered off, washed several times with small portions of water followed by ethanol, acetone, and diethyl ether, and dried under vacuum. The reaction yields were 72, 30, 95, and 85% for the compounds **1**, **2**, **4**, and **5**, respectively.

Complex **3** was prepared by adding an ethanolic solution (20 mL) of 0.624 g (4 mmol) of 2,2′-bipyridine to a water suspension (20 mL) of 0.509 g (1 mmol) of $[Cu(TPHA)]_2\cdot 2H_2O$, prepared according to known procedure.[8] Most of the solid was dissolved, and the color of the mixture turned dark blue. The solid was filtered off, and the filtrate upon ad-

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Table III. $\nu_{as}(CO_2^-)$ and $\nu_s(CO_2^-)$ Spectral Bands (cm^{-1}) of the Compounds Along with Their Differences and the Coordination Mode of the TPHA Ligand

compd	$\nu_{as}(CO_2^-)$	$\nu_s(CO_2^-)$	Δ ($\nu_{as} - \nu_s$)	coordn mode
$(TPHA^{2-})2K^+$	1580	1410	170	ionic
		1410	168	bidentate
1	1578			
		1372	206	monodentate
2	1576	1393	183	bidentate
3	1612	1370	242	monodentate
4	1595	1355	240	monodentate
5	1598	1354	244	monodentate

dition of 1.5 g of NH_4PF_6 gave complex **3** (yield 58%).

Elemental analyses for all complexes were satisfactory (Table I).[9]

Optical Measurements. Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer (4000–240 cm^{-1}) using KBr pellets.

Reflectance spectra in the range of 200–2000 nm were measured on Hitachi 356 and Beckman UV 5240 spectrometers by using Nujol films. Sr_2ZnTeO_6 and freshly sintered MgO were used as standards.

EPR spectra were recorded on a JEOL-JES-ME X-band (ν = 9.30 GHz) spectrometer using a nuclear magnetometer (MJ 11OR), a microwave frequency meter (JES-SH-30X), and EPR standards at both room temperature and 173 K.

Magnetic Measurements. Magnetic measurements were carried out on a Faraday type magnetometer using a sensitive Cahn RG-HV electrobalance in the temperature range of 4.2–295 K. The magnetic field applied was 6.25 kG. Mercury tetrakis(thiocyanato)cobaltate was used as a susceptibility standard. Corrections for diamagnetism were estimated as -323×10^{-6}, -387.5×10^{-6}, -620×10^{-6}, -792.5×10^{-6}, and -558×10^{-6} cm^3 mol^{-1} for compounds **1**–**5**, respectively. Magnetism of the samples was found to be field-independent. The TIP per copper(II) ion was assumed to be 60×10^{-6} cm^3 mol^{-1}. The effective magnetic moment was calculated by using the equation $\mu_{eff} = 2.83\ (\chi_M T)^{1/2}$, whereas the exchange parameters J were estimated with the computer program BGD-1/81 on an ODRA 1305 computer.

Computational Details. Calculations were carried out in the framework of the extended Hückel LCAO-MO[10] method with off-diagonal matrix elements given by the expression of Wolfsberg–Helmholz.[11] For the reasons described previously,[5] option 0 of the FORTICON-8 program[12] was used along with hypothetical nitrogen donor atoms possessing only one sp^3 doubly occupied hybridized orbital in the place of the terminal polyamine ligands. Furthermore, reasonable diagonal matrix elements (H_{dd} for Cu and H_{pp} for N and O atoms) along with the best K values, allowing for a good fit between experimental and theoretical ligand field transitions, were determined, by following a series of calculations. The deviations between the theoretical and experimental frequencies of the ligand field bands plotted against the H_{ii} and K values showed characteristic minima corresponding to the best values of the parameters. All these values of the different local geometries around the paramagnetic centers are collected in Table II.[9] The values of all other diagonal matrix elements H_{ii} for carbon and hydrogen were those given in the literature.[5,10,12] Orbital exponents for C, N, O, H, and Cu were those used previously.[5]

The structural parameters used for the regularized structure of each model compound investigated were obtained from analogous copper(II) complexes of known structures.[2,13,14] Thus, the Cu–O and Cu–N bond lengths were taken as 1.96 and 2.00 Å, respectively. For the unidentate mode of coordination of the terephthalato ligand the distance between the Cu(II) ion and the noncoordinated oxygen atom of the carboxylato group was taken as 2.75 Å. The terephthalato bridging unit was considered quite planar, and the local geometries around the magnetic centers were selected to represent the regular structures present in the structural pathway established for the Cu(II) polyamine complexes.[15]

Results and Discussion

Characterization and Properties of Complexes. All five homobinuclear copper(II) complexes investigated were light or dark blue microcrystalline solids, stable in air and insoluble in most of the common organic and inorganic solvents. The identification of compounds was based on elemental analysis and spectral studies (IR, UV–vis, and EPR).

The most relevant IR absorption bands of the complexes along with their assignments are shown in Table III. A thorough analysis of the IR data provided information about the nature of the coordination sphere and the coordination number of each magnetic center in the binuclear species. Thus, all five complexes exhibited the characteristic strong and broad $\nu_{as}(CO_2)$ and $\nu_s(CO_2)$ absorption bands due to the terephthalato ligand coordinated in an end-to-end fashion. However, the shape and the position of these bands were different for the five complexes, suggesting different coordination modes of the ligand. Complexes **3**–**5** showed two bands separated by ca. 240 cm^{-1}, which is consistent with an amphimonodentate bonding mode[16] of the terephthalato ligand with the copper centers. Two bands were also observed for complex **2**, separated by ca. 183 cm^{-1}, suggesting a bidentate coordination mode for both carboxylato groups. However, the $\nu_s(CO_2)$ band of complex **1** was split, the two $\nu_{as}(CO_2)-\nu_s(CO_2)$ values being 206 and 162 cm^{-1}, respectively. This calls for the coexistence of both bi- and unidentate carboxylato groups in the complex. The absorption bands associated with the polyatomic PF_6^- and ClO_4^- groups were typical[17-19] for ionic bonding. Moreover, all five complexes exhibited the characteristic bands along with their overtones due to the amino groups of the coordinated terminal polyamine ligands.

