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Synthesis, Magnetic Susceptibility, and Structure of Some Binuclear Copper(II), Nickel(II), and Cobalt(II) Fluorinated 1,3,5-Triketonates. Structural and Electronic Effects on Magnetic Exchange

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The structures of two binuclear complexes prepared from fluorinated 1,3,5-triketonate-type ligands were determined by single-crystal X-ray techniques. The complexes are $Cu_2(HXFDAA)_2(CH_3OH)_2$ containing the ligand 1,1,1,7,7,7-hexafluoro-2,4,6-heptanetrionate dianion and $Ni_2(TFDAA)_2(py)_4$ containing the ligand 1,1,1-trifluoro-2,4,6-heptanetrionate dianion. The complex $Cu_2(HXFDAA)_2(CH_3OH)_2$ contains two copper atoms, each coordinated to four equatorial ketonic oxygens and one methanolic oxygen in typical five-coordinate manner (*Cmca*, $a = 21.353$ (7) Å, $b = 7.623$ (2) Å, $c = 14.251$ (5) Å, $Z = 4$, $R = 0.064$). The complex $Ni_2(TFDAA)_2(py)_4$ contains two nickel atoms each coordinated to four equatorial ketonic oxygens and two axial pyridine nitrogens ($P2_1/c$, $a = 10.150$ (4) Å, $b = 19.969$ (5) Å, $c = 10.154$ (3) Å, $Z = 2$, $R = 0.065$). In addition $Cu_2(HXFDAA)_2(H_2O)_2$, $Cu_2(TFDAA)_2(CH_3OH)_2$, $Ni_2(HXFDAA)_2(H_2O)_4$, and $Co_2(TFDAA)_2(py)_4$ were prepared. The magnetic properties of these complexes, all of which exhibit antiferromagnetic exchange, were investigated. Comparisons with other 1,3,5-triketonate complexes show that, for a given metal ion, the coordination geometry is similar in all compounds. This allows discussion of magnetic differences in terms of the substituent group electronic effects.

Introduction

1,3,5-Triketones, as homologues of 1,3-diketones, are a versatile class of ligands with the capability of coordinating two metal ions per molecule. The resulting chelates are homologues of 1,3-diketonate chelates. Therefore, direct comparisons can be made concerning the physical and chemical effects of having two metal ions present rather than just one. In the extensive studies done on 1,3-diketonate chelates, it has been well established that substituent changes on the chelate rings may have profound effects on physical and chemical properties[1] such as solubility, volatility, crystallizability, spectral properties, metal ion stereochemistry, redox potentials of the metal ion, acidity of the metal ion, etc. Since the binuclear complexes of 1,3,5-triketonates have been studied for only a relatively short period of time, very little data of a comparable nature exist for these higher homologues. Part of the reason for undertaking this study was to determine some of the properties of a few fluorinated 1,3,5-triketonate binuclear chelates.

A feature of binuclear 1,3,5-triketonates which is obviously absent in mononuclear 1,3-diketonates is the antiferromagnetic exchange that takes place when the individual metal ions are paramagnetic. The magnitude of this exchange is a molecular property that can potentially be used to investigate such things as the electronic effects of the ligand substituent groups. Another reason for undertaking this project was to determine the relative importance of substituent electronic effects on the magnitude of magnetic exchange. A prerequisite for this determination is that intramolecular structural parameters such as M–O–M bridge angles, M–M distance, and mean deviation from similarly defined ligand planes within the series of compounds be essentially constant. In other words, the symmetry of the exchanging electrons must remain constant in order to observe effects due to substituent group changes within a series. At this point, sufficient structural information exists to make a preliminary discussion of substituent group effects possible. One prior report dealing with fluorinated 1,3,5-triketonate chelates[2] and our preliminary report of the structure and magnetic properties of a fluorinated bis(1,3,5-triketonato)dicopper(II) complex have appeared.[3]

Experimental Section

Ligand Synthesis. The sodium salt of 1,1,1,7,7,7-hexafluoro-2,4,6-heptanetrione, $Na_2(HXFDAA)$,[4] and the sodium salt of 1,1,1-trifluoro-2,4,6-heptanetrione, $Na_2(TFDAA)$,[4] were prepared by the general procedure of Miles, Harris, and Hauser.[5] The pure, protonated ligands were not isolated.

Bis(1,1,1,7,7,7-hexafluoro-2,4,6-heptanetrionato)diaquodicopper(II), $Cu_2(HXFDAA)_2(H_2O)_2$. Crude $Na_2(HXFDAA)$ (5.5 g) was dissolved in 150 mL of hot H_2O. To this was added a solution of $Cu(H_3C_2O_2)_2 \cdot H_2O$ (4.5 g in 100 mL of H_2O). The solution was stirred with gentle heating for 3 h after which it was filtered. The green solid collected on the filter was washed with H_2O, acetone, and diethyl ether. Evaporation of the combined acetone–ether washings yielded the green product which was recrystallized from a 3:1:1 $CH_3OH–CH_2Cl_2–CHCl_3$ mixed solvent. This product may be recrystallized from CH_3OH, yielding $Cu_2(HXFDAA)_2(CH_3OH)_2$ crystals. Anal. Calcd for $Cu_2(C_{14}H_4F_{12}O_6)(H_2O)_2$: C, 25.53; H, 1.22. Found: C, 25.31; H, 1.43.

Bis(1,1,1-trifluoro-2,4,6-heptanetrionato)bis(methanol)dicopper(II), $Cu_2(TFDAA)_2(CH_3OH)_2$. A solution of 2.4 g of crude $Na_2(TFDAA)$ in 150 mL of warm CH_3OH was added to a solution of 2.3 g of $CuBr_2$ in 150 mL of CH_3OH. The reaction mixture was refluxed for 1 h and filtered while still hot. A dark green solid which was not characterized remained on the frit. The filtrate was evaporated to dryness and the resulting solid dissolved in diethyl ether by means of a Soxhlet extractor. The green ether solution was evaporated to dryness, and the resulting green solid was vacuum-dried. Anal. Calcd for $Cu_2(C_{14}H_{10}F_6O_6)(CH_3OH)_2$: C, 33.28; H, 3.13; Cu, 22.01. Found: C, 33.89; H, 2.93; Cu, 21.57.

Bis(1,1,1-trifluro-2,4,6-heptanetrionato)tetrakis(pyridine)dinickel(II), $Ni_2(TFDAA)_2(py)_4$. A solution of 2.0 g of crude $Na_2(TFDAA)_2$ in 150 mL of warm CH_3OH was added to a stirred, refluxing solution of 2.0 g of $Ni(C_2H_3O_2)_2 \cdot 4H_2O$ in 200 mL of CH_3OH. The solution was refluxed for 45 min and concentrated to a small volume (about 15 mL). The resulting mixture was stirred in a 150 mL of H_2O/150 mL of diethyl ether mixture. A green ether layer was separated and the water layer extracted with two more 100-mL portions of ether. The combined ether extracts were evaporated to dryness. The resulting light green solid was crystallized twice from ethanol. Anal. Calcd for $Ni_3(C_{14}H_{10}F_6O_6)(OH)_2(H_2O)_6$:

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(1) See, for example: J. P. Fackler, *Prog. Inorg. Chem.*, **7**, 403 (1966); D. P. Graddon, *Coord. Chem. Rev.*, **4**, 1 (1969); Y. Y. Lim and R. S. Drago, *Inorg. Chem.*, **11**, 1334 (1972); G. H. Patterson and R. H. Holm, *ibid.*, **11**, 2285 (1972); R. F. Handy and R. L. Lintvedt, *ibid.*, **13**, 893 (1974).

