

Crystal Structure and Magnetic Properties of the Tetranuclear [Cu(SALMedpt)Cu(hfa)₂]₂·0.6CHCl₃ Complex, Formed by Hexafluoroacetylacetonate and by the Pentadentate *N,N'*-[4-Methyl-4-azaheptane-1,7-diyl]bis(salicylaldimine) Ligand

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The magnetic properties of the tetranuclear copper compound consisting of dimers of the Cu(SALMedpt)Cu(hfa)₂ complex (SALMedpt is the Schiff base formed by salicylaldehyde and bis(3-aminopropyl)methylamine, and hfa is hexafluoroacetylacetonate) formed by one pentadentate and two bidentate ligands are investigated by EPR and magnetic susceptibility measurements, in view of its structure determined by X-ray diffraction methods. Crystal data for the compound Cu(SALMedpt)Cu(hfa)₂·0.3CHCl₃: space group *P* $\bar{1}$ with *a* = 17.370 (6) Å, *b* = 13.374 (5) Å, *c* = 8.553 (4) Å, α = 93.14 (5)°, β = 99.54 (5)°, γ = 104.33 (5)°, *Z* = 2, and *V* = 1888.9 Å³. The structure solution based on 2928 reflections converged at *R* = 0.073 and *R*_w = 0.075. The two symmetry-independent metal atoms in the centrosymmetric tetranuclear complex are in five-coordinate environments with distorted-square-pyramidal geometries. The two inner copper atoms, bridged by salicylaldimine oxygens, are close to each other (Cu1...Cu1' = 3.176 (1) Å), whereas the outer copper atoms are separated by considerable distances (>6 Å) from the other metal centers in the structure. The magnetic exchange in the tetranuclear species is determined by the interaction of the two inner copper ions. It is antiferromagnetic, *J* = 6.6 cm⁻¹. The interaction between one inner and one outer copper has been found to be much smaller.

Introduction

Metal complexes of polydentate salicylaldimines are known to act as ligands toward transition-metal ions, yielding polynuclear complexes.¹ In all cases the polynuclear complexes are formed through the phenolic oxygen atoms of the salicylaldimine ligands.

Both homo- and heterodinuclear complexes can in principle be formed by reacting a suitable metal salicylaldimine with a suitable Lewis acid, and a few heterodinuclear complexes have been thoroughly characterized.²⁻⁵ In this respect the metal complexes of tri- and tetradentate salicylaldimine ligands appear to be better suited than those of bidentate ligands, for which to our knowledge no stable compounds containing dissimilar metal ions have been reported.

Tetradentate salicylaldimine ligands are the most studied ones, for the ease of formation of dinuclear complexes, but the square-planar geometry imposed on the metal ion sets strong limitations on the choice of possible metal complexes if one is interested in the study of magnetic exchange interactions.

To our knowledge no polynuclear compounds have been reported for metal complexes formed by pentadentate salicylaldimine ligands. In this case the parent mononuclear complexes are five-coordinate,^{6,7} with a geometry intermediate between the trigonal bipyramidal and the square pyramidal.^{8,9} The two oxygen atoms are rather far apart from each other, so that it is dubious whether they can chelate to another metal ion, M'. However, it appeared of interest to us to determine if even in this case polynuclear complexes can be formed by reacting the complexes with metal hexafluoroacetylacetonates, which are strong Lewis acids. We were not able to isolate any heterodinuclear complex, but from the reaction of Cu(SALMedpt) (SALMedpt is the Schiff base formed by salicyl-

aldehyde and bis(3-aminopropyl)methylamine) with Cu(hfa)₂ (copper hexafluoroacetylacetonate) a well-defined crystalline compound was formed, which we characterized through X-ray, EPR, and magnetic susceptibility measurements.

Experimental Section

Materials. All solvents and substances used in these preparations were reagent grade. Cu(SALMedpt) was synthesized according to literature methods.⁷ The complex Cu(hfa)₂ was synthesized according to Cotton and Holm.¹⁰

Synthesis of the Cu(SALMedpt)Cu(hfa)₂ Complex. This complex was prepared by mixing 2.0 mmol of Cu(SALMedpt) dissolved in 30 mL of hot chloroform with 20 mL of a hot methanolic solution containing an equimolar amount of Cu(hfa)₂. The solution was concentrated and then cooled slowly at room temperature. Deep green crystals began to appear after 1 h. They were filtered, washed with a 1:1 ethanol-ether mixture, and dried under vacuum. Anal. Calcd for Cu(SALMedpt)Cu(hfa)₂·0.3CHCl₃, C₃₁H₂₇N₃O₆F₁₂Cu₂·0.3CHCl₃: C, 40.49; H, 2.96; N, 4.53; Cu, 13.69. Found: C, 40.31; H, 2.93; N, 4.53; Cu, 13.45. In the analysis 0.3 mol of CHCl₃ was included, according to the X-ray results (see below). Similar results are obtained also by reacting Cu(SALMedpt) with CuCl₂, but in this case only microcrystalline compounds are obtained, which cannot be recrystallized due to their insolubility in the common organic solvents. Moreover, it was not possible to obtain satisfactory analytical data for such compounds. Attempts were also made to use different metal ions, but no new compounds were obtained. In fact reacting Ni(SALRdpt) (SALRdpt is the Schiff base formed by salicylaldehyde and bis(3-aminopropyl)alkylamine) with Cu(hfa)₂ only yielded Cu(SALRdpt)Cu(hfa)₂, showing that, even if a pentadentate ligand is used, the central metal ion may be replaced by copper. Similar results were obtained also by reacting Cu(SALMedpt) with Ni(hfa)₂. From Ni(SALMedpt) and Ni(hfa)₂ only the starting compounds were obtained.