Insight concerning the stereochemistry of each magnetic center for each complex was gained through the analysis of their electronic and EPR spectra. Complex **1** exhibited a broad-band envelope with a maximum at 15 870 cm^{-1} and two shoulders at 19 230 and 12 820 cm^{-1}. According to the electronic criterion established for Cu(II) polyamine complexes[20-22] this spectrum indicates the coexistence of a square-planar and a trigonal-bipyramidal chromophore. Surprisingly, complex **1** gave a single somewhat asymmetric EPR derivative at both room temperature and 173 K with g values of 2.099 and 2.098 (peak-to-peak line widths of 67 and 56 G, respectively). This could be attributed to the low resolution of X-band EPR for nearby signals.[23]

The ligand field broad-band envelope of complex **2**, exhibiting a maximum at 16 180 cm^{-1} and two shoulders at 17 700 and 14 810 cm^{-1}, strongly suggests a tetragonally distorted octahedral stereochemistry around both magnetic centers. Consistent with this stereochemistry was also the observed room-temperature axial powder EPR spectrum of **2** ($g_\parallel = 2.169$, $g_\perp = 2.070$; $g_{av} = 2.103$), which calls for[24] a $|x^2 - y^2\rangle$ ground state, as could be expected.

3 and **5** exhibited similar ligand field spectral broad-band envelopes with two distinct maxima of unequal intensity. These maxima, occurring at 14 810 and 9 940 cm^{-1} for complex **3** and 15 040 and 10 480 cm^{-1} for **5**, are characteristic[25] of Cu(II) chromophores with intermediate stereochemistries between those of the cis distorted octahedral and trigonal bipyramidal. The EPR spectrum of **3** was axial at both 295 K ($g_\parallel = 2.215$, $g_\perp = 2.109$; $g_{av} = 2.145$) and 173 K ($g_\parallel = 2.200$, $g_\perp = 2.097$; $g_{av} = 2.132$). This spectrum is not consistent with a $|z^2\rangle$ ground state, and its rhombicity was not resolved even at 173 K. In contrast, complex **5** gave a rhombic X-band EPR spectrum with $g_1 = 2.025$, $g_2 = 2.063$, and $g_3 = 2.209$. The high-field signal at $g = 2.025$ indicates

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Table IX. Exchange Parameters and Curie and Weiss Constants[a] of the Complexes

compd	J, cm^{-1}	C, cm^3 mol^{-1} K	Θ, K
1	−1.83	0.405	−2.14
2	−2.22	0.403	−3.6
3	−0.44	0.447	−4.03
4	−0.50	0.41	0.96
5	+1.11	0.43	0.18

[a] Data were fit from 4.2 to 290 K.

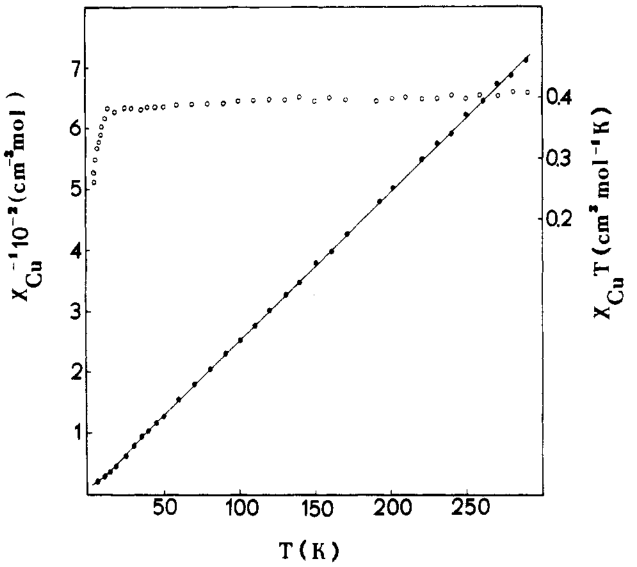

Figure 1. Temperature dependence of $\chi_M T$ and $1/\chi_M$ for complex **1**.

a $|z^2\rangle$ ground state,[24,26] consistent with a trigonal-bipyramidal stereochemistry around the two copper centers. Furthermore, the g_1 value for **5** was in better proximity to the g_e value of 2.0023 than the one of **3**, presumably reflecting a Cu(II) coordination geometry in the former that is closer to an idealized trigonal bipyramid.

The ligand field spectrum of **4**—a broad-band envelope with a maximum at 14 750 cm^{-1} and a shoulder at 13 420 cm^{-1}—strongly suggests five-coordinated Cu(II) chromophores possessing a distorted square-pyramidal (SBP) stereochemistry. The axial EPR spectrum ($g_\parallel$ = 2.245, $g_\perp$ = 2.081; g_{av} = 2.137) of **4** is more consistent with the proposed structure, as a $g_\parallel$ signal at about 2.24 supports[26] a fair degree of SBP character for the Cu(II) coordination geometry.

Finally, it should be noted that the EPR spectra of all five complexes did not exhibit any sign of exchange interaction or triplet ground state.

Magnetic Measurements. Variable-temperature (4.2–295 K) magnetic susceptibility data (Tables IV–VIII)[9] were collected for solid samples of all five binuclear Cu(II) complexes. These data were first fit to the Bleaney–Bowers equation[27] using the average g value obtained from EPR measurements.[26] Moreover, as the magnetic exchange interactions were small, it was felt that the magnetic susceptibility data could be also fit to the magnetization equation,[28] which includes the effect of Zeeman splitting of the triplet-state energy levels. The results obtained from both equations were essentially identical. A summary of the least-squares-fit exchange parameters J and Curie (C) and Weiss (Θ) constants, determined from the magnetic susceptibility data for the complexes under investigation, is presented in Table IX. Furthermore, the magnetic behavior of the complexes, in the form of $\chi_M T$ vs. T plot, χ_M being the molecular magnetic susceptibility and T the temperature, is depicted schematically in Figures 1–5.