(2) D. E. Fenton, S. E. Gayda, and P. Holmes, *Inorg. Chim. Acta*, **21**, 187 (1977).

(3) J. W. Guthrie, R. L. Lintvedt, and M. D. Glick, Abstracts, 174th National Meeting of the American Chemical Society, Chicago, Ill., Aug 1977, No. INOR 173.

(4) The abbreviations $Na_2(HXFDAA)$ and $Na_2(TFDAA)$ represent the trivial names sodium hexafluorodiacetylacetonate and sodium trifluorodiacetylacetonate.

(5) M. L. Miles, T. M. Harris, and C. R. Hauser, *J. Org. Chem.*, **30**, 1007 (1965).

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Table I. Atomic Parameters for $Cu_2(HXFDAA)_2(CH_3OH)_2$[a]

	x	y	z	B, Å^2
Cu	0.0 (0)	−0.1794 (2)	−0.0466 (1)	
O1	0.0652 (3)	−0.3090 (7)	−0.1053 (4)	3.92 (13)
O2	0.0563 (3)	0.0 (0)	0.0 (0)	
O3	0.0 (0)	−0.3340 (14)	0.0856 (8)	5.69 (23)
C1	0.1661 (5)	−0.3988 (15)	−0.1470 (8)	5.01 (23)
C2	0.1233 (4)	−0.2682 (11)	−0.0960 (6)	3.40 (16)
C3	0.1514 (4)	−0.1352 (12)	−0.0488 (7)	3.97 (18)
C4	0.1179 (5)	0.0 (0)	0.0 (0)	3.35 (22)
C5	0.0 (0)	−0.2766 (25)	0.1792 (13)	7.18 (43)
F1	0.1593 (4)	−0.5568 (9)	−0.1130 (6)	
F2	0.1532 (4)	−0.4086 (11)	−0.2348 (5)	
F3	0.2259 (3)	−0.3637 (12)	−0.1401 (7)	

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.0016 (0)	0.0141 (3)	0.0043 (1)	0.0 (0)	0.0037 (4)	−0.0019 (1)
O2	0.0012 (2)	0.0150 (16)	0.0057 (5)	0.0 (0)	0.0 (0)	−0.0013 (8)
F1	0.0064 (3)	0.0251 (18)	0.0146 (7)	0.0062 (6)	0.0037 (4)	−0.0000 (9)
F2	0.0051 (2)	0.0551 (24)	0.0060 (4)	0.0070 (7)	0.0006 (3)	−0.0054 (8)
F3	0.0023 (2)	0.0523 (24)	0.0174 (8)	0.0024 (5)	0.0012 (3)	−0.0154 (12)

[a] Standard deviations from the full variance–covariance matrix are given in parentheses for the least significant digit(s). The form of the anisotropic temperature factor is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

C, 23.80; H, 3.42; F, 16.14; Ni, 24.93. Found (lab 1): C, 24.42; H, 3.13; F, 15.55. Found (lab 2): C, 24.22; H, 3.21; Ni, 24.96. Although the nature of this complex is not known, dissolution and recrystallization of this material from pyridine yields crystals of $Ni_2(TFDAA)_2(py)_4$ suitable for single-crystal X-ray analysis. Elemental analysis of the pyridine adduct is consistent with the above formulation.

Bis(1,1,1,7,7,7-hexafluoro-2,4,6-heptanetrionato)tetraaquodinickel(II), $Ni_2(HXFDAA)_2(H_2O)_4$. A solution of 1.9 g of crude Na_2((HXFDAA) in 150 mL of H_2O was added to a refluxing solution of 3.1 g of $Ni(C_2H_3O_2)_2 \cdot 4H_2O$ in 150 mL of H_2O. A precipitate forms after all the ligand solution is added. The reaction mixture was refluxed for 1 h and filtered hot. The light green solid recovered was vacuum dried at room temperature. The crude solid was extracted with acetone in a Soxhlet extractor. The product was obtained as small green crystals by slow evaporation of the acetone extract. Anal. Calcd for $Ni_2(C_{14}H_4F_{12}O_6)(H_2O)_4$: C, 24.53; H, 1.76. Found: C, 25.05; H, 2.19.

Bis(1,1,1-trifluoro-2,4,6-heptanetrionato)tetrakis(pyridine)dicobalt(II), $Co_2(TFDAA)_2(py)_4$. A solution of 2.4 g of crude $Na_2(TFDAA)_2$ in 300 mL of hot CH_3OH was added to a refluxing solution of 2.5 g of $Co(C_2H_3O_2)_2 \cdot 4H_2O$ in 150 mL of CH_3OH. The solution was stirred for about 10 h at room temperature. It remains burgundy colored throughout this period, and no precipitate forms. The volume was reduced to 50 mL, and 100 mL of H_2O was added. The resulting mixture was heated and filtered. The recovered solid was extracted with acetone in a Soxhlet extractor. Evaporation of the acetone yielded an orange solid. The dried solid was dissolved in 50 mL of CH_3OH and the solution filtered. About 30 drops of pyridine was added to the CH_3OH solution and orange crystals of the pyridine adduct were obtained by slow evaporation. Anal. Calcd for $Co_2(C_{14}H_{10}F_6O_6)(C_5H_5N)_4$: C, 49.65; H, 3.68; N, 6.81; Co, 14.33. Found: C, 49.36; H, 3.76; N, 6.65; Co, 14.19.

Crystallography and Structure Determination[6]

1. $Cu_2(HXFDAA)_2(CH_3OH)_2$. Single crystals were obtained from methanol. An irregular hexagonal-prismatic crystal, with approximate dimensions of 0.60 × 0.23 × 0.08 mm, was mounted in a capillary tube with a small quantity of mother liquor to prevent solvent loss; crystals exposed to the air lost solvent and crumbled. Rotational and axial photographs of the crystal obtained on a Syntex $P2_1$ four-circle diffractometer, together with collection of a small data set, were consistent with orthorhombic symmetry. Lattice constants were obtained from least-squares refinement of 15 reflections which were automatically centered: $a = 21.353$ (7) Å, $b = 7.623$ (2) Å, $c = 14.251$ (5) Å, $Z = 4$, ρ(calcd) = 1.97 g cm^{-3}, and $V = 2320$ (1) Å^3.

