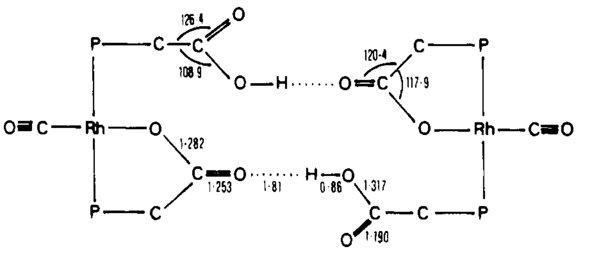
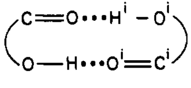


Figure 2. Hydrogen bonding in α-Rh(CO)A(HA).

is unique for the complex studied. By means of two intermolecular hydrogen bonds, the crystal structure consists of centrosymmetrical dimers (Figure 2), which are packed in the structure at van der Waals distances without any further significant intermolecular interaction. The central moiety of the double hydrogen bridge



comprises a plane within ±0.04 Å, which intersects the planes involving Rh and Rh^i at angles of ±20°. Hence, the whole dimer possesses a "chair" arrangement consisting of three planes, which contain Rh, the inversion center, and Rh^i. As a result, the RhA chelate ring adopts the δ-envelope conformation, which minimizes the strain involved between the planes.

The structures of the other modifications and solvates of the Rh(CO)A(HA) complex remain elusive, partly because they were not obtained as single crystals suitable for X-ray analysis. The ν(C=O) and δ(C=O) bands safely indicate that the Rh(I) core remains intact, and therefore the differences probably involve more subtle changes, e.g., in the hydrogen bonding, relative conformation of the trans phosphine ligands, packing of the phenyl rings, or ortho hydrogen–metal interaction. This situation seems to occur frequently in rhodium(I) phosphine complexes.[16,18,19] The various forms of the complex yield different patterns for the carboxyl region in the IR spectra, which might be taken as evidence that differences in hydrogen bonding are the main reason for the existence of the modifications. In the absence of firmer evidence, however, these changes cannot be safely correlated to any distinct structure.

Registry No. Rh(CO)Cl(HA)$_2$, 92763-41-2; Rh(CO)Br(HA)$_2$, 92763-42-3; Rh(CO)I(HA)$_2$, 92763-43-4; α-Rh(CO)A(HA), 92763-44-5; [Rh(CO)$_2$Cl]$_2$, 14523-22-9; [Rh(CO)$_2$Br]$_2$, 21475-96-7; [Rh(CO)$_2$I]$_2$, 21475-95-6; Rh(CO)$_2$acac, 14874-82-9.

Supplementary Material Available: Listings of structure factors, anisotropic thermal parameters of non-hydrogen atoms, distances and angles in phenyl rings, least-squares planes and deviations of atoms therefrom, analytical data, and properties of the complexes and a table comparing important distances and angles of α-Rh(CO)A(HA) with those of related complexes (27 pages). Ordering information is given on any current masthead page.

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Crystal Structures and Magnetic Properties of (μ-Terephthalato)bis[(*N,N,N',N'',N''*-pentamethyldiethylenetriamine)aquocopper(II)] Perchlorate and (μ-Terephthalato)bis[(*N,N,N',N'',N''*-pentaethyldiethylenetriamine)copper(II)] Perchlorate

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The two title compounds of formula [[Cu(pmedien)(H$_2$O)]$_2$tp](ClO$_4$)$_2$ (**1**) and [(Cu(petdien))$_2$tp](ClO$_4$)$_2$·H$_2$O (**2**) with pmedien = *N,N,N',N'',N''*-pentamethyldiethylenetriamine, petdien = *N,N,N',N'',N''*-pentaethyldiethylenetriamine, and tp = terephthalato have been synthesized and their structures solved at room temperature. **1** crystallizes in the monoclinic system, space group $P2_1/c$: a = 8.42 (5) Å, b = 14.40 (4) Å, c = 15.99 (5) Å, β = 100.65 (10)°, Z = 4. **2** crystallizes in the orthorhombic system, space group *Pbca*: a = 28.48 (1) Å, b = 26.363 (2) Å, c = 12.591 (5) Å, Z = 8. The structures of **1** and **2** consist of μ-terephthalato-bridged copper(II) binuclear complexes and noncoordinated perchlorate anions. In **1**, tp bridges in a bis monodentate fashion, and in **2**, in a bis bidentate fashion. In both compounds, the environment of the metal ions is intermediate between the square-based pyramid and the trigonal bipyramid, the trigonal-bipyramid character being more pronounced in **2**. The magnetic properties of **1**, **2**, and [[Cu(dien)(H$_2$O)]$_2$tp](ClO$_4$)$_2$ (**3**) have been investigated in the 4.2–300 K temperature range. The decrease of the product $\chi_M T$ of the molar magnetic susceptibility and the temperature upon cooling from 30 to 4.2 K in **1** and **3** is attributed to intermolecular interactions that vary according to **3** (dien) > **1** (pmedien) > **2** (petdien). The EPR spectra do not exhibit any evidence of triplet state. The unfavorable character of the terephthalato bridge to transmit the electronic effects over long distances is discussed.

Introduction

In the last few years, it has been shown that two paramagnetic centers could interact through extended bridging ligands, even if these centers were relatively far away from each other.[2] Restricting ourselves to copper(II) bimetallic complexes with a copper–copper separation larger than 5 Å, we can mention the end-to-end bis(μ-azido),[3] the μ-oxalato,[4-6]

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(2) "Magnetostructural Correlations in Exchange Coupled Systems"; Gatteschi, D., Kahn, O., Willett, R. D., Eds.; Reidel Publishing Co.: Dordrecht; Nato Adv. Study Inst. Ser., in press.