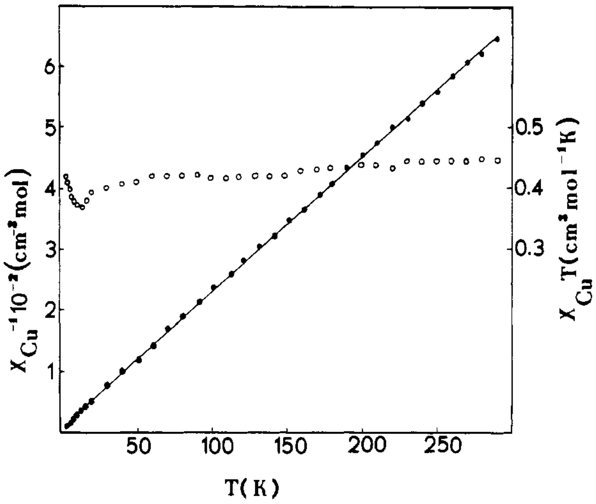

Figure 3. Temperature dependence of $\chi_M T$ and $1/\chi_M$ for complex **3**.

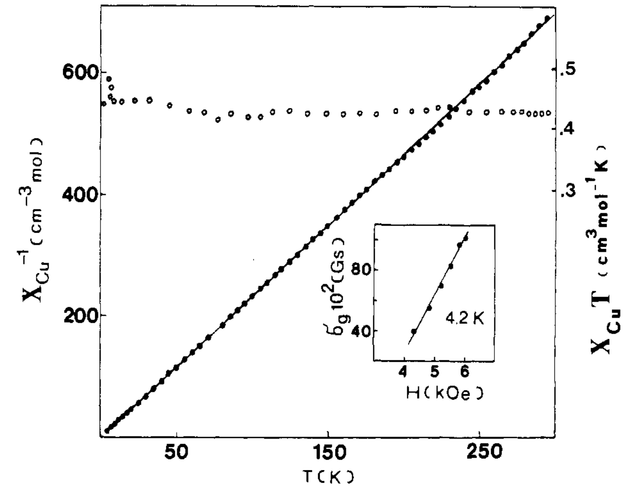

Figure 5. Temperature dependence of $\chi_M T$ and $1/\chi_M$ along with the isothermal of the magnetization at 4.2 K for complex **5**.

For complex **1** $\chi_M T$ decreased slightly upon cooling down (0.409 cm^3 mol^{-1} at 290 K and 0.378 cm^3 mol^{-1} K at 20 K) except below 20 K, where it decreased more drastically down to a value of 0.261 cm^3 mol^{-1} K at 4.2 K (Figure 1). This latter accounts for a very weak intermolecular antiferromagnetic interaction[29] below 14 K. The dependence of $1/\chi_M$ on T, shown also in Figure 1, was linear with only small anomalies at liquid-helium temperature. The lowering of the μ_{eff}/Cu(II) on cooling (1.81 μ_B at 290 K and 1.45 μ_B at 4.2 K) along with the minus sign of the Weiss constant value strongly suggest an antiferromagnetic interaction for **1**. The energy difference between the two thermally accessible spin states of **1**, i.e. the triplet excited state (S = 1) and the singlet ground state (S = 0), which is equal to $|2J|$, was found to be 3.66 cm^{-1}. The relatively small $|2J|$ value indicates that the triplet state depopulating could be observed below 20 K; below this temperature the magnetic moment declines down to 1.43 μ_B at 4.2 K. The interchain coupling between the dimers in the solid state is weak[30] as the interdimer exchange parameter J', estimated by the $J' = \gamma N g^2 \beta^2 / 2z$, was only −0.22 cm^{-1} (for z = 2), where all symbols have their usual meaning and z represents the number of nearest-neighbor Cu(II) ions.

Complex **2** exhibited analogous magnetic susceptibility data (Figure 2).[9] Thus, $\chi_M T$ decreased slightly on cooling down (0.401 cm^3 mol^{-1} K at 290 K and 0.373 cm^3 mol^{-1} K at 18 K) except below 18 K, where it decreased drastically down to a value of 0.227 cm^3 mol^{-1} K at 4.2 K. The μ_{eff}/Cu(II) values over the temperature

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range varied from 1.79 μ_B at 290 K to 1.35 μ_B at 4.2 K. These magnetic data call again for an antiferromagnetic interaction in complex **2**. Furthermore, the J' value of −0.70 cm^{-1} (for $z = 2$) supports a stronger interdimer coupling for **2** than **1**.

The magnetic behavior of **3** (Figure 3) was different. Both $\chi_M T$ and μ_{eff}/Cu(II) values decreased slightly upon cooling down (0.450 cm^3 mol^{-1} K, 1.90 μ_B at 290 K and 0.418 cm^3 mol^{-1} K, 1.83 μ_B at 12 K, respectively). These results could be combined with an antiferromagnetic interaction of **3** for the temperature range 290–12 K. In contrast, below 12 K, an increase of both values to 0.418 cm^3 mol^{-1} K and 1.83 μ_B, respectively at 4.2 K was observed. The very slight variation in the μ_{eff}/Cu(II) values observed indicates a very weak superexchange interaction. Moreover, a γ value of 0.07 cm^{-1} and a positive value of 0.029 cm^{-1} for the zJ' product were derived. This latter accounts well for the anomalous increase of the μ_{eff}/Cu(II) values observed below 12 K. Hence, a very weak intermolecular ferromagnetic interaction could be present below 12 K.