Intensity data were collected with Mo Kα radiation ($\lambda = 0.710\,69$ Å) by using the θ–2θ scan technique and a scan speed of 2°/min. The ratio of background/scan time was 0.5. During data collection, the intensities of three reflections were measured every 100 reflections. There was no indication of crystal movement or decomposition. A total of 1804 independent data were collected to $(\sin\theta)/\lambda < 0.53$. Standard deviations were assigned as $\sigma(I) = [\sigma_{\text{counter}}(I)^2 + (pI)^2]^{1/2}$, where $\sigma_{\text{counter}} = (I + K^2B)^{1/2}$, I = net intensity, B = total background counts, K is the ratio of scan time to background time, and p is an instability factor. The data were corrected for Lorentz and polarization effects, but no absorption corrections were applied. There were 630 data with $I > 2.5\sigma(I)$, of which 623 were used for the solution and refinement of the structure; seven reflections of very low intensity were removed. The data were consistent with the space group *Cmca*. Patterson and Fourier techniques yielded the positions of the nonhydrogen atoms with anisotropic thermal parameters for the copper and fluorine atoms and isotropic thermal parameters for the carbon and oxygen atoms, except for the central oxygen of the triketonate moiety which was treated anisotropically and yielded $R = \sum(||F_o| - |F_c||)/\sum|F_o| = 0.064$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.079$. The error of fit was 2.59. The backbone hydrogen was located in the final difference map. The methanol hydrogens were not located. The highest residual electron density was 1.29 e/Å^3 and was located near (<1.0 Å) the oxygen atom of the methanol. Atomic positional and thermal parameters are given in Table I.

2. $Ni_2(TFDAA)_2(py)_4$. Single crystals were obtained from pyridine. An irregular hexagonal-prismatic crystal with approximate dimensions 0.45 × 0.35 × 0.15 mm was sealed in a capillary tube in order to minimize solvent loss. Rotational and axial photographs indicated that the crystal belonged to a monoclinic space group. A preliminary intensity data set indicated that the space group was $P2_1/c$. Lattice constants were obtained from least-squares refinement of 15 reflections which were automatically centered: $a = 10.150$ (4) Å, $b = 19.969$ (5) Å, $c = 10.154$ (3) Å, $Z = 2$, ρ(calcd) = 1.523 g/cm^3, and $V = 1792$ (1) Å^3. The intensity data were collected as described earlier. Three check reflections measured every 100 data indicated that no significant crystal movement or decomposition occurred. A total of 2568 independent data were collected to $(\sin\theta)/\lambda < 0.54$. Standard deviations were assigned as was described for the previous structure determination. The data were corrected for Lorentz and polarization effects, but no absorption corrections were applied. There were 1379 data with $I > 2.5\sigma(I)$.

Patterson and Fourier techniques yielded the nonhydrogen positions. Full-matrix least-squares refinement on 26 atomic positions, using isotropic temperature factors for all atoms, resulted in R of 0.133.

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(6) Local versions of the following programs were used: (1) SYNCOR, W. Schmonsee's program for data reduction; (2) FORDAP, A. Zalkin's Fourier program; (3) ORFLS and ORFFE, W. Busing, K. Martin, and H. Levy's full-matrix least-squares program and function and error program; (4) ORTEP, C. K. Johnson's program for plotting; (5) HFINDR, A. Zalkin's program for calculating idealized hydrogen positions. An interactive graphics package written in our laboratory for a General NOVA-1200 computer and an Owen-Illinois plasma display panel was used. Scattering factors including real and imaginary anomalous scattering terms for the metal ion were taken from I. A. Ibers and W. C. Hamilton, Eds., "International Tables for X-ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974.

Table II. Atomic and Thermal Parameters for $Ni_2(TFDAA)_2(py)_4$

atom	x	y	z	B, Å^2
Ni	0.0000 (1)	0.0559 (1)	0.1101 (1)	
O1	0.1777 (8)	0.1011 (4)	0.1102 (7)	3.48 (15)
O2	−0.1479 (6)	0.0000 (3)	−0.0739 (7)	2.77 (14)
O3	−0.1774 (8)	−0.1012 (4)	−0.2876 (8)	3.63 (16)
C1	−0.4285 (17)	0.1330 (8)	0.0351 (18)	5.43 (32)
C2	−0.3181 (12)	0.0892 (6)	0.0116 (12)	3.77 (23)
C3	−0.3776 (11)	0.0439 (5)	−0.1044 (11)	3.36 (23)
C4	−0.2971 (11)	0.0005 (6)	−0.1490 (11)	3.45 (22)
C5	−0.3772 (11)	−0.0436 (5)	−0.2744 (11)	3.22 (22)
C6	−0.3192 (12)	−0.0880 (6)	−0.3316 (12)	3.68 (23)
C7	−0.4310 (16)	−0.1327 (7)	−0.4641 (17)	5.22 (32)
F1[a]	−0.5707 (15)	−0.1183 (10)	−0.5149 (19)	
F2	−0.3979 (16)	−0.1423 (10)	−0.5526 (16)	
F3	−0.4246 (17)	−0.1940 (8)	−0.3974 (18)	
F4	−0.5672 (15)	0.1181 (10)	−0.0536 (21)	
F5	−0.4199 (16)	0.1944 (8)	−0.0224 (20)	
F6	−0.3952 (16)	0.1434 (10)	0.1572 (17)	
N1	0.0006 (10)	−0.0167 (4)	0.2631 (9)	3.75 (18)
C8	−0.1266 (14)	−0.0398 (7)	0.2529 (14)	5.69 (32)
C9	−0.1292 (17)	−0.0827 (8)	0.3629 (18)	7.19 (37)
C10	0.0024 (17)	−0.1033 (7)	0.4811 (16)	6.18 (32)
C11	0.1330 (17)	−0.0835 (8)	0.4928 (16)	7.03 (36)
C12	0.1294 (14)	0.0407 (7)	0.3811 (15)	5.65 (31)
N2	−0.0012 (10)	0.1362 (4)	−0.0315 (10)	3.61 (18)
C13	−0.1303 (14)	0.1640 (7)	−0.1392 (15)	5.77 (30)
C14	−0.1332 (17)	0.2172 (8)	−0.2269 (17)	7.32 (38)
C15	−0.0052 (18)	0.2443 (7)	−0.2068 (16)	6.10 (30)
C16	0.1290 (16)	0.2174 (8)	−0.0984 (17)	7.17 (37)
C17	0.1258 (14)	0.1631 (7)	−0.0132 (14)	5.62 (30)
H1	−0.4961	0.0416	−0.1688	3.93
H2	−0.4983	−0.0420	−0.3285	3.78
H3	−0.2343	−0.0235	0.1574	6.98
H4	−0.2306	−0.0940	0.3654	8.32
H5	0.0031	−0.1389	0.5629	6.32
H6	0.2392	−0.0995	0.5875	8.02
H7	0.2353	−0.0255	0.3898	6.41
H8	−0.2386	0.1461	−0.1515	7.37
H9	−0.2422	0.2411	−0.3097	9.12
H10	−0.0020	0.2869	−0.2716	6.47
H11	0.2348	0.2377	−0.0803	7.92
H12	0.2314	0.1388	0.0629	6.66

atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	0.0076 (2)	0.0017 (0)	0.0094 (2)	−0.0001 (1)	0.0035 (1)	0.0000 (1)
F1[a]	0.0062 (20)	0.0065 (7)	0.0380 (40)	0.0006 (10)	−0.0023 (22)	−0.0105 (14)
F2	0.0183 (26)	0.0094 (10)	0.0126 (23)	−0.0075 (13)	0.0043 (21)	−0.0058 (13)
F3	0.0266 (33)	0.0039 (6)	0.0257 (33)	−0.0046 (11)	0.0056 (27)	−0.0031 (12)
F4	0.0075 (21)	0.0065 (8)	0.0472 (44)	−0.0003 (10)	0.0088 (25)	−0.0106 (16)
F5	0.0222 (30)	0.0040 (6)	0.0386 (41)	0.0045 (11)	0.0171 (29)	0.0007 (13)
*F6	0.0178 (25)	0.0096 (10)	0.0156 (25)	0.0080 (13)	0.0113 (21)	0.0026 (13)

[a] All fluorine atoms were half-weighted in the refinement.