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the μ-oxamato,[7,8] and the μ-dithiooxalato[10,11] complexes. A relatively large interaction was also achieved between copper(II) ions separated by about 7.5 Å through chloranilato and bromanilato bridges in one-dimensional compounds.[12] The question at hand is whether there is a limit beyond which the metal centers are too separated to interact. In order to answer this question, we decided to synthesize new copper(II) bimetallic complexes with very extended bridging ligands and to investigate their magnetic and EPR properties in relation with their structure. Our feeling, but it is still only a feeling, is that the limit, if any, is beyond what the relation proposed by Coffman and Buettner suggests.[13] This relation is

$$|J_{\mathrm{lim}}|/\mathrm{cm}^{-1} = 1.37 \times 10^7 \exp(-1.80R/\text{Å}) \qquad (1)$$

where J is the singlet–triplet energy gap and R the copper–copper separation. If we assume that the smallest $|J|$ value detectable by the usual magnetic techniques is about 0.1 cm^{-1}, R deduced from (1) is in the range 10–11 Å. This is why we focus on the synthesis of binuclear systems with such a separation between the metal centers. The terephthalato ion is an appropriate bridge to design such systems. In this paper, we report on our results concerning (μ-terephthalato)copper(II) binuclear complexes. Several new complexes have been synthesized and the crystal structure of two of them solved, namely $[[\mathrm{Cu(pmedien)(H_2O)}]_2\mathrm{tp}](\mathrm{ClO_4})_2$ (**1**) and $[(\mathrm{Cu(petdien)})_2\mathrm{tp}](\mathrm{ClO_4})_2\cdot\mathrm{H_2O}$ (**2**), with pmedien = *N,N,N′,N″,N″*-pentamethyldiethylenetriamine, petdien = *N,N,N′,N″,N″*-pentaethyldiethylenetriamine, and tp = terephthalato. To our knowledge, only one μ-terephthalato bimetallic complex has already been reported, namely (μ-terephthalato)bis(dicyclopentadienyltitanium(III)).[14] Its crystal structure has not been determined.

Experimental Section

Syntheses. The two compounds **1** and **2** were prepared in a similar way. In a first step, the piperidinium terephthalate was obtained as a white powder by mixing equimolecular solutions of terephthalic acid and freshly distilled piperidine in dimethylformamide. Then, 337 mg (10^{-3} mol) of piperidinium terephthalate was dissolved in 100 mL of methanol. A solution of 741 mg (2×10^{-3} mol) of copper(II) perchlorate in 100 mL of methanol was added to a solution of 3×10^{-3} mol of the triamine (347 mg for pmedien and 487 mg for petdien). The two solutions were filtered, and the latter was slowly added to the former. In both cases, single crystals suitable for X-ray investigation were obtained by slow evaporation at room temperature. In the case of the petdien compound, **2**, two kinds of crystal appeared, blue-violet needles and transparent bright blue platelets, with the same chemical analysis. The structural and magnetic investigations were performed on the blue-violet crystals. Anal. Calcd for $\mathrm{C_{26}H_{54}N_6O_{14}Cl_2Cu_2}$ (**1**): C, 35.78; H, 6.24; N, 9.63; Cl, 8.12; Cu, 14.56. Found: C, 36.18; H, 6.19; N, 9.28; Cl, 8.76; Cu, 14.22. Calcd for $\mathrm{C_{36}H_{72}N_6O_{13}Cl_2Cu_2}$ (**2**): C, 43.45; H, 7.29; N, 8.44; O, 20.90; Cl, 7.13; Cu, 12.77. Found: C, 44.37; H, 7.17; N, 8.52; O, 19.48; Cl, 7.50; Cu, 12.78.

Table I. Atomic Coordinates[a] for 1

atom	x/a	y/b	z/c
Cu	−0.02813 (6)	0.23637 (4)	0.11802 (4)
Cl	−0.5149 (2)	0.36412 (9)	0.33397 (9)
O_1	−0.2074 (4)	0.3195 (2)	0.0809 (2)
O_2	−0.1739 (5)	0.4355 (3)	0.1759 (3)
O_3	0.0373 (5)	0.3058 (3)	0.2443 (3)
O_4	0.440 (1)	0.3683 (6)	0.2459 (4)
O_5	0.3423 (8)	0.3549 (5)	0.3660 (5)
O_6	−0.4328 (8)	0.4452 (4)	0.3656 (5)
O_7	−0.419 (1)	0.2863 (5)	0.3560 (5)
N_1	−0.1814 (5)	0.1368 (3)	0.1490 (3)
N_2	0.1410 (5)	0.1344 (3)	0.1319 (3)
N_3	0.1096 (5)	0.3001 (3)	0.0399 (3)
C_1	−0.0798 (6)	0.0540 (4)	0.1804 (4)
C_2	0.0524 (7)	0.0442 (4)	0.1297 (4)
C_3	0.2276 (7)	0.1438 (4)	0.0590 (4)
C_4	0.2629 (7)	0.2455 (4)	0.0481 (4)
C_5	−0.2729 (8)	0.1670 (5)	0.2152 (5)
C_6	−0.2951 (7)	0.1145 (5)	0.0695 (4)
C_7	0.2583 (6)	0.1411 (4)	0.2130 (4)
C_8	0.019 (1)	0.2041 (7)	0.4507 (4)
C_9	0.1487 (9)	0.3981 (4)	0.0638 (5)
C_{10}	−0.2434 (6)	0.3983 (3)	0.1095 (3)
C_{11}	−0.3803 (5)	0.4502 (3)	0.0527 (3)
C_{12}	−0.4418 (6)	0.5308 (3)	0.0816 (3)
C_{13}	−0.4395 (6)	0.4187 (3)	−0.0290 (3)

[a] Standard deviations on the last significant figures are given in parentheses.

$[[\mathrm{Cu(dien)(H_2O)}]_2\mathrm{tp}](\mathrm{ClO_4})_2$ (3), with dien = diethylenetriamine, was prepared in a similar way as **1** and **2**, but we were unable to grow single crytals suitable for a structural investigation. Anal. Calcd for $\mathrm{C_{16}H_{34}N_6O_{14}Cl_2Cu_2}$ (**3**): C, 26.24; H, 4.68; N, 11.47; Cl, 9.68; Cu 17.35. Found: C 27.97; H, 4.40; N, 11.48; Cl, 9.89; Cu, 18.96.