$\chi_M T$ of complex **4** (Figure 4)[9] remained essentially constant throughout the temperature range of 295 K (0.417 cm^3 mol^{-1} K) to 9 K (0.419 cm^3 mol^{-1} K) except below 9 K, where it decreased to a value of 0.385 cm^3 mol^{-1} K at 4.2 K. Moreover, the μ_{eff}/Cu(II) values ranged from 1.85 μ_B at 295 K to 1.75 μ_B at 4.2 K. A weak antiferromagnetic exchange interaction could also be suggested for **4** along with a very weak interdimer coupling ($J' = -0.18$ cm^{-1} for $z = 2$).

Finally, the magnetic behavior of **5** shown in Figure 5 was as follows: $\chi_M T$ increased slightly upon cooling down from 295 K (0.428 cm^3 mol^{-1} K) to 5 K, appeared to reach a maximum equal to 0.495 cm^3 mol^{-1} K at 5 K, and decreased slightly to a value of 0.441 cm^3 mol^{-1} K at 4.2 K. This behavior is characteristic for a ferromagnetic coupling[29,31] between the Cu(II) ions stabilizing the triplet state in regard to the singlet one. Furthermore, the decrease of $\chi_M T$ below 5 K suggests that a very weak intermolecular antiferromagnetic interaction superimposes itself on the intramolecular ferromagnetic coupling.

The magnetic susceptibility results of the five (μ-terephthalato)copper(II) dimers under investigation establish weak antiferromagnetic exchange interactions for all but complex **5**, which exhibited a weak ferromagnetic one. Moreover, the magnetic exchange parameters, J (Table IX) estimated for all complexes, do reflect the variation in the local geometry of the magnetic centers for this class of compounds. Therefore, the experimentally derived J parameter trend was

$$J_{\text{TDO-TDO}} > J_{\text{SP-TBP}} > J_{\text{TBP-TBP}} \simeq J_{\text{SBP-SBP}}$$

where the subscripts TDO, SP, TBP, and SBP were the abbreviations used for the stereochemistries tetragonally distorted octahedral, square planar, trigonal bipyramidal, and square-based pyramidal around each magnetic center, respectively.

At first sight, the observed trend in the magnitude of the exchange parameters could be explained on the grounds of the electronic (basicity)[32] and steric effects of the terminal nitrogen donor ligands as well as the bonding mode of the terephthalato ligand and the nature of the counteranions—ClO$_4^-$ or PF$_6^-$—of the complexes. Therefore, attempts have been made to find some correlation between the stereochemistries around each magnetic center and the exchange parameters, based on quantum-chemical calculations of the EHMO type.

Quantum-Chemical Interpretations and Mechanism of Superexchange Interactions. The EHMO calculations, performed on model (μ-terephthalato)copper(II) dimers, were selected to represent all possible regular stereochemistries of Cu(II) complexes. Furthermore, the intervening terephthalato ligand was considered to be coordinated either in its bis(monodentate) or bis(bidentate) bonding mode.

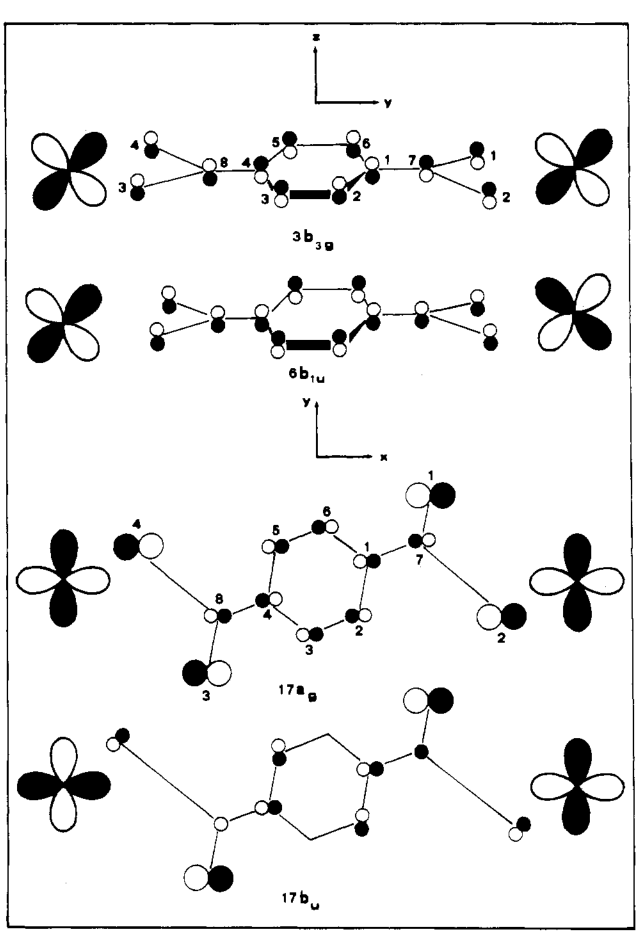

Figure 6. Schematic representation of the molecular orbitals, singly occupied in the triplet state, of the T_d–T_d model dimers.

Following the line of the molecular orbital analysis of superexchange interactions, suggested by Hoffmann et al.,[33] the orbital energy splitting term $(\epsilon_1 - \epsilon_2)^2$ (ϵ_1 and ϵ_2 being the symbols used for the eigenvalues of the symmetric and antisymmetric MO's where the unpaired electrons reside), was used as a qualitative measure of the magnetic exchange interaction in a series of analogous magnetic systems. In the light of these results (Table X), the following trend of the J parameters with regard to the stereochemistry of the magnetic centers and the bonding mode of the terephthalato bridging unit could be proposed:

$$J_{T_d\text{-}T_d}(\text{bi}) > J_{T_d\text{-}T_d}(\text{uni}) > J_{O_h\text{-}O_h}(\text{bi}) > J_{\text{SP-SP}}(\text{uni}) > J_{O_h\text{-}O_h}(\text{uni}) > J_{\text{TBP-TBP}}(\text{uni}) > J_{\text{TBP-TBP}}(\text{bi}) > J_{\text{SBP-SBP}}(\text{uni}) \gg J_{\text{SBP-SBP}}(\text{bi}) \simeq J_{\text{SP-SP}}(\text{bi})$$