Magnetic Measurements. Magnetic susceptibility data were obtained with a Faraday balance equipped with a Bruker electromagnet operating at 2.7 T and a R-100 Cahn microbalance. The cooling apparatus was a CF 200 flow cryostat from Oxford Instruments Co. Electronic spectra were recorded on a Cary 17 spectrophotometer and the EPR spectra with a Varian E-9 spectrometer equipped with X-band (9 GHz) and an Oxford ESR 9 continuous-flow cryostat.

X-ray Structural Determination. Diffraction data for the compound Cu(SALMedpt)Cu(hfa)₂·0.3CHCl₃ were collected at 22 ± 2 °C on a Philips PW 1100 automated diffractometer using graphite-mono-

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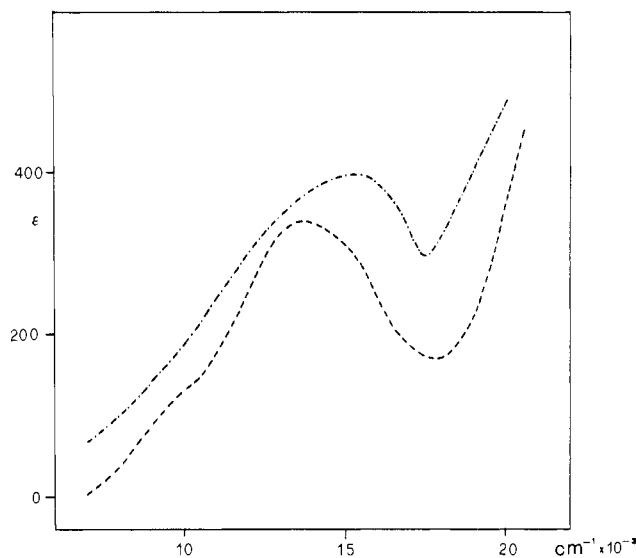
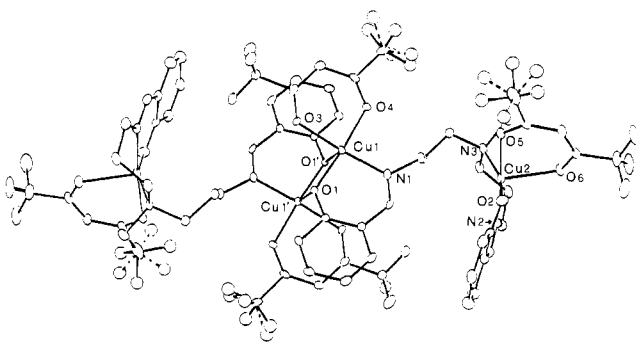
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Table I. Summary of Crystal Data, Intensity Collection, and Structure Refinement

formula	$C_{31}H_{27}Cu_2F_{12}N_3O_6 \cdot C_0.3H_{0.3}Cl_{0.9}$
fw	928.5
space group	$P\bar{1}$
<i>a</i> , Å	17.370 (6)
<i>b</i> , Å	13.374 (5)
<i>c</i> , Å	8.553 (4)
α , deg	93.14 (5)
β , deg	99.54 (5)
γ , deg	104.33 (5)
<i>V</i> , Å ³	1888.9
<i>Z</i>	2
density, g cm ⁻³	1.63 (calcd) 1.62 (obsd, by flotation)
cryst size, mm	0.22 × 0.13 × 0.40
μ (Mo K α), cm ⁻¹	12.9
scan type	ω -2 θ
scan width ($\Delta(2\theta)$), deg	1.00 + 0.30 θ
scan speed, deg min ⁻¹	5.4
bkgd/scan time ratio	0.5
2 θ limits, deg	5–50
data collection range	$\pm h, \pm k, +l$
no. of unique data	6611
no. of data $F_o^2 > 3\sigma(F_o^2)$	2928
no. of variables	504
<i>R</i>	0.073
<i>R_w</i>	0.075

chromated Mo K α radiation ($\lambda = 0.7107$ Å). Crystals of the compound were not very suitable for X-ray diffraction work due to large mosaic spread. Details on crystal data, intensity collection, and refinement are reported in Table I. Lattice constants were obtained by a least-squares fit to 24 reflections in the range $30^\circ < 2\theta < 40^\circ$. The intensities of three standard reflections measured every 90 min showed small oscillations (<2%) about their average values but no systematic trend. Data were processed with use of a 0.05 value for *p* in the calculation of the $\sigma(I)$'s.¹¹ Corrections for Lorentz and polarization effects as well as for absorption (the transmission coefficients ranging from 0.75 to 0.86) were applied.¹²