Crystal Structure Refinement. $[[\mathrm{Cu(pmedien)(H_2O)}]_2\mathrm{tp}](\mathrm{ClO_4})_2$ (1). The crystal selected for X-ray analysis was a 0.2-mm high hexagonal prism with a 0.25-mm average basal edge. It was screened with varnish and set up on the goniometric head along a basal diagonal.

Preliminary Laüe and precession photographs led to a monoclinic unit cell: $P2_1/c$, $a = 8.42$ (5) Å, $b = 14.40$ (4) Å, $c = 15.99$ (5) Å, $\beta = 100.65$ (10)°, $V = 1904.81$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.45 \times 10^3$ kg m^{-3}, $\rho_{\mathrm{measd}} = 1.52 \times 10^3$ kg m^{-3} (measured by flotation in a trichloromethane–dibromoethane mixture).

Intensity data were collected on a homemade automatic diffractometer: radiation, Mo Kα; takeoff angle, 1°; crystal–focus distance, 230 mm; crystal–counter distance, 230 mm; θ–2θ scan with 1.25° min^{-1} in Bragg angle; scan length, 1.4°, plus a correction for Kα_1–Kα_2 dispersion; background measurements, 10 s in fixed positions before and after every scan. The scintillation counter was connected to a pulse height analyzer set on Mo Kα energy so that 90% of the intensity was counted. A graphite monochromator was set in front of the counter window. The standard reflections, 400 and 080, were measured every 100 reflections; no significant intensity decrease was observed. A total of 2622 independent reflections have been collected at room temperature to $\theta_{\mathrm{Bragg}} = 23°$, and the 2588 reflections with intensity higher than 3σ have been kept for refinement. Intensities were corrected for Lorentz and polarization factors.

The absorption coefficient is equal to 14.3 cm^{-1}; no absorption correction has been carried out because of this low value, and the nearly regular standard deviation σ was computed ($\sigma = F_0(\Delta c)/c$, where c is the integrated intensity and Δc the error. Atomic form factors were taken from the International Tables for all the atoms. All atoms, except hydrogens, were corrected for the real and imaginary parts of anomalous dispersion. Refinements were carried out with the SHELX 76 computing program minimizing the R_w factor ($R_w = [\sum_i w_i(F_o - F_c)^2/\sum_i w_i F_o{}^2]^{1/2}$, where w_i is $1/\sigma^*$).

A three-dimensional Patterson map showed copper and chlorine atoms. Refinement of their coordinates gave $R = 0.38$. Successive

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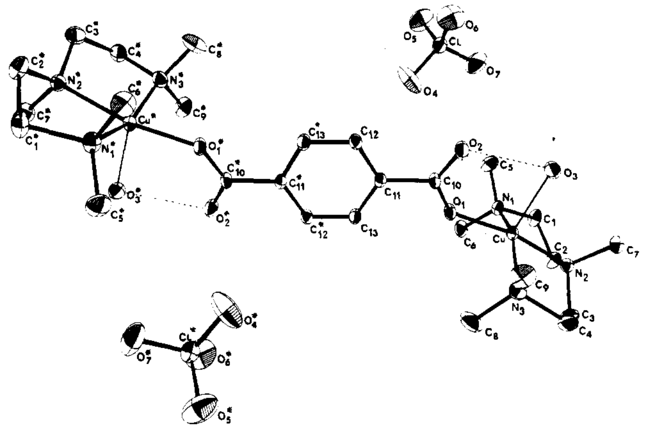

Figure 1. Perspective view of the structure of [[Cu(pmedien)(H_2O)]$_2$tp](ClO_4)$_2$ (**1**).

Fourier syntheses and refinements dropped *R* to 0.10 with isotropic temperature factors and to 0.071 with anisotropic temperature factors for the 25 atoms other than hydrogens. Hydrogen atoms of the benzene ring and CH_2 groups were added in calculated positions and allowed to shift according to the movement of the parent C atoms with a refineable overall isotropic thermal parameter. The CH_3 groups were refined as rigid groups with the AFIX option of SHELX 76 program. *R* dropped to 0.058. Correction for secondary extinction was performed, and the two water hydrogen atoms were then localized from a difference Fourier synthesis. Final factors were as follows: nonweighted *R*, excluding zeros, 0.049; weighted *R*, excluding zeros, 0.052; *F*(000) = 864. The atomic parameters are shown in Tables I and VII.[18]

[(Cu(petdien))$_2$tp](ClO$_4$)$_2$ (2). The crystal selected for X-ray analysis was roughly parallelepiped shaped with 0.25 × 0.5 × 0.6 mm dimensions. It was set up on the goniometric head along its 001 axis. Preliminary Laue and precession photographs led to an orthorhombic cell: *Pbca*, $a = 28.48$ (1) Å, $b = 26.363$ (2) Å, $c = 12.591$ (5) Å, $V = 9453$ Å^3, $Z = 8$, $\rho_{calcd} = 1.36 \times 10^3$ kg m^{-3}, $\rho_{measd} = 1.40 \times 10^3$ kg m^{-3} (measured by flotation in a toluene–trichloromethane mixture). Intensity data were collected on a Philips PW 1100 diffractometer: radiation, Cu Kα; takeoff angle, 3°; θ–2θ scan, with 1.8° min^{-1} in Bragg angle; $0.9 + 0.3$ (tan θ); scan length, background measurements, half of the scan time, before and after every scan. Three standard reflections, 226, 0,16,0, and $\bar{2}\bar{2}\bar{6}$, were measured every other hour. A total of 2833 independent reflections have been collected at room temperature to $\theta_{Bragg} = 50°$, and the 2760 reflections with intensity higher than 3σ were kept for refinement. Intensities were corrected for Lorentz and polarization factors. The absorption coefficient is 27.2 cm^{-1}; absorption corrections have been carried out. Minimal and maximal transmission factors are respectively 0.268 and 0.595. The refinement method was the same as for compound **1**. A three-dimensional Patterson map showed copper atoms. Refinement of their coordinates gave $R = 0.52$. Successive Fourier syntheses and refinements dropped *R* to 0.15 with isotropic temperature factors and to 0.10 with anisotropic temperature factors for the 59 atoms other than hydrogens. All hydrogen atoms but water ones were introduced in the refinement in the same way as for **1**. *R* dropped to 0.065. Hydrogen atoms of water molecule could not be found in a difference Fourier map. No weighting scheme gave an improvement of *R* value. Final reliability factors were as follows: nonweighted *R*, excluding zeros, 0.065; *F*(000) = 4176. Atomic parameters are shown in Tables II and VIII.[18]

Magnetic Measurements. They were carried out on a Faraday type magnetometer with a He continuous-flow cryostat in the 4.2–300 K temperature range. Mercury tetrakis(thiocyanato)cobaltate was used as a susceptibility standard. Corrections for diamagnetism were estimated as -473×10^{-6}, -566×10^{-6}, and -234×10^{-6} cm^3 mol^{-1} for **1**–**3**, respectively.