An inspection of the series clearly demonstrates the great importance of both the local geometries of the two paramagnetic centers and the coordination mode of the bridging terephthalato ligand on the magnitude of the magnetic exchange interactions. Thus, as far as the binuclear complexes with four-coordinated magnetic centers are concerned, those possessing tetrahedral local geometries are predicted to exhibit much stronger antiferromagnetic exchange interactions than the square-planar ones. In particular, the T_d–T_d(bi) model is at the top of the series, whereas the SP–SP(bi) is at the bottom. The relative magnetic exchange parameter value of the latter is estimated to be only 0.025 for the T_d–T_d(bi) model (its relative J value was taken as 100). Moreover, it should exhibit a very weak AF interaction or even a ferromagnetic one, as its orbital energy splitting value is almost zero. The magnetic behavior of all four model compounds, exhibiting four-coordinated magnetic centers, could implicitly be accounted for on the grounds of the form of the symmetric and antisymmetric frontier MO's, where the unpaired electron resides. These singly occupied molecular orbitals (SOMO's) for the tetrahedral and

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Table X. Orbital Energy Splitting Values $\epsilon_1 - \epsilon_2$, Along with Their Squares and the Relative J Values of the Model Compounds

model	energy, eV HOMO	energy, eV NHOMO	$\epsilon_1 - \epsilon_2$	$(\epsilon_1 - \epsilon_2)^2 \times 10^8$	rel J
SP–SP(bi)	-10.132 7	-10.213 57	0.000 3	9	0.025
T_d–T_d(bi)	-11.426 78	-11.445 68	0.018 9	35721	100.0
O_h–O_h(bi)	-10.117 94	-10.127 74	0.009 8	9604	27.0
SBP–SBP(bi)	-10.515 18	-10.515 50	0.000 32	10	0.028
TBP–TBP(bi)	-10.569 13	-10.573 07	0.003 94	1552	4.3
SP–SP(uni)	-10.103 78	-10.110 85	0.007 07	4998	14.0
T_d–T_d(uni)	-11.633 64	-11.646 94	0.013 30	17689	50.0
O_h–O_h(uni)	-10.166 10	-10.172 02	0.005 92	3505	10.0
SBP–SBP(uni)	-9.874 19	-9.876 4	0.002 21	448	1.3
TBP–TBP(uni)	-10.099 68	-10.105 16	0.005 48	3003	8.4

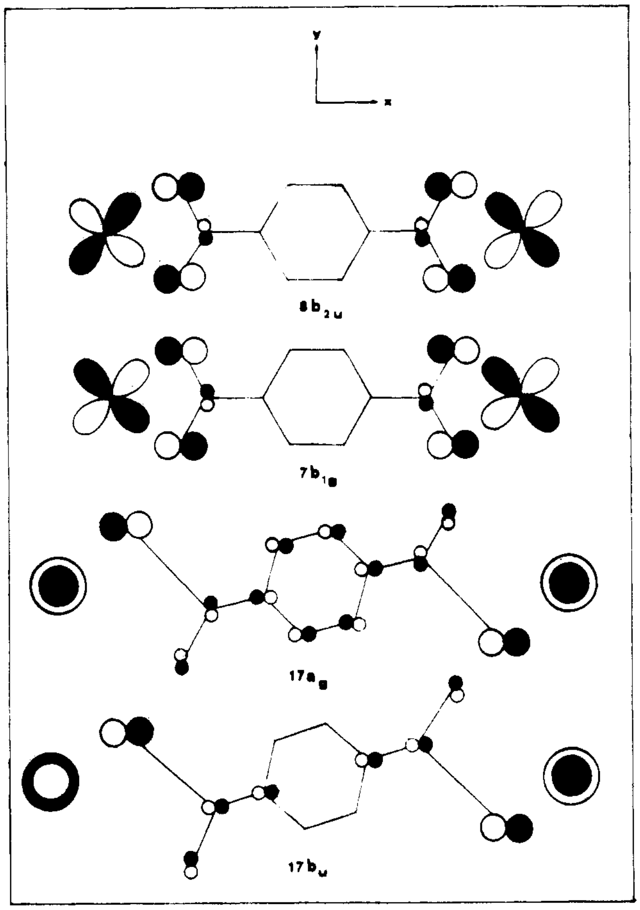

Figure 7. Schematic representation of the molecular orbitals, singly occupied in the triplet state, of the SP–SP model dimers.

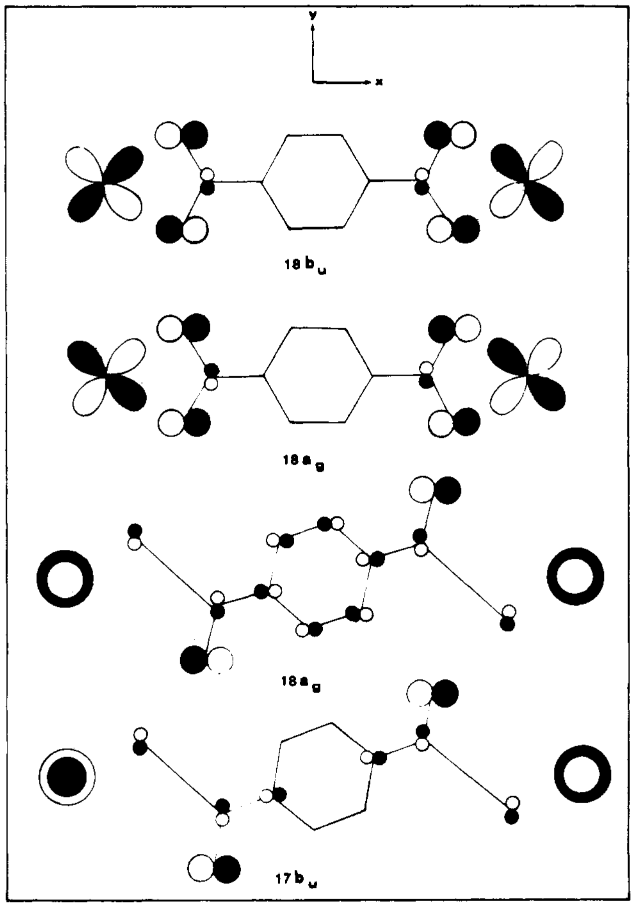

Figure 8. Schematic representation of the molecular orbitals, singly occupied in the triplet state, of the SBP–SBP model dimers.