The structure was solved by heavy-atom procedures. A Patterson synthesis yielded the positions of the two metal atoms in the asymmetric unit. The positions of the other nonhydrogen atoms, except for those of the atoms of the solvent molecule, were determined from Fourier syntheses. The choice of the centrosymmetric $P\bar{1}$ space group, initially made, was later proved to be correct by the successful refinement. In the blocked-cascade least-squares refinement (ca. 270 parameter blocks) the function $\sum w(|F_o| - |F_c|)^2$ was minimized with weight $w = 1/\sigma^2(F_o)$. The scattering factors of the neutral atoms were taken from ref 13, and anomalous dispersion terms for the metal atoms were included in F_c .¹⁴ All non-hydrogen atoms were refined anisotropically, except for the solvent (vide infra) and the fluorine atoms of the two CF₃ groups, which were refined as described below. The two groups of fluorine atoms, namely, F4–F6 and F7–F9, which were mostly affected by librational motion or rotational disorder about the respective C–C bond direction, were considered to be distributed between two positions whose occupancy factors were refined. The six C–F and, separately, the six F–F distances within the two fractions of each of these CF₃ groups were constrained to be identical, and an overall temperature factor was applied to the six F “atoms” of each group. A difference Fourier calculated at the conventional *R* value of 0.093 showed numerous broad peaks in the proximity of an inversion center, which, on the basis of their heights and of geometrical considerations, were attributed to the non-hydrogen atoms of a disordered CHCl₃ solvate molecule, predominantly occupying two positions in the asymmetric unit with essentially equal probability (therefore occupy four positions in the centrosymmetric cavity, which could not accommodate more than one CHCl₃ molecule; the overall occupancy

**Figure 1.** Diffuse-reflectance (---) and 1,2-dichloroethane solution (---) spectra of Cu(SALMedpt)Cu(hfa)₂. The absorbance scale is arbitrary.**Figure 2.** Perspective view of the Cu(SALMedpt)Cu(hfa)₂ molecule. The two sets of C–F bonds in the distorted C–F₃ groups (see text) are marked differently in this and following drawings of the structure.

was, however, estimated to be less than 1, on the basis of the elemental analysis and density data). Two CCl₃ pyramidal fragments, each with fixed 0.15 population parameter, were finally included in the model, with identical C–Cl and Cl...Cl distances and an overall temperature factor, whose values were refined applying a damping factor to the shifts. The values of these parameters were not allowed to change in the final cycles. Although such a model for the solvent was not very accurate, it accounted reasonably well for the elemental analysis and density data and for the electron density distribution in the ΔF map. Hydrogen atoms of the SALMedpt and hfa ligands were introduced in calculated positions (C–H = 1.00 Å) and assigned isotropic thermal parameters ca. 20% larger than those of the relative carbon atoms. In the final least-squares cycle no shift/error ratio was higher than 0.20. The final values of the discrepancy indices, defined by $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2}$, were $R = 0.073$ and $R_w = 0.075$. The highest peaks ($< 1 e \text{ \AA}^{-3}$) in a difference Fourier map calculated at the end of the refinement were located in the regions occupied by the solvent molecule and by the disordered CF₃ groups. The final atomic positional and thermal parameters for the non-hydrogen atoms are listed in Table II. A listing of the observed and calculated structure amplitudes is available.¹⁵

Results and Discussion

The diffuse-reflectance and the solution spectra of the Cu(SALMedpt)Cu(hfa)₂ complex are shown in Figure 1. The solid-state spectra show a peak at 16 000 cm⁻¹ on an asymmetric band. The solution spectra show a red shift of the main peak (to 13 800 cm⁻¹) and a shoulder at ca. 10 000 cm⁻¹,

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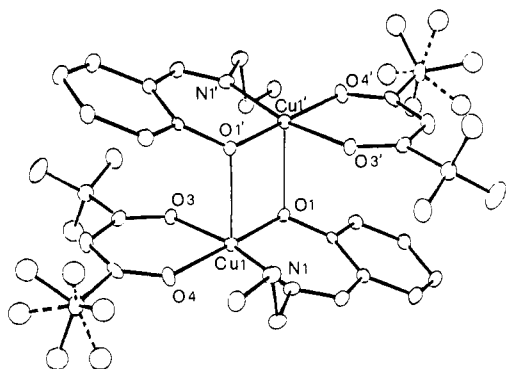


Figure 3. Perspective view of the inner part of the Cu(SALMedpt)Cu(hfa)₂ molecule.

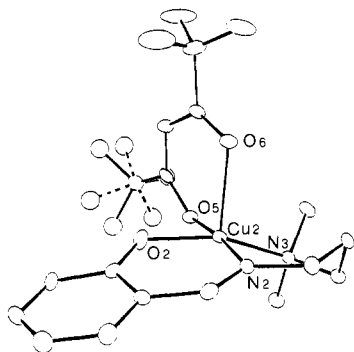


Figure 4. View of the outer metal atom environment in the Cu(SALMedpt)Cu(hfa)₂ molecule.

indicating that different species are present in solution.

Although the analytical data suggest a dinuclear structure, the room-temperature magnetic moments are practically normal and also the EPR spectra are not very diagnostic, showing at room temperature a broad signal, centered at $g = 2.13$, typical of exchange narrowing¹⁶ operative between copper centers.

The structure is formed by centrosymmetric dimers of the dinuclear species of formula [Cu(SALMedpt)Cu(hfa)₂]₂ and by CHCl₃ solvent molecules, which occupy in a disordered fashion a region of space surrounding an inversion center. A perspective view of the molecule is shown in Figure 2. The four metal atoms in the tetranuclear species are related in pairs by the inversion center. Two, lying close to each other (3.176 Å) in the core of the tetranuclear molecule, are bridged by salicylaldehyde oxygen atoms. Those of the other pair occupy peripheral positions which are separated by rather large distances (>6 Å) from the other metal sites in the structure. Although the environment of the two copper atoms in the symmetry-independent part of the tetranuclear species is different, the coordination geometry approaches that of an axially elongated square pyramid in both cases.