Addition of anisotropic thermal parameters for Ni(II) and the three fluorine positions yielded an R of 0.126. The relatively high R and the deviant C–F distances led to the consideration of 1:1 disorder. This type of disorder was considered since hydrogen and fluorine occupy similar volumes. Placement of six fluorines with half-weighted occupancy factors at both terminal carbon atoms improved the R value greatly and improved the C–F bond distances slightly. The use of (1) half-weighted occupancy factors for fluorines at both terminal carbon atoms, (2) anisotropic thermal parameters for Ni(II) and the F's and isotropic thermal parameters for all other nonhydrogen atoms, and (3) H atoms located by using program HFINDR with thermal parameters assigned 10% larger than that for the attached atom and kept invariant gave a final R of 0.065 and R_w of 0.079 after several cycles of full-matrix least-squares refinement. The error of fit was 1.75. The maximum residual electron density was 0.48 e/Å^3. Atomic and thermal parameters are given in Table II.

Magnetic Susceptibility. Magnetic susceptibility measurements were performed by using the Faraday technique. $Hg[Co(SCN)_4]$ was used as a standard for calculation of a magnet constant.[7] Temperature measurements were made with a Leeds-Northrup temperature potentiometer in conjunction with a copper–constantan thermocouple for which the precision is ±0.5 K. Temperatures above ambient were obtained by using a heating tape. Temperatures between ambient and liquid N_2 were obtained with the use of "slush" baths. The system used for magnetic measurements consisted of a Varian Associates power supply modified to allow digital readout of current, Varian Associates Model V-4004 4-in. electromagnet with a 2-in. pole gap, Cahn RG electrobalance, and Hewlett-Packard Model 7123A recorder. The resulting fields are about 8000 G. Pascal's constants were used for diamagnetic corrections.[8]

Results

Structure of $Cu_2(HXFDAA)_2(CH_3OH)_2$. Figure 1 shows the molecular structure of the monomeric, binuclear, 5-coordinate copper(II) triketonate. The binuclear complex is located on a crystallographic inversion center. Each Cu(II) is bonded equatorially to four ketonic oxygens of the triketonate moieties and axially to a methanol oxygen (O3). The carbons (C5) of the methanols, located above and below the

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(7) H. St. Rade, *J. Phys. Chem.*, 77, 424 (1973).

(8) E. A. Boudreaux and L. N. Mulay, "Theory and Applications of Molecular Paramagnetism", Wiley, New York, 1976.

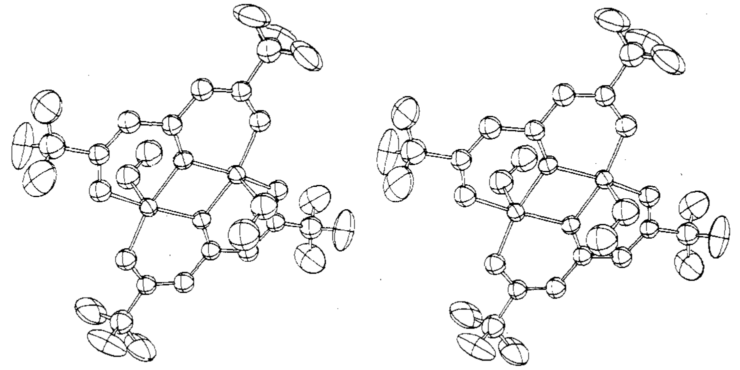

Figure 1. Stereoscopic view of a molecule of [$Cu_2(HXFDAA)_2(CH_3OH)_2$] with thermal ellipsoids.

Table III. Selected Distances (Å) between Nonbonded Atoms $Cu_2(HXFDAA)_2(CH_3OH)_2$

	A. Intermolecular[a]		
O3–O1^{I,II}	3.070 (10)	C5–O1^{III,IV}	3.435 (18)
O3–Cu^{I}	3.751 (11)	C5–O1^{I,II}	3.609 (19)
Cu–Cu^{I}	5.065 (3)	F2–F3^{V}	3.156 (10)
	B. Intramolecular[b]		
Cu–Cu′	3.040 (3)	O1–O3	3.062 (12)
O1–O2	2.799 (6)	O2–O3	3.069 (10)
O1–O1″	2.784 (11)	O1–C5	4.294 (19)
O2–O2″	2.405 (14)	O2–C5	3.523 (18)
F3–C3	2.694 (11)		

[a] Roman numerical superscripts denote the following equivalent positions relative to x, y, z: (I) $-x, -y - 1, -z$; (II) $x, -y - 1, -z$; (III) $x, -y - {}^1/_2, z + {}^1/_2$; (IV) $-x, -y - {}^1/_2, z + {}^1/_2$; (V) $-x + {}^1/_2, y, -z - {}^1/_2$. [b] See Figure 4 caption for relationship of primed to unprimed atoms.

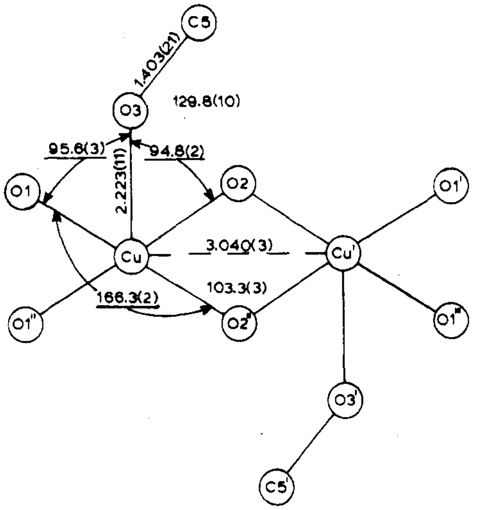

Figure 2. Distances and angles in the coordination environment of [$Cu_2(HXFDAA)_2(CH_3OH)_2$]. Singly, doubly, and triply primed atoms are related to unprimed atoms by the 2, *m*, and 2/*m* symmetry operators, respectively.

Table IV. Deviations (Å) from Mean Planes for $Cu_2(HXFDAA)_2(CH_3OH)_2$[a]

	I	II	III	IV
Cu	−0.18*	−0.21*	−0.22*	
O1	0.00	−0.06		−0.09*
O2	0.00	0.01	0.00	0.00
O1″	0.00	−0.06		−0.09*
O2″	0.00	0.01	0.00	0.00
C1		0.05	0.02	0.02
C2		0.00	−0.02	−0.02
C3		−0.01	−0.00	−0.00
C4		0.01	0.00	0.00
C1″		0.05	0.02	0.02
C2″		0.00	−0.02	−0.02
C3″		−0.01	−0.00	−0.00
C4″		0.01	0.00	0.00

[a] Each plane is defined by ligand atoms (without asterisks) for which displacements are listed. Asterisked displacements are perpendicular distances from the defined mean plane. The estimated error for each displacement is about 0.01 Å.

plane of the Cu–O2–Cu′–O2″ ring, point toward an imaginary axis which intersects perpendicularly the Cu_2O_2 ring at its midpoint. Generation of a packing diagram by the translation of two non-*C*-centered molecules one negative unit in *y* gives an interesting view of the packing. A methanol of one binuclear molecule has its oxygen atom directed midway between the terminal oxygen atoms of a second molecule at a distance of 3.070 Å. The same methanol has its carbon atom directed midway between the terminal oxygen atoms of a third molecule at a distance of 3.435 Å. The interlocking "zipper-like" arrangement suggests the presence of hydrogen-bonded interactions. Observed distances for such interactions are about 2.7 Å for the oxygen to oxygen distance in O–H···O type interactions and about 3.2 Å for the carbon to oxygen distance in C–H···O type interactions.[9] The corresponding distances in this complex are longer but do not preclude weak intermolecular hydrogen-bonded interactions.