square-planar model compounds are depicted schematically in Figures 6 and 7, respectively. Proper orbital pathways, providing suitable "channels" in transmitting the electronic effects, are involved in both tetrahedral model compounds. Actually, the bidentate μ-terephthalato ligand provides a π-type orbital pathway involved in the $6b_{1u}$ SOMO, which could support intramolecular magnetic exchange interactions via the "channel" involving the atoms O_1–O_2–C_7–C_1–C_4–C_8–O_3–O_4. On the other hand, the unidentate μ-terephthalato ligand provides a σ-type orbital pathway, involved in the $17a_g$ SOMO, supporting superexchange interactions via the O_2–C_2–C_3–C_4–C_8–O_4 and O_4–C_5–C_6–C_1–C_7–O_2 channels. Owing to the more delocalized character of the π-type orbital pathway, as compared to the σ-type one, it would be expected that the former is the more favorable channel in transmitting the electronic effect. Actually, the relative magnetic exchange parameter value of the T_d–T_d(uni) model was estimated to be only 50. However, it is worth noting that all proper orbital pathways are expected to support only weak intramolecular magnetic exchange interactions, due to the low overlap density values between some of the basis functions involved and/or the presence of nodal planes.

The SP–SP(bi) model does not exhibit any proper orbital pathway, since both $8b_{2u}$ and $7b_{1g}$ SOMO's are localized on the magnetic center's chromophores CuO_2N_2. Moreover, any overlapping between the basis functions located on the oxygen donor atoms (p_xAO's) should be zero owing to the very large separation between the oxygen atom pairs O_1,O_4 and O_2,O_3. In contrast, the SP–SP(uni) model possesses two incomplete orbital pathways involved in the $17a_g$ SOMO. These two "channels" involve the atoms O_2–C_2–C_3–C_4 and O_4–C_5–C_6–C_1, respectively. The incomplete orbital pathways present, the almost negligible orbital overlaps, and the increase of the unpaired electron density on the xy plane (due to the admixture of the $|x^2 - y^2\rangle$, $|z^2\rangle$ and $|xy\rangle$ AO's) account well for the moderately higher relative J value (=14) predicted for this model.

The consideration of the frontier SOMO's of the binuclear model compounds exhibiting five-coordinated magnetic centers accounts well for the relative magnitude of their magnetic exchange interactions predicted. The $18b_u$ and $18a_g$ SOMO's of the SBP–SBP(bi) model is quite analogous to the ones of the SP–SP(bi) model. Consequently, it should also exhibit very weak magnetic exchange interaction. Furthermore, the relative J value

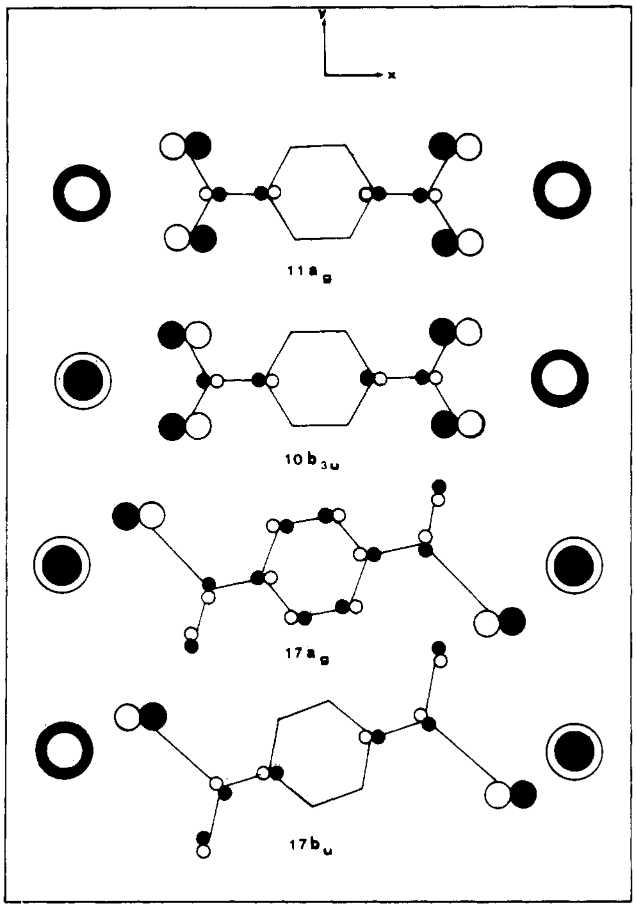

Figure 9. Schematic representation of the molecular orbitals, singly occupied in the triplet state, of the TBP–TBP model dimers.

of the model is only 0.03, which in turn is very close to the relative J value of the SP–SP(bi) model. Very weak magnetic exchange interaction (relative J value of 1.3) should also be expected for the SBP–SBP(uni) model (Figure 8), because of modal planes being in its $18a_g$ and $17b_u$ SOMO'S. However, the TBP–TBP(bi) model (Figure 9) should exhibit stronger antiferromagnetic interaction because of the orbital pathway C_7–C_1–C_4–C_8 involved in the $11a_g$ SOMO. The small but positive oxygen–oxygen overlaps along with the low unpaired electron density in the xy plane account for the relative J value of 4.30 estimated for this model. Finally, the TBP–TBP(uni) model involves analogous orbital pathways as the SP–SP(uni) one. This accounts well for the more favorable transmission of the electronic effects (relative J value of 8.4) of the former.