The copper atom lying close to the inversion center (inner copper) is bound (Figure 3) by the oxygen and the iminic nitrogen atoms of a SALMedpt ligand, by the two oxygen atoms of a hfa ligand, and in the axial position by one oxygen atom of the second SALMedpt molecule. The two oxygen atoms of the SALMedpt ligands are symmetry related.

The second copper atom in the dimer (outer copper) is surrounded by the remaining donor atoms (Figure 4), namely, one oxygen and two nitrogens of the pentadentate ligand and by the two oxygen atoms of the second hfa molecule. One of these oxygens lies in the axial position.

A schematic representation of the tetranuclear species is given in Figure 5, from which it is apparent that the outer

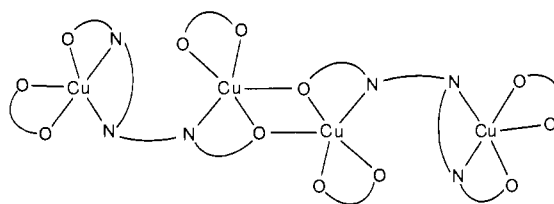


Figure 5. Schematic representation of the tetranuclear molecule Cu(SALMedpt)Cu(hfa)₂.

copper atoms are bound to a hfa and to a SALMedpt molecule that is acting as a tridentate ligand, while the inner copper atoms are bound to a hfa and to a SALMedpt that is acting as a bidentate ligand. Although tetranuclear complexes are not uncommon for copper(II), usually the observed arrangement of metal ions is of the cubane type,¹⁷⁻²⁰ whereas in the present compound the arrangement of copper ions is almost linear.²¹⁻²³

Bond distances and angles within the ligand molecules are in the normal range. Values of bond distances and angles around the metal ions are listed in Table III.

The metal to phenolic oxygen and iminic nitrogen distances are very similar in the two copper environments (1.903 (6) and 1.892 (9) Å for Cu-O, 1.966 (9) and 1.974 (11) Å for Cu-N). The same is true for one of the copper to hfa oxygen distances (2.015 (6) and 2.024 (9) Å) but not for the other one: in fact, in the outer copper environment the oxygen atom of the hfa ligand occupies the axial position of the square pyramid so that such a Cu-O distance is rather long (2.276 (9) Å). In the inner copper environment, on the other hand, the oxygen atom is occupying an equatorial position and the bond distance is therefore rather short (1.937 (7) Å). The longest distance in the coordination environment is that of the inner copper to the bridging oxygen (2.398 (6) Å), which compares well with the longest values reported for similar dinuclear copper complexes.²⁴ In the two square pyramids the copper atoms deviate from the least-squares planes through the four basal ligands by 0.12 and 0.21 Å in the inner and outer environments, respectively. The angle between such planes is 89.7°.

The Cu-O-Cu angle of 94.3° is in the usual range found for similar complexes.²⁴

With the structural data available it appeared interesting to undertake a characterization of the magnetic properties of the polynuclear complex. Polycrystalline powder EPR spectra do not show many features down to liquid-helium temperature. At 4.2 K the spectra can be interpreted with $g_{\parallel} = 2.05$ and $g_{\perp} = 2.18$. A similar pattern of g values can be expected as arising from the interaction of two antiferrodistortively coupled copper ions.^{25,26} As a matter of fact the elongation axes of the inner and the outer chromophores are almost exactly orthogonal to each other.

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Table II. Positional Parameters and Temperature Factors for $\text{Cu}_2(\text{SALMedpt})(\text{hfa})_2 \cdot 0.3\text{CHCl}_3^{a-c}$