A listing of some intermolecular distances appears in Table IIIA. Another close intermolecular approach besides that described above is the F2–F3^{V} distance of 3.156 Å. The intermolecular Cu–Cu^{I} distance of 5.065 Å is long which makes it possible to ignore any consideration of intermolecular magnetic interactions.

A skeletal view that emphasizes the axial coordination parameters is depicted in Figure 2. The Cu to coordinated methanol oxygen (O3) distance is rather short at 2.223 Å. The angles about the Cu atom indicate that it does not lie exactly in the plane of the ketonic oxygens but somewhat above it toward the coordinated methanol oxygen. Table IV contains the results of plane calculations, indicating that one Cu atom lies 0.18–0.22 Å above the best plane while the other Cu lies an equivalent distance below the plane. Planes II–IV show the degree of planarity of the triketonate moiety. Significant deviations from mean plane II occur for O1 and O1″ and for C1 and C1′, the terminal oxygens and carbons, respectively. Plane IV shows clearly that it is the terminal oxygens that deviate significantly from the mean ligand plane.

Figure 2, Figure 3, and Table IIIB contain more data that characterize the coordination environment and the ligand configuration.

Structure of $Ni_2(TFDAA)_2(py)_4$. Figure 4 shows the molecular structure for this binuclear 6-coordinate nickel(II) triketonate. The average binuclear complex is located on a

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(9) W. C. Hamilton and J. C. Ibers, "Hydrogen Bonding in Solids", W. A. Benjamin, New York, 1968.

Table V. Temperature-Dependent Magnetic Properties of $Co_2(TFDAA)_2(py)_4$[a]

T, K	$10^6\chi_m'$,[b] cgsu	μ_{eff},[c] μ_B
340	8 031	4.67
301	8 860	4.62
203	12 763	4.55
150	15 422	4.30
77	22 753	3.74

[a] All magnetic data are presented on a per mole of Co(II) basis. [b] $\chi_m' = \chi_m - \chi_D$; $\chi_D = -180 \times 10^{-6}$ cgsu; $N\alpha$ neglected. [c] $\mu_{eff} = 2.83(\chi_m'T)^{1/2}$ μ_B

crystallographic inversion center in the 1:1 disordered structure. Each Ni(II) is bonded equatorially to four ketonic oxygens of two triketonate moieties; the central oxygen of each serves as a bridge between the Ni(II) ions. The six oxygens and two nickels are essentially coplanar. Each Ni(II) is bonded axially to the nitrogens of two pyridine rings. The important distances and angles without the pyridine are given in Figure 5 along with the atom numbering scheme. The C–F bond distances and angles are not shown due to the disorder problem.

Figure 6 presents a skeletal view of the coordination environment of the metal ions with an emphasis on the axial bonding to the pyridine nitrogens. The nonbonded oxygen–oxygen distances (in Å) are 2.869 (9) (O1···O2), 2.870 (9) (O2···O3), 3.121 (9) (O1···O3′), and 2.600 (11) (O2···O2′). The closest intermolecular contact of 2.615 Å is between fluorines (or hydrogens).[10] Other relatively short intermolecular distances are fluorine (or hydrogen) to pyridine carbons which are about 3.1 Å. The intermolecular Ni–Ni distances are greater than 5.5 Å. None of these are considered chemically significant.

The orientation of the pyridine rings within the molecule and within the unit cell is interesting. The pyridine rings of a given molecule are almost perpendicular to the plane of the oxygens and the Ni(II) ions. Adjacent pyridines are, however, bent away from each other. This is clearly shown by the angles shown in Figure 6 and by a comparison of the distances between the nitrogens and the carbons para to them. The distance between nitrogens of adjacent rings (N1–N2′) is 3.352 Å while the distance between the adjacent para carbons (C10–C15′) is 3.970 Å. Both of these distances exceed the 3.161 Å separation of the Ni(II) ions significantly. Since the sum of the van der Waals π radii for two pyridines is 3.4 Å,[11] π–π repulsions are perhaps responsible for this structural feature.

A packing diagram shows an interesting alignment of pyridine rings between adjacent molecules in which molecules that are related to one another by a translation of one unit in *c* have pyridine rings that are essentially parallel and surprisingly close. The nitrogen to para carbon and para carbon to nitrogen distances between adjacent pyridines on adjacent molecules are both 3.545 Å. Thus, there are four essentially parallel and equally spaced pyridines on two otherwise independent molecules.

Magnetic Properties. Table V contains the magnetic data for the binuclear cobalt(II) fluorinated triketonate, $Co_2(TFDAA)_2(py)_4$, in the temperature range 350–77 K. The magnetic moment decreases from 4.67 μ_B at 340 K to 3.74 μ_B at 77 K which is a greater decrease than could be expected for high-spin Co(II), even in a highly distorted octahedral environment.[12] Therefore, a net antiferromagnetic exchange interaction is indicated.

Table VI. Temperature-Dependent Magnetic Properties of $Ni_2(TFDAA)_2(py)_4$[a]

T, K	$10^6(\chi_m' - N\alpha)_{obsd}$,[b] cgsu	$10^6(\chi_m' - N\alpha)_{calcd}$,[c] cgsu	μ_{eff} (obsd),[d] μ_B
300	3703	3687	2.97
199	5055	5054	2.84
185	5266	5306	2.79
176	5559	5477	2.80
166	5688	5675	2.75
77	10309		2.52

[a] All magnetic data are presented on a per mole of Ni(II) basis. [b] $\chi_m' = \chi_m - \chi_D$; $\chi_D = -180 \times 10^{-6}$ cgsu; $N\alpha = 250 \times 10^{-6}$ cgsu. [c] $\chi_m' = [3K/(T - \Theta_i)]\,[[1 + 5\exp(4J/kT)]/[3 + 5\exp(4J/kT) + \exp(-2J/kT)]] + N\alpha$; $K = N\beta^2g^2/3k$, $\Theta_i = 0$ (i.e., intermolecular interactions are neglected), and $g = 2.39$. [d] $\mu_{eff} = 2.83[\chi_m' - N\alpha)T]^{1/2}$ μ_B.