The SOMO'S of the two model compounds possessing six-coordinated magnetic centers are depicted schematically in Figure 10. Both possess proper orbital pathways for intradimer magnetic exchange interactions. In the $11a_g$ SOMO of the O_h–O_h(bi) model the two channels present involve the atoms O_1–C_6–C_5–O_4 and O_2–C_2–C_3–O_3, respectively. This could be the main reason for the higher relative J value of 27 estimated for this model. On the contrary, the O_h–O_h(uni) model involves analogous orbital pathways as the SP–SP(uni) one. As a consequence, they both exhibit analogous magnetic exchange interactions (relative J values of 10 for the former and 14 for the latter).

Insight concerning the mechanism of the superexchange interactions of the μ-terephthalato binuclear magnetic systems could be gained in the light of the theoretical and experimental results discussed above. As a matter of fact, there is a clear evidence for *intramolecular* magnetic exchange interactions in the complexes under consideration, since the experimentally derived trend of the exchange parameter J agrees with the theoretically established one. This is further supported by the magnetic and structural results available for four other μ-terephthalato dimers[2,3] of Ti(III) and Cu(II). Actually, the Ti(III) complex[3] exhibits a J value of -0.7 cm^{-1}, consistent with a tetrahedrally distorted square-planar configuration around each magnetic center. Moreover, complex **3** of ref 2 gave a $2J$ value that is essentially identical with the one of our complex **1** and that is in excellent agreement with our theoretical predictions. On the other hand, for complexes **1** and **2** of ref 4, exhibiting intermediate configurations between those of SBP and TBP around the magnetic centers, the authors asserted that if there is an intramolecular interaction, this will be more important in **2** than in **1**, because of the bis(bidentate) bonding mode of the terephthalato ligand in **2** and the bis(unidentate) one in **1**. However, according to our theoretical predictions, the bis(unidentate) bonding mode of the terephthalato ligand in binuclear complexes with five-coordinated magnetic centers provides more favorable orbital pathways in propagating the electronic effects than the bis(bidentate) one. This is in excellent agreement with the $2J$ values of -2.7 cm^{-1} and 0 cm^{-1} determined experimentally for complexes **1** and **2** of ref 2, respectively, and further verifies the intramolecular nature of the magnetic exchange interactions.

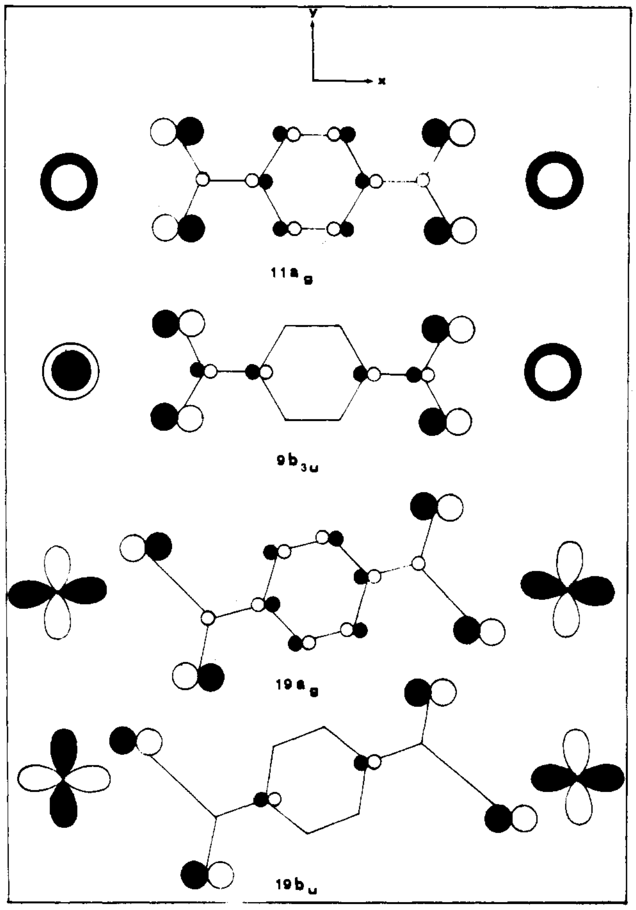

Figure 10. Schematic representation of the molecular orbitals, singly occupied in the triplet state, of the O_h–O_h model dimers.

The possibility of intermolecular exchange interactions is further examined in the (μ-terephthalato)copper(II) dimers, because such interactions could not be excluded on the basis of their experimental magnetic data. In accordance with the results of our quantum-chemical calculations the frontier MO'S of all five complexes and of the model compounds with T_d, O_h, and TBP surroundings, of the Cu(II) ions are not appropriate for intermolecular orbital interactions. This is also true for dimers with distorted SBP magnetic centers, and this is the case for complexes **1** and **2** of ref 2. In all these dimers, owing to steric and crystal packing effects, the shortest Cu··Cu interdimer distance is about 8 Å. According to the relation proposed by Coffman and Buettner,[4] such a distance gives an intermolecular contribution to the magnetic exchange interaction of about 0.25 cm^{-1}. On the contrary, the dimers with SP or regular SBP magnetic centers possess frontier orbitals suitable for intermolecular orbital interactions. Therefore, it should be expected to exhibit stronger antiferromagnetic interactions mainly of intermolecular nature. Actually, this is the case of the dimer $[Cu_2(\mu\text{-TPHA})(bpy)_2(H_2O)_2](ClO_4)_2$, prepared by us,[7] which indeed showed stronger magnetic interaction ($J \simeq -26$ cm^{-1}). Finally, it is worth noting that the magnetic exchange interactions, if any, of the μ-terephthalato dimers that do not possess suitable orbital pathways must be mainly intermolecular. However, it seems clear that the terephthalato dianion, under certain conditions, is an appropriate bridging unit to design magnetic systems with expected magnetic properties.

Registry No. **1**, 103817-49-8; **2**, 103817-51-2; **3**, 103834-81-7; **4**, 103817-53-4; **5**, 103817-55-6.