A. Positional Parameters and Isotropic Temperature Factors									
atom	x	y	z	$U, \text{\AA}^2$	atom	x	y	z	$U, \text{\AA}^2$
Cu1	0.0300 (1)	0.1033 (1)	0.1186 (2)		C6	-0.1001 (7)	-0.1640 (9)	0.2782 (14)	
Cu2	0.3949 (1)	0.1674 (1)	0.4264 (2)		C7	-0.0312 (6)	-0.0829 (8)	0.2587 (13)	
F1	-0.2030 (4)	0.1381 (6)	-0.1871 (10)		C8	0.3784 (7)	-0.0519 (11)	0.4319 (15)	
F2	-0.1870 (4)	0.2770 (7)	-0.0420 (10)		C9	0.3310 (7)	-0.0576 (11)	0.5579 (14)	
F3	-0.1507 (5)	0.2833 (8)	-0.2636 (10)		C10	0.2976 (9)	-0.1589 (12)	0.5982 (17)	
F41 ^d	0.1836 (7)	0.4323 (9)	0.1834 (11)	0.105 (3)	C11	0.2540 (10)	-0.1721 (16)	0.7152 (20)	
F51 ^d	0.1892 (7)	0.3972 (9)	-0.0578 (14)	0.105 (3)	C12	0.2391 (8)	-0.0848 (15)	0.7925 (18)	
F61 ^d	0.1154 (6)	0.4923 (9)	0.0013 (15)	0.105 (3)	C13	0.2713 (7)	0.0139 (13)	0.7559 (14)	
F42 ^e	0.1278 (14)	0.4431 (18)	-0.1028 (17)	0.105 (3)	C14	0.3204 (7)	0.0291 (11)	0.6391 (14)	
F52 ^e	0.2128 (8)	0.3941 (17)	0.0613 (30)	0.105 (3)	C15	0.2030 (6)	0.1538 (10)	0.2908 (14)	
F62 ^e	0.1423 (14)	0.4866 (13)	0.1439 (3)	0.105 (3)	C16	0.2420 (7)	0.1410 (10)	0.1494 (14)	
F71 ^f	0.3723 (8)	0.4669 (12)	0.8129 (13)	0.106 (3)	C17	0.3147 (7)	0.2335 (7)	0.1373 (16)	
F81 ^f	0.2700 (6)	0.3903 (12)	0.6391 (18)	0.106 (3)	C18	0.4558 (8)	0.0108 (11)	0.2404 (16)	
F91 ^f	0.3614 (9)	0.5101 (10)	0.5777 (16)	0.106 (3)	C19	0.4865 (7)	0.1076 (11)	0.1659 (16)	
F72 ^g	0.3825 (9)	0.5187 (9)	0.7483 (17)	0.106 (3)	C20	0.4181 (7)	0.1509 (11)	0.0896 (14)	
F82 ^g	0.3044 (9)	0.3700 (10)	0.7502 (18)	0.106 (3)	C21	0.4547 (8)	0.3234 (10)	0.2181 (18)	
F92 ^g	0.2975 (9)	0.4475 (12)	0.5414 (15)	0.106 (3)	C22	-0.0700 (6)	0.2224 (11)	-0.0548 (13)	
F10	0.6348 (6)	0.4274 (10)	0.8651 (16)		C23	-0.0052 (8)	0.3099 (10)	-0.0536 (15)	
F11	0.6707 (6)	0.3301 (11)	0.7194 (15)		C24	0.0711 (7)	0.3098 (9)	0.0274 (15)	
F12	0.6110 (8)	0.2718 (13)	0.8921 (19)		C25	-0.1543 (7)	0.2294 (11)	-0.1416 (16)	
O1	-0.0402 (4)	-0.0281 (5)	0.1358 (8)		C26	0.1407 (7)	0.4107 (9)	0.0388 (10)	
O2	0.3532 (5)	0.1231 (7)	0.6090 (9)		C27	0.4020 (7)	0.3577 (10)	0.6125 (17)	
O3	-0.0687 (4)	0.1413 (8)	0.0062 (8)		C28	0.4781 (8)	0.3716 (10)	0.7081 (16)	
O4	0.0932 (4)	0.2418 (6)	0.0994 (10)		C29	0.5310 (6)	0.3156 (10)	0.6719 (15)	
O5	0.3680 (4)	0.3011 (6)	0.4889 (10)		C30	0.3497 (7)	0.4282 (9)	0.6608 (11)	
O6	0.5214 (4)	0.2474 (7)	0.5623 (10)		C31	0.6139 (9)	0.3385 (18)	0.7867 (22)	
N1	0.1217 (5)	0.0806 (8)	0.2678 (11)		C32 ^h	0.0275 (7)	0.5165 (13)	0.5035 (12)	0.186 (2)
N2	0.4094 (5)	0.0298 (8)	0.3649 (11)		C33 ^h	0.0057 (9)	0.5169 (13)	0.4631 (12)	0.186 (2)
N3	0.3952 (5)	0.2199 (7)	0.2059 (11)		Cl1 ^h	-0.0366 (8)	0.4494 (13)	0.3617 (11)	0.186 (2)
C1	0.1129 (7)	0.0096 (10)	0.3614 (14)		Cl2 ^h	-0.1170 (7)	0.5103 (14)	0.5113 (13)	0.186 (2)
C2	0.0407 (6)	-0.0716 (9)	0.3678 (13)		Cl3 ^h	-0.0010 (9)	0.5255 (13)	0.6670 (10)	0.186 (2)
C3	0.0447 (8)	-0.1355 (10)	0.4901 (15)		Cl4 ^h	-0.0236 (9)	0.4420 (12)	0.3053 (10)	0.186 (2)
C4	-0.0216 (9)	-0.2119 (11)	0.5083 (15)		Cl5 ^h	0.0987 (7)	0.5461 (13)	0.5325 (13)	0.186 (2)
C5	-0.0936 (8)	-0.2253 (9)	0.3988 (15)		Cl6 ^h	-0.0520 (8)	0.5020 (13)	0.5876 (12)	0.186 (2)