Table VII. Temperature-Dependent Magnetic Properties of $Cu_2(HXFDAA)_2(OH_2)_2$[a]

T, K	$10^6(\chi_m' - N\alpha)_{obsd}$[b]	$10^6(\chi_m' - N\alpha)_{cor}$[b,c]	$10^6(\chi_m' - N\alpha)_{calcd}$[d]	μ_{eff}(cor)[e]	μ_{eff}(calcd)
295	239	232	232	0.74	0.74
188	84	72	71	0.33	0.33
163	64	51	40	0.26	0.23
154	19	5	31	0.08	0.20
130	19	2	12	0.05	0.11
77	40	11	<1	0.08	~0.01

[a] All data are presented on a per mole of Cu(II) basis. Molar susceptibilities are in cgsu and magnetic moments are in μ_B. [b] $\chi_m' = \chi_m - \chi_D$; $\chi_D = -112 \times 10^{-6}$ cgsu; $N\alpha = 100 \times 10^{-6}$ cgsu. [c] Corrected for 0.5% paramagnetic mononuclear impurity where $\chi_m'(\text{impurity}) = (\mu^2/2.83^2)(1/T) = 0.451T^{-1}$ for $\mu = 1.90$. [d] Calculated by using the Bleaney–Bowers[13] equation with g fixed at 2.10, $N\alpha$ fixed at 100×10^{-6} cgsu, and $2J = -626$ (±15) cm^{-1}. [e] $\mu_{eff} = 2.83[(\lambda_m' - N\alpha)T]^{1/2}$ μ_B.

Table VIII. Temperature-Dependent Magnetic Properties of $Cu_2(TFDAA)_2(CH_3OH)_2$[a]

T, K	$10^6 \times \chi_m'{}_{obsd}$[b]	$10^6 \times \chi_m'{}_{calcd}$[c]	μ_{eff}(obsd)[d]
298	128	128	0.55
244	94	72	0.43
227	60	55	0.33
196	44	31	0.25
179	13	19	0.14
151	−7	7	
77	−29	<<1	

[a] All magnetic data are presented on a per mole of Cu(II) basis. Susceptibilities are in cgsu, and magnetic moments are in μ_B. [b] $\chi_m' = \chi_m - \chi_D$; $\chi_D = -117 \times 10^{-6}$ cgsu. [c] Calculated by using the Bleaney–Bowers[13] equation with g fixed at 2.10, $N\alpha$ fixed at 0.0, and $2J = -776$ (±15) cm^{-1}. [d] $\mu_{eff} = 2.83(\chi_m'T)^{1/2}$ μ_B.

Magnetic data for $Ni_2(TFDAA)_2(py)_4$ are contained in Table VI for the temperature range 300–77 K. The magnetic moment decreases from 2.97 μ_B at 300 K to 2.52 μ_B at 77 K. A least-squares plot of $(\chi_m' - N\alpha)$ vs. T (exclusive of the 77 K value) is linear ($r = 0.999$, $\Theta_p = -80$ K, $C = 1.41$). The Weiss constant, Θ_p, obtained by extrapolation of the least-squares plot, indicates a net antiferromagnetic exchange interaction. The susceptibilities for the temperature range 300–166 K are reproduced very well with $J = -26$ cm^{-1} (−37 K), a g value fixed at 2.39, and $N\alpha$ fixed at 250×10^{-6} cgsu/mol of Ni(II); R, the discrepancy index, is 0.0078, where $R = \sum|(\chi_m' - N\alpha)_{obsd} - (\chi_m' - N\alpha)_{calcd}|^2/\sum|(\chi_m' - N\alpha)_{obsd}|^2]^{1/2}$. For this paramagnetic region, an average g value can be determined from the equation $g = 3kC/N\beta^2S(S+1)^{1/2} = 2.37$. The g value of 2.39 used to calculate the susceptibilities is in good agreement with the experimentally determined value of 2.37.

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(10) This ambiguity is a result of the disorder.

(11) L. Pauling, "The Nature of the Chemical Bond", 3rd ed., Cornell University Press, Ithaca, N.Y., 1960.

(12) B. N. Figgis, M. Gerlock, J. Lewis, F. Mabbs, and G. A. Webb, *J. Chem. Soc. A*, 2086 (1968); F. A. Cotton and J. S. Wood, *Inorg. Chem.*, 3, 245 (1964).

Table IX. Structural Data Associated with the Metal Ion Coordination Sphere in Various Bis(1,3,5-triketonato)dimetal(II) Complexes

compd	distances, Å[a]						M dev from L plane, Å	angles, deg[a]				ref
	M-M	$M-O_b$	$M-O_t$	O_b-O_b	O_t-O_b	O_t-O_t		$M-O_b-M$	O_b-M-O_b	O_t-M-O_b	O_t-M-O_t	
					Copper							
$Cu_2(BAA)_2(py)_2$	3.05	1.95	1.91	2.41	2.77	2.81	0.23	103.4	76.6	92.8	94.3	15
$Cu_2(DTFACP)_2(H_2O)_2$	3.06	1.95	1.91	2.37	2.78	2.89	0.10	103.7	75.1	92.5	98.8	15
$Cu_2(DAA)_2(py)_2$	3.05	1.95	1.91	2.41	2.78	2.80	0.28	103	77	93	94	16
$Cu_2(HXFDAA)_2(CH_3OH)_2$	3.04	1.94	1.90	2.41	2.80	2.78	0.20	103.3	76.7	93.6	94.1	this work
					Nickel							
$Ni_2(DBA)_2(py)_4$	3.17	2.04	2.01	2.59	2.85	3.13	0.01	101.5	78.5	89.6	102.2	17
$Ni_2(TFDAA)_2(py)_4$	3.16	2.05	2.02	2.60	2.87	3.12	0.01	101.1	78.9	89.9	101.4	this work
					Cobalt							
$Co_2(DBA)_2(py)_4$	3.27	2.09	2.01	2.62	2.85	3.22	0.0	102.7	77.3	88.1	106.6	18

[a] Where appropriate, these are average values. [b] Abbreviations not described in the body of the paper are BAA^{2-} = 1-phenyl-1,3,5-hexanetrionato, $DTFACP^{2-}$ = 2,5-bis(trifluoroacetylcyclopentanedionato), DAA^{2-} = 2,4,6-heptanetrionato, and DBA^{2-} = 1,5-diphenyl-1,3,5-pentanetrionato.

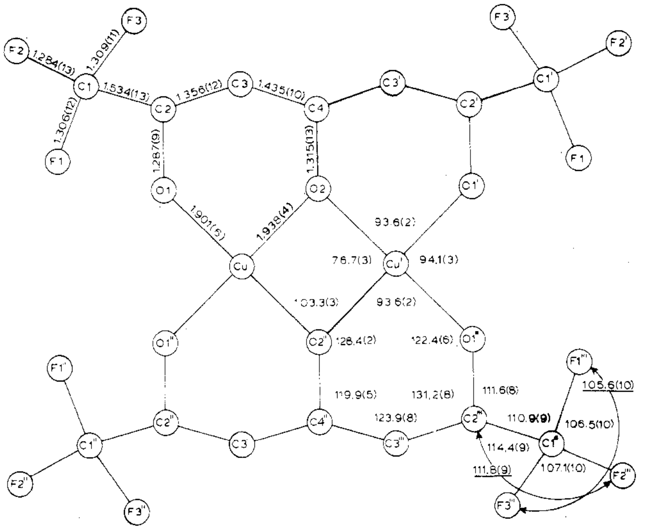

Figure 3. Distances and angles for $[Cu_2(HXFDAA)_2(CH_3OH)_2]$ excluding CH_3OH. See Figure 4 caption for relationships of primed to unprimed atoms.