Supplementary Material Available: Table I (analytical data), Table II (extended Hückel parameters), Tables IV–VIII (variable-temperature magnetic susceptibility data), and Figures 2 and 4 (temperature dependence of $\chi_M T$ and $1/\chi_M$ for **2** and **4**) (15 pages). Ordering information is given on any current masthead page.

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Metal Complexes Containing the Trimethylamine–Carboxylatoborane Ligand: Synthesis and Characterization of $[M_3O((CH_3)_3N{\cdot}BH_2CO_2)_6R_3]^+X^-$ (M = Cr(III), Fe(III); R = H_2O, CH_3OH; X^- = NO_3^-, Cl^-)

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The coordination chemistry of Cr(III) and Fe(III) with the trimethylamine–carboxylatoborane ligand $[(CH_3)_3N{\cdot}BH_2CO_2^-]$ has been studied by using magnetic moments and infrared, proton and boron-11 NMR, and visible spectroscopies. The complexes have the formulation $[M_3O((CH_3)_3N{\cdot}BH_2CO_2)_6(R)_3]^+X^-$ (M = Cr(III), Fe(III); R = H_2O, CH_3OH; X^- = NO_3^-, Cl^-). The proposed structure contains three metal ions lying at the apices of an equilateral triangle, each coordinated to an oxygen atom located at the center of the triangle and each bridged by two acetate ligands. The carboxylatoborane ligand behaves similarly to carbon carboxylato ligands.

Introduction

The synthesis of trimethylamine–carboxyborane, $(CH_3)_3N{\cdot}BH_2COOH$, the protonated boron analogue of the amino acid betaine, $(CH_3)_3N^+CH_2COO^-$, has been reported by Spielvogel.[1] Both $(CH_3)_3N{\cdot}BH_2COOH$ and its *N*-ethylamide derivative, $(CH_3)_3N{\cdot}BH_2C(O)NHC_2H_5$, have demonstrated significant biological activity, with $(CH_3)_3N{\cdot}BH_2COOH$ showing 82% inhibition of tumor growth in the Ehrlich Ascites screen[2] and lowering serum cholesterol levels by 49% at low dosages.[3] The copper(II) complex of $(CH_3)_3N{\cdot}BH_2COOH$ shows increased biological activity compared to that of the free acid.[4] In addition to these biological studies, a study[5] of the basicity of $(CH_3)_3N{\cdot}BH_2COOH$ showed that replacement of the methylene group in betaine by the negatively charged BH_2 group increases the basicity of the carboxylate moiety by about 6 log units; e.g., the pK_a value for $(CH_3)_3NCH_2COOH$ is 1.83, whereas the corresponding value for $(CH_3)_3N{\cdot}BH_2COOH$ is 8.38. The latter observations coupled with questions arising during the study in our laboratory of the coordination chemistry of a boron analogue of a hydroxamic acid, $(CH_3)_3N{\cdot}BH_2C(O)NHOH{\cdot}HCl$,[6] necessitated a thorough study of the coordination chemistry of $(CH_3)_3N{\cdot}BH_2COOH$. Although Scheller et al. have reported[5] some stability constants of various boron analogues of glycine and *N*-methylated glycines $[(CH_3)_x NH_{3-x}{\cdot}BH_2COOH$ (x = 0–3)] with Zn(II) in solution, these complexes were not isolated. To date, only one example of an isolated coordination complex of $(CH_3)_3N{\cdot}BH_2COOH$ with a metal ion (Cu^{2+}) has been reported.[4] We here report the synthesis and characterization of Cr(III) and Fe(III) complexes of $(CH_3)_3N{\cdot}BH_2COOH$, both of which contain the cation $[M_3O((CH_3)_3N{\cdot}BH_2CO_2)_6R_3]^+$.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 599 spectrometer. Solid samples were prepared as KBr disks. Proton and boron-11 NMR spectra were obtained on a JEOL FX90Q spectrometer. Standards were Me_4Si, DSS (^1H), and $Et_2O{\cdot}BF_3$ (^{11}B). Visible spectra were recorded on a Beckman Model 35 spectrophotometer with the concentration of the solutions being 1×10^{-2} M unless otherwise indicated. Room-temperature magnetic moments were determined by the relative Guoy method.[7] The Guoy calibrant was mercury(II) tetrakis(thiocyanato)cobaltate(II). All calculations, including diamagnetic corrections, were done according to standard procedure.[8] The following compounds were purchased and used without further purification: $(CH_3)_3N{\cdot}HCl$ (Aldrich), $NaBH_3CN$ (Aldrich), $Cr(NO_3)_3{\cdot}9H_2O$ (J. T. Baker), $Fe(NO_3)_3{\cdot}9H_2O$ (J. T. Baker), $FeCl_3{\cdot}6H_2O$ (J. T. Baker). $(CH_3)_3N{\cdot}BH_2COOH$ was prepared[2] from the reaction of $(CH_3)_3N{\cdot}BH_2CN$[9] and $(C_2H_5)_3OBF_4$[10] followed by hydrolysis. Melting points were determined on a Thomas-Hoover capillary apparatus and are uncorrected. Metal analyses for Fe(III) and Cr(III) were performed in our laboratory according to standard procedures.[11] Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ, or by Dr. David Holah, Lakehead University, Thunder Bay, Ontario, Canada.

Preparation of $(CH_3)_3N{\cdot}BH_2CO_2^-Na^+{\cdot}0.25CH_3OH$ (1). A solution of Na_2CO_3 (0.53 g, 5.0 mmol) in water (10 mL) was added to a stirred solution of $(CH_3)_3N{\cdot}BH_2COOH$ (0.58, 5.0 mmol) in warm water (25 mL). The resulting mixture was kept at 35 °C for 0.5 h. The solvent was then removed by rotary evaporation to give a white solid, **1**, and the impurity $NaHCO_3$. The crude product was dissolved in methanol (15 mL), the insoluble $NaHCO_3$ (IR) filtered off, and the solvent removed under reduced pressure. An analytical sample was prepared by recrys-

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