B. Anisotropic Temperature Factors

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu1	0.0298 (7)	0.0406 (8)	0.0532 (9)	0.0048 (6)	0.0028 (6)	0.0041 (6)
Cu2	0.0341 (8)	0.0526 (9)	0.0550 (9)	0.0064 (7)	0.0067 (6)	-0.0067 (7)
F1	0.060 (5)	0.075 (6)	0.131 (7)	0.018 (5)	-0.023 (5)	0.015 (5)
F2	0.066 (5)	0.110 (7)	0.124 (7)	0.046 (5)	0.023 (5)	0.005 (5)
F3	0.089 (6)	0.160 (9)	0.106 (7)	0.044 (6)	0.014 (5)	0.074 (7)
F10	0.096 (8)	0.169 (11)	0.246 (14)	0.035 (7)	-0.074 (8)	-0.130 (11)
F11	0.046 (6)	0.242 (15)	0.202 (12)	0.027 (7)	-0.018 (7)	-0.081 (11)
F12	0.146 (12)	0.252 (18)	0.215 (15)	-0.032 (11)	-0.089 (11)	0.109 (14)
O1	0.034 (4)	0.038 (4)	0.047 (5)	0.006 (3)	-0.001 (3)	0.009 (4)
O2	0.089 (7)	0.066 (6)	0.052 (5)	0.031 (5)	0.026 (5)	-0.003 (5)
O3	0.035 (4)	0.048 (5)	0.058 (5)	0.018 (4)	0.008 (4)	0.017 (4)
O4	0.045 (5)	0.033 (5)	0.090 (6)	0.004 (4)	0.005 (4)	0.013 (4)
O5	0.043 (5)	0.065 (6)	0.078 (6)	0.009 (4)	0.006 (4)	-0.017 (5)
O6	0.043 (5)	0.071 (6)	0.082 (6)	0.016 (4)	0.006 (4)	-0.024 (5)
N1	0.033 (5)	0.059 (7)	0.047 (6)	0.007 (5)	0.004 (5)	-0.002 (5)
N2	0.035 (5)	0.065 (7)	0.048 (6)	0.012 (5)	0.007 (5)	-0.001 (5)
N3	0.033 (5)	0.055 (6)	0.065 (7)	0.003 (5)	0.011 (5)	-0.001 (5)
C1	0.038 (7)	0.062 (9)	0.050 (8)	0.028 (7)	-0.004 (6)	-0.001 (7)
C2	0.035 (7)	0.045 (7)	0.051 (7)	0.011 (6)	0.006 (6)	0.007 (6)
C3	0.048 (8)	0.074 (10)	0.063 (9)	0.026 (7)	0.002 (7)	0.015 (7)
C4	0.084 (11)	0.071 (10)	0.053 (9)	0.029 (9)	0.010 (8)	0.024 (8)
C5	0.066 (9)	0.043 (8)	0.065 (9)	0.007 (7)	0.026 (7)	0.016 (7)
C6	0.046 (8)	0.045 (7)	0.060 (8)	0.001 (6)	0.015 (6)	0.005 (6)
C7	0.043 (7)	0.031 (6)	0.043 (7)	0.015 (5)	0.009 (5)	0.001 (5)
C8	0.052 (8)	0.062 (9)	0.064 (9)	0.029 (7)	0.004 (7)	-0.010 (7)
C9	0.039 (7)	0.062 (9)	0.057 (8)	0.004 (6)	0.003 (6)	0.003 (7)
C10	0.098 (12)	0.073 (11)	0.067 (10)	0.015 (9)	0.022 (9)	0.006 (9)
C11	0.089 (12)	0.098 (15)	0.089 (13)	0.016 (10)	0.021 (10)	0.027 (11)
C12	0.053 (9)	0.122 (15)	0.070 (11)	0.005 (10)	0.018 (8)	0.029 (11)
C13	0.059 (9)	0.097 (12)	0.044 (8)	0.023 (8)	0.019 (7)	0.000 (8)
C14	0.047 (8)	0.066 (10)	0.045 (8)	0.021 (7)	-0.004 (6)	0.008 (7)
C15	0.037 (7)	0.070 (11)	0.053 (8)	0.001 (6)	-0.001 (6)	0.008 (7)
C16	0.038 (7)	0.069 (9)	0.058 (8)	0.009 (7)	0.004 (6)	0.004 (7)
C17	0.054 (8)	0.067 (10)	0.072 (10)	0.019 (7)	0.008 (7)	0.017 (8)
C18	0.046 (8)	0.087 (11)	0.080 (10)	0.024 (8)	0.021 (8)	-0.021 (9)
C19	0.039 (8)	0.088 (11)	0.073 (9)	0.004 (8)	0.027 (7)	-0.018 (8)
C20	0.050 (8)	0.090 (11)	0.051 (8)	-0.003 (8)	0.010 (7)	0.009 (8)

Table II (Continued)

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C21	0.059 (10)	0.070 (10)	0.094 (12)	-0.010 (8)	0.028 (8)	0.010 (9)
C22	0.045 (7)	0.074 (10)	0.047 (7)	0.027 (7)	0.014 (6)	0.017 (7)
C23	0.063 (9)	0.055 (9)	0.084 (10)	0.022 (8)	0.029 (8)	0.024 (8)
C24	0.054 (8)	0.028 (7)	0.075 (9)	-0.002 (6)	0.030 (7)	-0.030 (6)
C25	0.049 (8)	0.062 (10)	0.073 (10)	0.020 (8)	0.010 (7)	0.017 (8)
C26	0.141 (15)	0.078 (11)	0.077 (11)	0.063 (11)	0.021 (10)	0.036 (9)
C27	0.037 (7)	0.056 (9)	0.088 (10)	0.001 (6)	0.034 (7)	-0.009 (8)
C28	0.053 (9)	0.073 (10)	0.071 (9)	0.007 (8)	0.002 (7)	-0.018 (8)
C29	0.037 (7)	0.064 (9)	0.077 (10)	-0.005 (7)	0.008 (7)	-0.018 (8)
C30	0.097 (13)	0.140 (16)	0.086 (12)	-0.042 (12)	0.032 (10)	-0.008 (11)
C31	0.061 (12)	0.134 (17)	0.095 (14)	0.014 (12)	-0.021 (10)	-0.036 (13)

^a Standard deviations in the last significant digits are in parentheses. ^b Isotropic temperature factors are of the form $\exp[-8\pi^2 U(\sin^2 \theta)/\lambda^2]$, and anisotropic temperature factors are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{12}hka^*b^* + \dots)]$. ^c Atoms O1, O2, and N1-C21 belong to the SALMedpt ligand, atoms F1-F12, O3-O6, and C22-C31 to the two hfa ligands, and atoms C32-Cl6 to the solvate CHCl₃ molecule. ^d Value of population parameter (pp) 0.69. ^e pp = 0.31. ^f pp = 0.52. ^g pp = 0.48. ^h pp = 0.15.