The magnetic properties of $Ni_2(HXFDAA)_2(H_2O)_4$ do not vary greatly from those of $Ni(TFDAA)_2(py)_4$. At 300 K $\chi_g = 11.83 \times 10^{-6}$ cgsu, giving $\mu_{eff} = 3.05\ \mu_B$, and at 77 K $\chi_g = 34.26 \times 10^{-6}$ cgsu, giving $\mu_{eff} = 2.67\ \mu_B$.

The magnetic data for $Cu_2(HXFDAA)_2(H_2O)_2$ and $Cu_2(TFDAA)_2(CH_3OH)_2$ are contained in Tables VII and VIII, respectively. Duplicate results were obtained for samples of different sizes and on samples obtained from different preparations. Differential error analyses performed on these results gave estimated errors in the susceptibilties of about $\pm 10 \times 10^{-6}$ cgsu near room temperature and $\pm 50 \times 10^{-6}$ cgsu at temperatures below 160 K. For this reason the most reliable values of $2J$ are obtained from the high-temperature values. The estimated error in $2J$ for these compounds is ± 15 cm^{-1} on the basis of the susceptibility errors. With the temperature-independent paramagnetism, $N\alpha$, fixed at 100×10^{-6} cgsu and paramagnetic impurity estimated to be 0.5%, the calculated susceptibility approximates zero at about 77 K. With use of the Bleaney–Bowers equation[13] with the g value fixed at 2.10, the best fit to the observed data is obtained for $2J = -626\ (\pm 15)$ cm^{-1}. For $Cu_2(TFDAA)_2(CH_3OH)_2$, the observed susceptibility decreases to zero in the 180–150 K range without any corrections. Therefore, no temperature-independent paramagnetic or paramagnetic impurity corrections were made in fitting the data to theory. The absence of TIP is unusual but not unprecedented.[14] We are not aware of an adequate explanation at this time. With use of the Bleaney–Bowers equation[13] and by fixing g at 2.10, the best fit is obtained for $2J = -776\ (\pm 15)$ cm^{-1}.

Discussion

Because of the unusual versatility of 1,3,5-triketones as a class of binucleating ligands, it appears possible through systematic ligand and metal ion variations to assess the importance of such factors as donor-atom electron density changes and unpaired electron orbital symmetry on the magnitude of magnetic exchange. An objective of this work is to determine whether the substituent group electronic effects have a significant influence on the antiferromagnetic exchange observed in binuclear triketonate chelates. A prerequisite for this determination is that substituent groups can be changed without changing the intramolecular structural parameters associated with the magnetically coupled metal ions, e.g., M–O–M bridging angles, M–M distance, deviation of M from the ligand plane, etc. Concisely stated, the symmetry of the exchanging electrons must remain constant in order to observe differences due to substituent electronic effects. This type of data is summarized in Table IX for complexes that have been structurally characterized to date.

On the basis of the data in Table IX for the copper complexes it is reasonable to conclude that substituent group changes have no structural effect on the metal ion environment within experimental error. The only parameters that vary significantly are the metal deviation from the ligand plane and the O_t–M–O_t angle in $Cu_2(DTFACP)_2(H_2O)_2$. Both of these are explained by the fact that it is a dimer in the solid state and there is a weak sixth bond to each Cu(II) causing it to more nearly lie in the plane of the ligands. With the exception of knowing whether or not dimers are present and the resulting ambiguity in deviation from the ligand plane, it is safe to say that on the basis of the similarities of known structures these parameters can be very accurately predicted for other bis(1,3,5-triketonato)dicopper(II) molecules.

An even stronger statement about the similarity of the binuclear nickel(II) triketonates is probably justified since there

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(13) B. Bleaney and K. D. Bowers, *Proc. R. Soc. London, Ser. A*, **214**, 451 (1952).

(14) B. N. Figgis and C. M. Harris, *J. Chem. Soc.*, **855** (1959).

(15) R. L. Lintvedt, M. D. Glick, B. K. Tomlonovic, D. P. Gavel, and J. M. Kuszaj, *Inorg. Chem.*, **15**, 1633 (1976).

(16) A. B. Blake and L. R. Fraser, *J. Chem. Soc., Dalton Trans.*, 2554 (1974).

(17) R. L. Lintvedt, L. L. Borer, D. P. Murtha, J. M. Kuszaj, and M. D. Glick, *Inorg. Chem.*, **13**, 18 (1974).

(18) J. M. Kuszaj, B. K. Tomlonovic, D. P. Murtha, R. L. Lintvedt, and M. D. Glick, *Inorg. Chem.*, **12**, 1297 (1973).

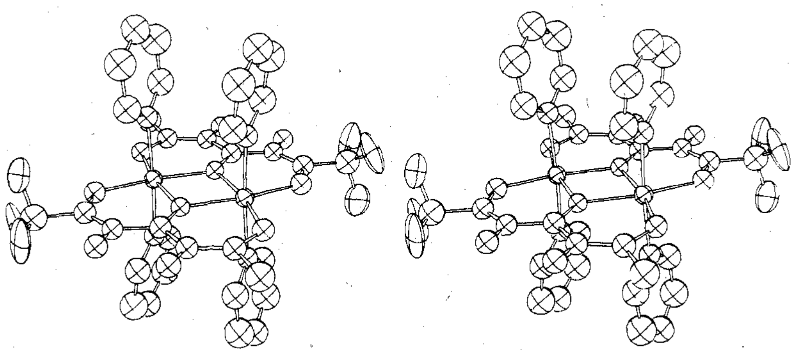


Figure 4. Stereoscopic view of a molecule of $[Ni_2(TFDAA)(py)_4]$ with thermal ellipsoids.

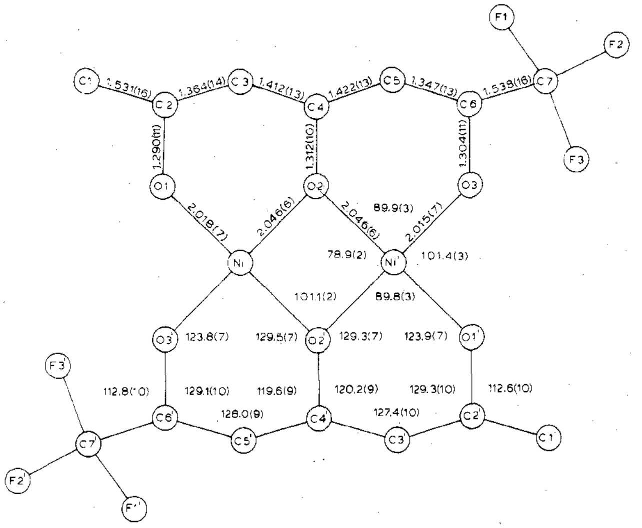


Figure 5. Distances and angles for $[Ni_2(TFDAA)_2(py)_4]$ excluding pyridines. Primed atoms are related to unprimed atoms by an inversion operation.