EPR. The spectra were recorded in the 4.2–300 K temperature range with a Bruker X-band ER 200 D spectrometer equipped with a continuous-flow cryostat, a Hall probe, and a Hewlett-Packard frequency meter.

Table II. Atomic Coordinates[a] for **2**

atom	*x*/*a*	*y*/*b*	*z*/*c*
Cu_1	0.00646 (4)	0.15211 (5)	0.2465 (1)
N_{11}	0.0360 (3)	0.2018 (4)	0.1438 (7)
N_{12}	−0.0543 (3)	0.1852 (3)	0.2173 (8)
N_{13}	−0.0308 (3)	0.0842 (3)	0.2522 (7)
C_{12}	−0.0044 (5)	0.2255 (6)	0.092 (1)
C_{13}	−0.0489 (4)	0.2249 (5)	0.139 (1)
C_{14}	−0.0875 (3)	0.1450 (5)	0.1813 (9)
C_{15}	−0.0808 (4)	0.0993 (4)	0.253 (1)
C_{16}	0.0614 (4)	0.1728 (4)	0.0632 (8)
C_{17}	0.0807 (5)	0.2013 (6)	−0.031 (1)
C_{18}	0.0627 (7)	0.2429 (6)	0.183 (1)
C_{19}	0.1080 (6)	0.2332 (8)	0.223 (1)
C_{110}	−0.0705 (4)	0.2111 (4)	0.317 (1)
C_{111}	−0.1166 (5)	0.2402 (6)	0.312 (1)
C_{112}	−0.0210 (4)	0.0547 (4)	0.1538 (9)
C_{113}	0.0285 (4)	0.0368 (4)	0.142 (1)
C_{114}	−0.0216 (4)	0.0536 (4)	0.3489 (9)
C_{115}	−0.0482 (5)	0.0044 (5)	0.360 (1)
C_{11}	0.0562 (4)	0.1411 (4)	0.4089 (9)
O_{11}	0.0645 (2)	0.1270 (2)	0.3137 (6)
O_{12}	0.0197 (2)	0.1658 (3)	0.4283 (5)
C_1	0.0908 (4)	0.1292 (3)	0.4949 (8)
C_2	0.1368 (4)	0.1210 (3)	0.4685 (7)
C_3	0.1692 (3)	0.1102 (3)	0.5468 (8)
C_4	0.1548 (4)	0.1069 (3)	0.6515 (8)
C_5	0.1088 (4)	0.1156 (3)	0.6787 (7)
C_6	0.0771 (3)	0.1262 (3)	0.5996 (8)
C_{21}	0.1891 (4)	0.0948 (4)	0.7378 (9)
O_{21}	0.1840 (2)	0.1147 (2)	0.8292 (5)
O_{22}	0.2229 (3)	0.0668 (3)	0.7203 (5)
Cu_2	0.24327 (4)	0.09250 (5)	0.89544 (9)
N_{21}	0.2781 (4)	0.1609 (3)	0.8779 (8)
N_{22}	0.3058 (3)	0.0635 (4)	0.9352 (7)
N_{23}	0.2147 (3)	0.0358 (3)	0.9862 (6)
C_{22}	0.3289 (4)	0.1491 (5)	0.894 (1)
C_{23}	0.3346 (4)	0.1065 (5)	0.9704 (9)
C_{24}	0.2984 (4)	0.0292 (5)	1.0241 (9)
C_{25}	0.2553 (5)	−0.0001 (5)	1.0076 (9)
C_{26}	0.2706 (4)	0.1902 (5)	0.779 (1)
C_{27}	0.2888 (5)	0.1649 (6)	0.677 (1)
C_{28}	0.2649 (6)	0.1952 (7)	0.967 (1)
C_{29}	0.2216 (6)	0.2149 (8)	0.967 (1)
C_{210}	0.3260 (4)	0.0369 (4)	0.8375 (8)
C_{211}	0.3736 (4)	0.0115 (5)	0.852 (1)
C_{212}	0.1768 (4)	0.0061 (4)	0.9333 (9)
C_{213}	0.1558 (5)	−0.0372 (5)	0.996 (1)
C_{214}	0.2000 (4)	0.0564 (5)	1.0877 (9)
C_{215}	0.1604 (5)	0.0901 (6)	1.086 (1)
Cl_1	−0.0368 (2)	0.1208 (2)	−0.1732 (3)
O_{13}	−0.0179 (5)	0.1665 (4)	−0.1867 (9)
O_{14}	−0.0490 (7)	0.0981 (6)	−0.258 (1)
O_{15}	−0.0667 (6)	0.1180 (8)	−0.101 (1)
O_{16}	−0.0025 (8)	0.0926 (6)	−0.135 (2)
Cl_2	0.2689 (1)	0.1389 (1)	1.3000 (3)
O_{23}	0.3014 (3)	0.1179 (5)	1.2348 (9)
O_{24}	0.2899 (4)	0.1628 (5)	1.3857 (8)
O_{25}	0.2408 (6)	0.1710 (5)	1.245 (1)
O_{26}	0.2387 (4)	0.1009 (5)	1.3291 (8)
O	−0.0598 (3)	0.1493 (4)	0.5517 (8)

[a] Standard deviations on the last significant figures are given in parentheses.