Table III. Selected Bond Distances (Å) and Angles (Deg)^a

Cu1-O1	1.903 (6)	Cu2-O2	1.892 (9)
Cu1-N1	1.966 (9)	Cu2-N2	1.974 (11)
Cu1-O3	2.015 (6)	Cu2-N3	2.049 (10)
Cu1-O4	1.937 (7)	Cu2-O5	2.024 (9)
Cu1-O1'	2.398 (6)	Cu2-O6	2.276 (9)
Cu1-O1-Cu1'	94.3 (2)	O6-Cu2-O2	95.1 (3)
O1'-Cu1-O1	85.7 (3)	O6-Cu2-N2	100.3 (4)
O1'-Cu1-N1	104.8 (3)	O6-Cu2-N3	103.1 (4)
O1'-Cu1-O3	87.1 (3)	O6-Cu2-O5	84.9 (3)
O1'-Cu1-O4	96.2 (3)	O2-Cu2-N2	93.0 (4)
O1-Cu1-N1	94.2 (3)	O2-Cu2-N3	157.8 (4)
O1-Cu1-O3	86.8 (3)	O2-Cu2-O5	83.8 (3)
O1-Cu1-O4	175.0 (3)	N2-Cu2-N3	96.1 (4)
N1-Cu1-O4	89.9 (4)	N2-Cu2-O5	174.2 (4)
N1-Cu1-O3	168.0 (4)	N3-Cu2-O5	85.2 (4)
O3-Cu1-O4	88.6 (3)		

^a Primed atoms are related to the corresponding unprimed atoms by the inversion center at the origin.

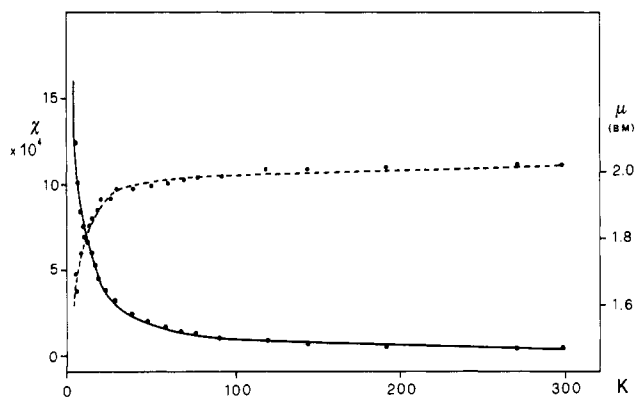
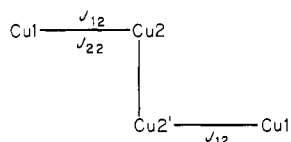


Figure 6. Temperature dependence of the magnetic susceptibility (—) and of the magnetic moment (---) of Cu(SALMedpt)Cu(hfa)₂. The curve through the experimental points was calculated with the Bleaney-Bowers equation (see text).

The temperature dependence of the magnetic susceptibility of Cu(SALMedpt)Cu(hfa)₂ is shown in Figure 6. The data were analyzed at two different levels of sophistication. The structure of the tetranuclear unit can be schematicized as shown as far as the magnetic coupling is concerned:



Therefore, at the lowest approximation only the J_{22} interaction may be considered to be different from zero, since the J_{12}

interactions are presumably very small, because the inner and outer metal ions are very far away from each other (6.27 Å) and they are bridged through polyatomic bridges.²⁷ In this approximation the data can be handled by using the simple Bleaney-Bowers equation²⁸ for dinuclear complexes. The best fit curve obtained through a least-squares procedure is shown in Figure 6. The corresponding parameters are $g = 2.25$ and $J = 6.6 \text{ cm}^{-1}$ (the interaction Hamiltonian is defined as $J \cdot (S_1 \cdot S_2)$).

The curve was also fit with use of a more complex model, appropriate to a linear tetranuclear species, with the exchange Hamiltonian

$$H = J_{12}(S_1 \cdot S_2) + J_{22}(S_2 \cdot S_2') + J_{12}(S_2' \cdot S_1') \quad (1)$$

where advantage was taken of the symmetry of the species. The matrix elements of the Hamiltonian (1) within the total spin S wave functions were evaluated through irreducible tensor operator techniques²⁹ and are reported in the Appendix. The magnetic susceptibility of the tetranuclear species was calculated by applying the Van Vleck equation to the resulting energy levels, by assuming one g value. The experimental data were fit by allowing the J_{12} , J_{22} , and g parameters to vary. The J_{12} and J_{22} parameters are strongly correlated, in the sense that increasing J_{22} (making it more antiferromagnetic) demands a more negative J_{12} value (more ferromagnetic) to yield a comparable fit. The best fit values are $J_{22} = 7.5 \pm 1.5 \text{ cm}^{-1}$ and $J_{12} = -1.5 \pm 1.5 \text{ cm}^{-1}$. In any case the tetranuclear model did not give any improvement in the quality of the fit so that the simpler model seems to be equally adequate. The exchange interaction between the two inner copper(II) ions is in the range usually found for square-pyramidal complexes bridged in an axial-equatorial way.^{19,30,31} Since the unpaired electrons are expected to be in practically parallel planes with the magnetic orbitals not overlapping appreciably, the exchange can be either ferro- or antiferromagnetic but in any case weak,³² as observed.

Appendix

The matrix elements were considered in the coupling scheme for which S_1 and S_2 are coupled first, the resulting states are coupled to S_2' , and finally S_1' is considered:

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These matrix elements can be expressed as products of phase factors and $6-j$ coefficients according to standard procedures.²⁹

The energies of the total spin state $S = 2$ were calculated through the expression

$$E(S = 2) = \frac{1}{2}J_{12} + \frac{1}{4}J_{22'}$$

The energies of the $S = 1$ and $S = 0$ states were obtained by diagonalization of the Hamiltonian matrices

$$E(S = 1) = \begin{vmatrix} -\frac{1}{6}J_{12} + \frac{1}{4}J_{22'} & \frac{2}{3}J_{12} & 0 \\ \frac{2}{3}J_{12} & \frac{1}{6}J_{12} - \frac{1}{2}J_{22'} & \frac{3}{4}J_{22'} \\ 0 & \frac{3}{4}J_{22'} & -\frac{1}{2}J_{12} \end{vmatrix}$$

$$E(S = 0) = \begin{vmatrix} \frac{1}{2}J_{12} - \frac{1}{2}J_{22'} & \frac{3}{4}J_{22'} \\ \frac{3}{4}J_{22'} & -\frac{3}{2}J_{12} \end{vmatrix}$$

Registry No. [Cu(SALMedpt)Cu(hfa)₂]₂·6CHCl₃, 82598-70-7; Cu(SALMedpt), 15378-53-7; Cu(hfa)₂, 14781-45-4.

Supplementary Material Available: A listing of structure factor amplitudes (17 pages). Ordering information is given on any current masthead page.

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Preparation and Structure of *cis*-Chlorodiammine(*N*²,*N*²-dimethyl-9-methylguanine)platinum(II) Hexafluorophosphate. A Model for the Intermediate in the Proposed Cross-Linking Mode of Action of Platinum(II) Antitumor Agents

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The synthesis and molecular and crystal structure of *cis*-chlorodiammine(*N*²,*N*²-dimethyl-9-methylguanine)platinum(II) hexafluorophosphate, *cis*-[Pt(NH₃)₂(Dmmg)Cl](PF₆), are reported. The compound crystallizes in the monoclinic system, space group *P*₂₁/*c*, with *a* = 5.467 (2) Å, *b* = 9.784 (5) Å, *c* = 32.309 (17) Å, β = 92.20 (4)°, *V* = 1726.9 Å³, *Z* = 4 [based on a formula weight of 602.78 for [Pt(NH₃)₂(C₈N₅H₁₁O)Cl](PF₆)], *D*_{meas} = 2.34 (1) g cm⁻³, and *D*_{calcd} = 2.32 g cm⁻³. A structural model was obtained by conventional Patterson and Fourier methods and refined by full-matrix least-squares techniques to an *R* value of 0.054 based on 4554 counter-collected *F*_o's. The *cis*-[Pt(NH₃)₂(Dmmg)Cl]⁺ complex cation is four-coordinate with the Dmmg base bound through the N(7) position of the five-membered imidazole ring. Principal geometrical parameters for the primary coordination sphere are as follows: Pt-N(ammine trans to the chloro ligand) = 2.059 (6) Å; Pt-N(ammine trans to the Dmmg base) = 2.027 (7) Å; Pt-N(7)(Dmmg) = 2.035 (6) Å; Pt-Cl = 2.300 (2) Å; base/PtN₃Cl coordination plane dihedral angle = 81.3°. The significant difference in the two Pt-NH₃ bond lengths is attributable to a greater structural trans effect for the chloro ligand over that of the N(7)-bound purine base. The molecular dimensions of the coordinated Dmmg ligand are in excellent agreement with those reported for the free base. The crystal structure is stabilized by hydrogen bonding between the exocyclic oxygen atom O(6) of the Dmmg ligand as an acceptor and the coordinated ammine ligands as donors and by general electrostatic interactions. The complex cation affords a model for a species of the type *cis*-[Pt(NH₃)₂(N(7)-bound guanine)Cl]⁺, where the guanine residue is part of a polynucleotide chain. Such species have been postulated as possible intermediates in the reaction sequence leading to the cross-linking of DNA by the antitumor agent *cis*-[Pt(NH₃)₂Cl₂].

Introduction

The class of coordination compounds typified by *cis*-[Pt(NH₃)₂Cl₂] (cisplatin) are clinically successful antineoplastic agents.² Diverse experimental evidence implicates that the primary targets for these drugs are regions of DNA rich in guanine-cytosine residues.³ These findings have stimulated considerable research into the chemistry of platinum compounds containing nucleic acid components as ligands. These investigations have led to numerous proposals for ways in which platinum compounds may bind to the nucleobases of DNA so as to cause mutagenesis (by inducing base mispairing) or cell death (by introducing one or more different kinds of "defects" that cancer cells may find difficult or impossible to repair). Both the *cis* and *trans* isomers of these platinum compounds are mutagenic, and to some extent carcinogenic,

but only the *cis* isomers have significant antitumor activity.^{2,4} This suggests a structural basis for the antineoplastic properties of the *cis* compounds. Consequently, many structural studies have been performed on model systems containing two nucleic acid constituents bound to a *cis*-A₂Pt^{II} moiety, where A = NH₃ or A₂ = a bidentate chelate such as ethylenediamine (en) or trimethylenediamine (tn).^{5,6} All of these systems model potential products of bifunctional attack of *cis*-A₂PtCl₂ on a DNA polymer, with the replacement of the two chloro ligands by donor atoms from two nucleic acid bases. The ultimate product is envisioned as a DNA polymer containing a metal-mediated intrastrand or interstrand cross-link.

To a much lesser extent, attention has been directed toward the structural characterization of possible intermediate species. For example, one postulated mechanism for the antineoplastic

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