Description of the Structures

For both compounds, the structure consists of binuclear cations with copper(II) ions bridged by the terephthalato ligand and noncoordinated perchlorate anions. The terephthalato ligand bridges in a bis monodentate fashion in the pmedien derivative and in a bis didentate fashion in the petdien derivative. The environment of the metal ions, in both cases, is intermediate between the square-based pyramid and the trigonal bipyramid, with trigonal-bipyramidal character more pronounced in the petdien compound than in the pmedien one. Let us examine now each of the structures in more details.

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(18) Supplementary material.

Table III. Main Interatomic Distances (Å) for **1**[a]

Cu–Cu

Cu–Cu = 11.129 (1) (binuclear unit)

Cu–Cu = 7.840 (1) (shortest distance between two (binuclear units)

	Cu Environment		
Cu-N_1	2.051 (4)	Cu-O_1	1.931 (3)
Cu-N_2	2.029 (4)	Cu-O_3	2.225 (4)
Cu-N_3	2.067 (4)		
	pmdien		
N_1-C_1	1.500 (7)	N_1-C_5	1.479 (8)
C_1-C_2	1.503 (8)	N_1-C_6	1.482 (8)
C_2-N_2	1.493 (7)	N_2-C_7	1.482 (7)
N_2-C_3	1.494 (7)	N_3-C_8	1.497 (9)
C_3-C_4	1.510 (9)	N_3-C_9	1.482 (9)
C_4-N_3	1.495 (7)		
	tp		
O_1-C_{10}	1.279 (6)	C_{11}-C_{12}	1.383 (7)
O_2-C_{10}	1.237 (6)	C_{11}-C_{13}	1.390 (7)
C_{10}-C_{11}	1.522 (7)	C_{12}-C_{13}	1.384 (7)
	Hydrogen Bond		
O_2-O_3	2.672 (6)		
	Perchlorate Anion		
Cl-O_4	1.390 (6)	Cl-O_6	1.403 (6)
Cl-O_5	1.399 (6)	Cl-O_7	1.389 (7)

[a] Standard deviations on the last significant figures are given in parentheses.

Table IV. Main Bond Angles (deg) for **1**[a]

	Cu Environment		
N_1-Cu-O_1	90.9 (2)	N_3-Cu-O_1	91.9 (2)
N_1-Cu-O_3	99.1 (2)	N_3-Cu-O_3	105.9 (2)
N_2-Cu-O_1	167.1 (2)	N_3-Cu-N_1	154.7 (2)
N_2-Cu-O_3	100.0 (2)	N_3-Cu-N_2	85.8 (2)
N_2-Cu-N_1	85.8 (2)		
	Perchlorate Anion		
O_5-Cl-O_4	106.6 (6)	O_7-Cl-O_4	109.0 (6)
O_4-Cl-O_6	110.8 (5)	O_7-Cl-O_5	109.2 (5)
O_6-Cl-O_5	110.3 (5)	O_7-Cl-O_6	110.9 (5)

[a] Standard deviations on the last significant figures are given in parentheses.

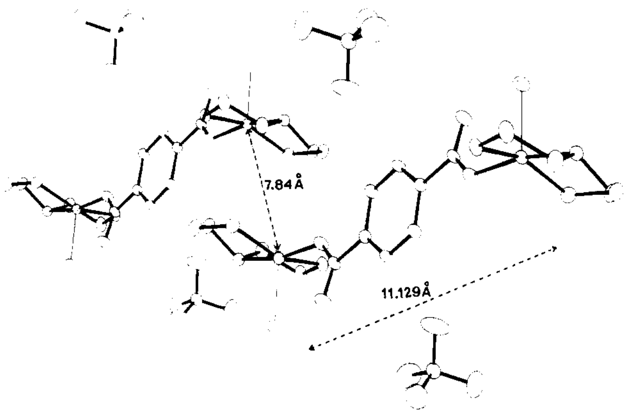


Figure 2. Perspective view showing the closest contacts between two binuclear units of **1**.

Table V. Main Interatomic Distances (Å) for **2**[a]

Cu–Cu

Cu_1–Cu_2 = 10.710 (2) (binuclear unit)

Cu_1–Cu_2 = 8.215 (2) } (two shortest distances between two

Cu_1–Cu_1 = 8.140 (2) } binuclear units)

	Cu Environment		
Cu_1-N_{11}	2.024 (9)	Cu_2-N_{23}	2.050 (8)
Cu_1-N_{12}	1.972 (8)	Cu_2-N_{22}	2.000 (8)
Cu_1-N_{13}	2.083 (8)	Cu_2-N_{21}	2.069 (9)
Cu_1-O_{11}	1.972 (6)	Cu_2-O_{21}	1.971 (6)
Cu_1-O_{12}	2.347 (6)	Cu_2-O_{22}	2.379 (6)
	pedien		
N_{11}-C_{12}	1.46 (2)	N_{23}-C_{25}	1.52 (2)
C_{12}-C_{13}	1.40 (2)	C_{25}-C_{24}	1.46 (2)
C_{13}-N_{12}	1.44 (2)	C_{24}-N_{22}	1.45 (2)
N_{12}-C_{14}	1.49 (2)	N_{22}-C_{23}	1.47 (2)
C_{14}-C_{15}	1.52 (2)	C_{23}-C_{22}	1.48 (2)
C_{15}-N_{13}	1.48 (1)	C_{22}-N_{21}	1.49 (2)
	tp		
O_{11}-C_{11}	1.28 (1)	C_1-C_2	1.37 (1)
O_{12}-C_{11}	1.25 (1)	C_2-C_3	1.38 (1)
C_1-C_{12}	1.50 (2)	C_3-C_4	1.38 (1)
O_{21}-C_{21}	1.27 (1)	C_4-C_5	1.37 (1)
O_{22}-C_{21}	1.23 (1)	C_5-C_6	1.37 (1)
C_4-C_{21}	1.49 (2)	C_6-C_1	1.38 (1)
	Hydrogen Bonds		
O-O_{12}	2.78 (1)	O-O_{14}	2.77 (2)
	Perchlorate Anion		
Cl_1-O_{13}	1.33 (1)	Cl_2-O_{23}	1.36 (1)
Cl_1-O_{14}	1.28 (1)	Cl_2-O_{24}	1.38 (1)
Cl_1-O_{15}	1.25 (2)	Cl_2-O_{25}	1.35 (1)
Cl_1-O_{16}	1.32 (2)	Cl_2-O_{26}	1.37 (1)

[a] Standard deviations on the last significant figures are given in parentheses.

[[Cu(pmedien)(H_2O)]$_2$tp](ClO_4)$_2$ (1). The monoclinic cell contains two binuclear cations $[[Cu(pmedien)(H_2O)]_2tp]^{2+}$ and four noncoordinated perchlorate anions. A perspective view is shown in Figure 1. Selected distances and angles are given in Tables III and IV. A crystallographic inversion center is located at the center of the benzene ring of the tp ligand. The surroundings of the copper(II) ions may be described by a slightly distorted square-based pyramid with the three nitrogen atoms, N_1, N_2, and N_3, of pmedien and one of the oxygen atoms, O_1, of the carboxylic group in the basal plane and the oxygen atom O_3 of a water molecule in apical position. The average deviation of N_1, N_2, N_3, and O_1 with regard to the mean basal plane is 0.104 Å. The copper(II) ion is displaced toward the apical site by 0.35 Å. The Cu–O_3 apical bond length is 2.225(4) Å.

A trigonal-bipyramid description would place N_1, N_3, and O_3 in the basal plane and N_2 and O_1 in axial positions. The metal ion deviates only by 0.061 Å from this trigonal plane, and the trigonal axis does not show too much distorsion from linearity, N_2–Cu–O_1 being 167.1 (2)°. However, the angles in the trigonal plane depart significantly from the theoretical 120° value, with values of 154.7 (2), 99.1 (2), and 105.9 (2)°.

Referring again to the square-based pyramid description of each copper of the binuclear cation, the two mean basal planes make a dihedral angle of 7.9° and are nearly perpendicular to the benzene ring. The Cu···Cu distance inside a same binuclear entity is 11.129 (1) Å. The shortest Cu···Cu distance, equal to 7.840 (1) Å, involves metal ions belonging to two different binuclear units, as shown in Figure 2. Concerning the terephthalato ligand, its eight carbon atoms are strictly coplanar, with a 0.006-Å mean deviation from the plane. The oxygen atoms O_1 and O_2 of carboxylate groups are respectively at 0.16 and 0.22 Å from this plane, which involves a dihedral angle of 10.4° between the carboxylate plane and the benzene ring.

It is worthwhile to point out the existence of a hydrogen bond between the oxygen atom O_3 of the water molecule and the noncoordinated oxygen atom O_2 of the carboxylic group; the distance O_3–O_2 is 2.672 (6) Å and the O_3–H–O_2 angle is 146°. Moreover, a weak hydrogen bond may be expected through the second hydrogen atom of that water molecule with the O_5 oxygen atom of a perchlorate anion; indeed, the distance O_3–O_5 is 3.005 Å, and the O_3–H–O_5 angle is 158°.

[(Cu(petdien))$_2$tp](ClO_4)$_2$·H_2O (2). The orthorhombic cell contains eight symmetry-related binuclear cations [(Cu(pet-

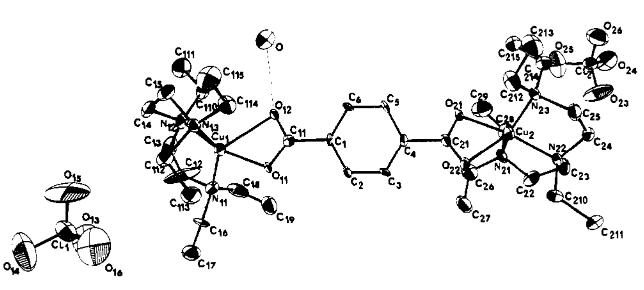


Figure 3. Perspective view of the structure of of [(Cu(petdien))$_2$tp](ClO$_4$)$_2$·H$_2$O (**2**).

Table VI. Main Bond Angles (deg) for **2**[a]

	Cu Environment		
N_{12}–Cu_1–N_{13}	86.5 (3)	N_{22}–Cu_2–N_{21}	86.2 (4)
N_{12}–Cu_1–N_{11}	87.7 (4)	N_{22}–Cu_2–N_{23}	86.3 (3)
N_{11}–Cu_1–N_{13}	142.2 (4)	N_{23}–Cu_2–N_{21}	152.2 (4)
O_{11}–Cu_1–N_{13}	97.1 (3)	O_{21}–Cu_2–N_{21}	96.1 (3)
O_{11}–Cu_1–N_{12}	164.6 (3)	O_{21}–Cu_2–N_{22}	168.8 (3)
O_{11}–Cu_1–N_{11}	98.2 (3)	O_{21}–Cu_2–N_{23}	96.5 (3)
O_{11}–Cu_1–O_{12}	59.9 (3)	O_{21}–Cu_2–O_{22}	58.9
O_{12}–Cu_1–N_{13}	100.4 (3)	O_{22}–Cu_2–N_{21}	105.5
O_{12}–Cu_1–N_{12}	104.8 (3)	O_{22}–Cu_2–N_{22}	109.9
O_{12}–Cu_1–N_{11}	117.2 (3)	O_{22}–Cu_2–N_{23}	102.2
	Perchlorate Anion		
O_{13}–Cl_1–O_{14}	115.3 (9)	O_{23}–Cl_2–O_{24}	111.3 (7)
O_{13}–Cl_1–O_{15}	115 (1)	O_{23}–Cl_2–O_{25}	110.6 (8)
O_{13}–Cl_1–O_{16}	105 (1)	O_{23}–Cl_2–O_{26}	106.9 (8)
O_{14}–Cl_1–O_{15}	113 (1)	O_{24}–Cl_2–O_{25}	111.5 (8)
O_{14}–Cl_1–O_{16}	104 (1)	O_{24}–Cl_2–O_{26}	113.3 (7)
O_{15}–Cl_1–O_{16}	102 (1)	O_{25}–Cl_2–O_{26}	102.8 (8)

[a] Standard deviations on the last significant figures are given in parentheses.

dien))$_2$tp]$^{2+}$, 16 noncoordinated perchlorate anions, and eight noncoordinated water molecules. A perspective view is shown in Figure 3. Selected distances and angles are given in Tables V and VI. The binuclear cations are not centrosymmetric; this fact may be related to the presence of a water molecule on one side of the cation. The environment of each metal ion is difficult to describe in a simple way. Three ideal structures may be envisaged, namely a square-based pyramid, a trigonal bipyramid, or a tetrahedron.[19]

A square-based pyramid description of the surrounding of the copper Cu$_1$ places N$_{11}$, N$_{12}$, and N$_{13}$ belonging to petdien and O$_{11}$ of the carboxylic group in the basal plane and the second oxygen atom O$_{12}$ of the carboxylic group in apical position. Around Cu$_2$, the basal plane is made of N$_{21}$, N$_{22}$, N$_{23}$, and O$_{21}$, and the apex is occupied by O$_{22}$. The average deviations of the atoms in the basal plane with regard to the mean plane are 0.45 and 0.33 Å, respectively. The copper(II) ion is displaced from the mean plane toward the apical site by 0.182 and 0.132 Å, respectively. The apical bond lengths are Cu$_1$–O$_{12}$ = 2.347 (6) Å and Cu$_2$–O$_{22}$ = 2.379 (6) Å.

A trigonal-biyramidal description places N$_{11}$, N$_{13}$, and O$_{12}$ (or N$_{21}$, N$_{23}$, and O$_{22}$) in the trigonal plane and N$_{12}$ and O$_{11}$ (or N$_{22}$ and O$_{21}$) along the trigonal axis. Cu$_1$ and Cu$_2$ deviate from the trigonal planes by 0.056 and 0.028 Å, respectively, and the trigonal axes are close to the linearity with N$_{12}$–Cu$_1$–O$_{11}$ = 164.6 (3)° and N$_{22}$–Cu$_2$–O$_{21}$ = 168.8 (3)°. The angles in the trigonal planes are 142.2 (4), 117.2 (3), and 100.4 (3)° on one side and 152.2 (4), 105.5 (3), and 102.2 (3)° on the other side. In each trigonal plane, one of the distances (Cu$_1$–O$_{12}$ and Cu$_2$–O$_{22}$) is much longer than the other two. The two trigonal planes are nearly parallel with a dihedral angle of 2.8°. The angles between these planes and the benzene ring are 68.7° for Cu$_1$ and 70.7° for Cu$_2$.

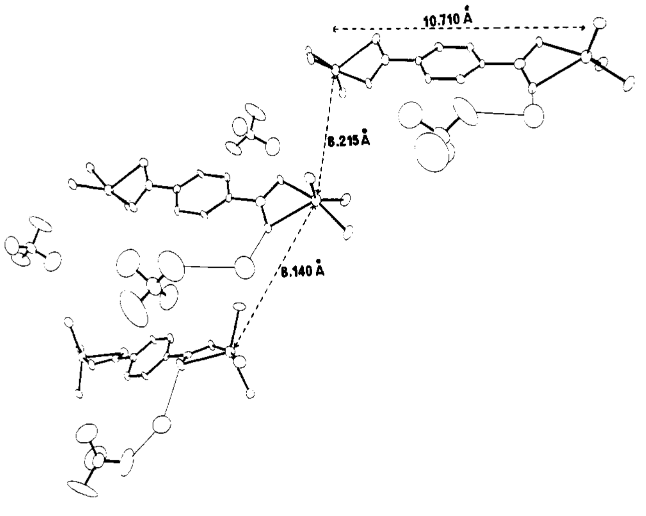


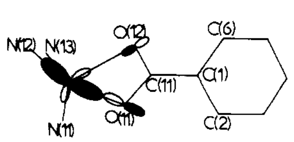
Figure 4. Perspective view showing the closest contacts between two binuclear units of **2**.

As for the tetrahedral description, N$_{11}$, N$_{12}$, N$_{13}$, and O$_{11}$ (or N$_{21}$, N$_{22}$, N$_{23}$, and O$_{21}$) would occupy the vertices of a distorted tetrahedron. The bond angles within the tetrahedron around Cu$_1$ are 87.7 (4), 86.5 (3), 97.1 (3), and 98.2 (3)°. They deviate significantly from the ideal value of 109.8°. The sum, 369.5°, shows however that the tetrahedral distortion actually does exist. The situation is much the same around Cu$_2$. The tetrahedral description requires the intrusion of a fifth ligand O$_{13}$ (or O$_{23}$) in the coordination spheres.

The intramolecular Cu··Cu distance is 10.710 (2) Å, the shortest Cu··Cu distances being 8.140 (2) and 8.215 (2) Å (see Figure 4). The terephthalato ligand presents nearly the same geometry as in **1**. The mean deviation from the plane is 0.005 Å for the eight carbon atoms, but the oxygen atoms are further away from this plane, i.e. 0.46 Å for O$_{11}$ and O$_{12}$ and 0.61 and 0.57 Å, respectively, for O$_{21}$ and O$_{22}$. Consequently, the dihedral angle between the ring plane and the carboxylate groups are respectively 25.0° for C$_{11}$–O$_{11}$–O$_{12}$ and 33.0° for C$_{21}$–O$_{21}$–O$_{22}$. These values are higher than in the first compound, certainly related to the bidentate behavior of the carboxylate groups. The noncoordinated water molecule contracts two hydrogen bonds with the oxygen atom O$_{12}$ (O–O$_{12}$ = 2.78 (1) Å) and with one of the oxygen atoms of ClO$_4^-$ (O–O$_{14}$ = 2.77 (2) Å).

Magnetic and EPR Properties

Before the magnetic data are examined, it is important to realize that, if there is an intramolecular interaction, this interaction will be more important in **2** than in **1**. Indeed, in **2**, tp bridges in a bis bidentate fashion instead of a bis monodentate fashion as in **1**. Moreover, the more pronounced trigonal-bipyramid character increases the admixture of d$_{z^2}$-type orbital in the ground state and gives a delocalization of the spin density on the two oxygen atoms of the carboxylic group (see **4**). Such a role of petdien with regard to pmedien



4

was first reported by Hendrickson et al.[15]

For **1**, the molar magnetic susceptibility χ_M follows the Curie law from room temperature down to 30 K. Below 30 K the product $\chi_M T$, T being the temperature, decreases from 0.93 cm^3 mol^{-1} K at 30 K to 0.71 cm^3 mol^{-1} K at 4.2 K. In contrast, in **2**, the magnetic susceptibility follows the Curie

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(19) We are grateful to one of the reviewers who pointed out that a tetrahedral description could be also envisaged.

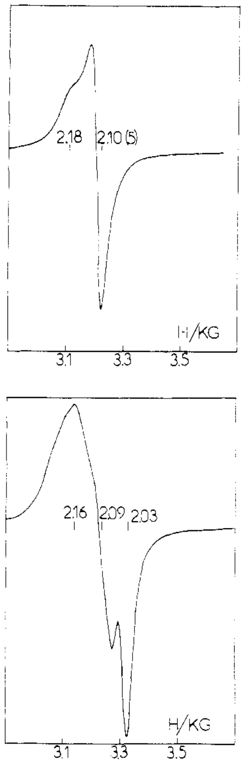
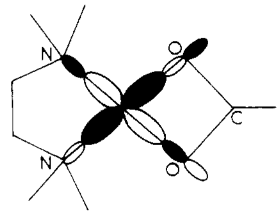


Figure 5. X-band EPR spectra of $[(Cu(petdien))_2tp](ClO_4)_2{\cdot}H_2O$ (**2**) at 80 K: (top) powder spectrum; (bottom) methanol–toluene glass spectrum.

law $\chi_MT = 0.91$ cm^3 mol^{-1} K down to liquid-helium temperature. This result is in apparent contradiction with the assertion at the beginning of this section. In fact, these magnetic data can be understood when the compound $[[Cu(dien)(H_2O)]_2tp](ClO_4)_2$ (**3**) is also compared. For this compound, the decrease of χ_MT upon cooling is more pronounced than in **1** with $\chi_MT = 0.91$ cm^3 mol^{-1} K at 30 K and 0.63 cm^3 mol^{-1} K at 4.2 K. The magnetic data could be fitted by a dimer law[5] with $J = -3.3$ cm^{-1} for **3** (dien), -2.7 cm^{-1} for **1** (pmedien), and zero for **2** (petdien). However, it is most likely that, in fact, the interaction is *intermolecular* instead of intramolecular, the more pronounced effect being obtained with the less bulky terminal triamine.

The X-band powder EPR spectra, investigated at 4.2 K and room temperature, do not exhibit any sign of exchange interaction. For **1** and **2**, the spectra are characteristic of uncoupled copper(II) in distorted-tetragonal elongated environments. For **1**, we found $g_\parallel = 2.21$ and $g_\perp = 2.07$, and for **2**, $g_\parallel = 2.18$ and $g_\perp = 2.10$ (5). The difference $g_\parallel - g_\perp$, more important in **1** than in **2**, confirms that the distortion toward the trigonal bipyramid is more pronounced in the latter compound. The EPR spectrum of **2**, which is much more soluble than **1** and for which a very weak interaction could be expected, was also studied in a methanol–toluene mixture between 4.2 and 300 K. At high temperature, the rhombicity is resolved with $g_x = 2.03$, $g_y = 2.09$, and $g_z = 2.16$, but again, there is no evidence of triplet state. Powder and glass EPR spectra are shown in Figure 5. Our goal in synthesizing these complexes was to see whether the benzene ring could play a role in the transmission of the electronic effects on long distances. The absence of any intramolecular interaction is not surprising for **1**, but somewhat disappointing for **2**. Indeed, if we assume that the interaction between two copper(II) ions very far away from each other can only be of antiferromagnetic nature,[16] the magnitude of this interaction is proportional to the square of the overlap integral between the magnetic orbitals.[17] In other words, there is interaction when the overlap density between these magnetic orbitals is different from zero in some points of the bridging region. In our case, this would require a delocalization of each magnetic orbital schematically shown in **4** beyond O_{11} and O_{12} (or O_{21} and O_{22}) toward the carbon atoms of the aromatic ring.

Due to the large separations of the type O_{11}–C_2 and O_{12}–C_6, this delocalization apparently does not occur. A more favorable situation could be expected with tmen = *N*,*N*,*N'*,*N'*-tetramethylethylenediamine as terminal ligands. In this case, the environment of the copper(II) ions would be planar with the two nitrogen atoms of tmen and the two oxygen atoms of a carboxylic group as nearest neighbors.[5] The spin density would be equally delocalized on the oxygen atoms, as shown in **5**.



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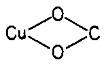
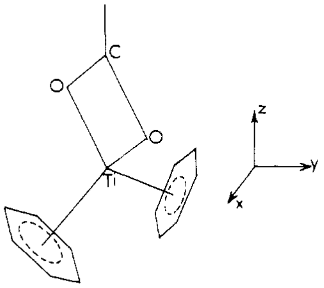
In spite of many attempts, we were unable to synthesize the complex with tmen, likely because the four-membered network



would be too constrained.

Finally, it must be noticed that a weak intramolecular interaction was reported for (μ-terephthalato)bis[dicyclopentadienyltitanium(III)], of which the EPR spectrum exhibits the features characteristic of a triplet state.[15] The environment of the titanium(III) ion may be described as a distorted tetrahedron. Accordingly, as the distortion corresponds to an elongation or a compression, the unpaired electron of Ti(III) occupies an *xy*- or a z^2-type magnetic orbital (referring to the axes shown in **6**). Neither situation is favorable for an intramolecular interaction. Recently, Hendrickson himself suggested that the interaction in (μ-terephthalato)bis[dicyclopentadienyltitanium(III)] could be largely intermolecular in nature.[9]



6

Acknowledgment. We are most grateful to P. Georget for her efficient help in the synthetic aspect of this work and to D. Jacquot.

Registry No. **1**, 93110-59-9; **2**, 93134-20-4; **3**, 93110-61-3.

Supplementary Material Available: Listings of structure factor amplitudes and atomic thermal parameters (Tables VII and VIII) (31 pages). Ordering information is given on any current masthead page.