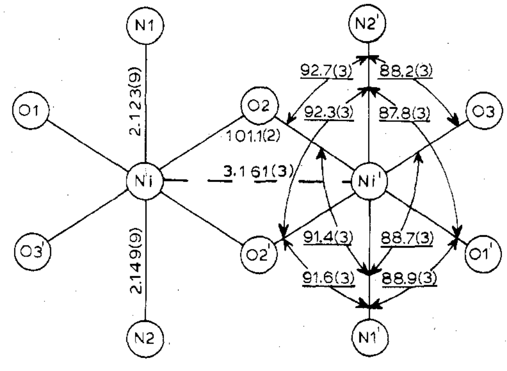
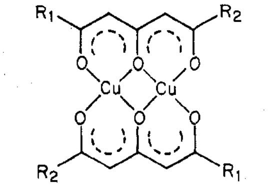


Figure 6. Distances and angles in the coordination environment of $[Ni_2(TFDAA)_2(py)_4]$. The relationship of primed to unprimed atoms is as in Figure 5.

Table X. Comparison of Magnetic Exchange as a Function of Ligand Substituents for Some Copper(II) Triketonates



compd	R_1	R_2	g	$\lvert 2J \rvert$, cm^{-1}	ref
$Cu_2(PAA)_2$[a]	CH_3	$C(CH_3)_3$	2.10	800	19
$Cu_2(DAA)_2(py)_2$	CH_3	CH_3	2.09	690	16
$Cu_2(BAA)_2(py)_2$	CH_3	C_6H_5	2.10	800	15
$Cu_2(TFDAA)_2(CH_3OH)_2$[a]	CH_3	CF_3	2.10	780 (±15)	this work
$Cu_2(DTFACP)_2(H_2O)_2$	CF_3	CF_3	2.12	740	15
$Cu_2(HXFDAA)_2(CH_3OH)_2$	CF_3	CF_3	2.10	630 (±15)	this work

[a] Structure has not been determined.

is not likely to be any ambiguity about the coordination number of Ni(II) with such ligands. However, since the structures of only two compounds have been reported, such a statement may be a bit premature. The values reported in Table IX do indicate that substituent group changes have no structural effect on the coordination sphere of the nickels within experimental error. Although only one binuclear Co(II) compound has been structurally characterized, it is clear that the structure is very similar to the Ni(II) complexes. The differences that do exist are explained by the slightly larger size of the Co(II) vs. the Ni(II) ion.

Recognizing that the structural parameters considered to be important in superexchange interactions are essentially constant in bis(1,3,5-triketonato)dicopper(II) complexes, one can proceed to investigate the magnetic properties. The antiferromagnetic exchange in all of the binuclear copper(II) triketonates is exceedingly strong, in some cases resulting in diamagnetism at room temperature.[19] Therefore, any effect of substituent group changes would be expected to be a small perturbation on a very large exchange interaction.

Table X summarizes the single–triplet energy separation ($-2J$) for several recently studied binuclear copper(II) triketonates. All but two of the compounds have been structurally characterized. The only unanswered structural question is the planarity of the Cu(II) ions in $Cu_2(PAA)_2$ since there are no apparent fifth bonds to the coppers. It is possible, however, that oxygens of a second molecule are bonded in a dimer arrangement. The compounds in Table X are arranged in the expected order of increasing electron-withdrawing ability of the substituent groups. There is a strong hint of a general trend of decreasing strength of magnetic exchange as one goes down the list with obvious exception of $Cu_2(DAA)_2(py)_2$.

The two compounds with the most similar structural parameters are $Cu_2(BAA)_2(py)_2$ and $Cu_2(HXFDAA)_2(CH_3OH)_2$. However, the expected electronic effects of CH_3, C_6H_5 and CF_3, CF_3 substituent groups are quite different, and there is a significant difference in the value of $|2J|$, 800 and 630 cm^{-1}, respectively. In view of the structural similarities, it would seem that the only plausible reason for the magnetic differences is the electron-withdrawing ability of the CF_3 groups which ought to decrease electron density on the bridging oxygens.

A few of the results in Table X, including the somewhat deviant behavior of $Cu_2(DAA)_2(py)_2$, might be explained on

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(19) R. L. Lintvedt, B. K. Tomlonovic, D. E. Fenton, and M. D. Glick, *Adv. Chem. Ser.*, No. **150**, 407 (1976).

Table XI. Comparison of Magnetic Properties for Some Binuclear Nickel(II) Triketonates

compd	temp range, K	Θ_p, K	g_{av}[a]	g[b]	J, cm^{-1}	ref
$[Ni_2(DBA)_2(py)_4]\cdot 4py$	77–298			2.0	−13	17
$[Ni_2(BAA)_2(OH_2)_4]\cdot H_2O$	77–400	−30	2.42	2.40	−10	17
$[Ni_2(DBA)_2(OH_2)_4]$	297–421	−30	2.46	2.46	−8	17
$[Ni_2(TFDAA)_2(py)_4]$	166–300	−80	2.37	2.39	−26	this work

[a] Calculated from $C = N\beta^2 g^2[S(S+1)]/3k$ for the paramagnetic region. $S = 1$. [b] This is the g value used to determine J.

the basis of structural factors. The only structural factor that is a variable in the copper compounds is the deviation of the coppers from the ligand plane, and the deviation is greatest for $Cu_2(DAA)_2(py)_2$. In addition, $Cu_2(DTFACP)_2(H_2O)_2$ and $Cu_2(HXFDAA)_2(CH_3OH)_2$ both contain CF_3 substituent groups and have very similar structural parameters except for a marked difference in coplanarity (0.10 vs. 0.20 Å deviation from planarity). Yet, the strength of the magnetic exchange is appreciably different; the more planar arrangement exhibits the strongest exchange. This trend is reasonable since one would expect a more favorable orbital overlap in the planar case. Thus, one expects that the anomalous behavior of $Cu_2(DAA)_2(py)_2$ is due to the coppers being 0.28 Å out of the ligand plane and that this factor is considerably more important than the electronic effects of the CH_3 groups.

Pertinent magnetic data for four binuclear nickel(II) triketonates have been collected in Table XI. Based on the structural data available (Table IX) it is reasonable to presume that the in-plane environments of the Ni(II) ions are virtually identical in the four compounds. There are some problems with the direct comparison of the properties of $Ni_2(DBA)_2(py)_4$ and the other three compounds since the value of g required in the calculation of J is unusually low. In addition, there is a peculiar temperature dependence for $Ni_2(DBA)_2(H_2O)_4$ that is difficult to explain,[17] since it is not possible to fit the experimental results in the 4.2–421 K range with single values of g and/or J. The values shown in Table XI for $Ni_2(DBA)_2(H_2O)_4$ are for the generally more reliable high-temperature region. These problems and the lack of sufficient data make strong conclusions impossible. However, qualitatively it appears at this point that in binuclear Ni(II) complexes the trifluoromethyl-substituted compounds exhibit exchange at least as strong as the others.

No detailed analysis of the complex d^7–d^7 exchange in the binuclear cobalt(II) triketonates has been reported. Still a direct comparison between the $Co_2(DBA)_2(py)_4$[18] magnetic moments and those of $Co_2(TFDAA)_2(py)_4$ should be instructive since the structures are likely to be extremely similar. For $Co_2(DBA)_2(py)_4$, the μ_{eff} is 4.07 μ_B at 300 K and 3.36 μ_B at 77 K. For $Co_2(TFDAA)_2(py)_4$, the μ_{eff} is 4.62 μ_B at 300 K and 3.74 μ_B at 77 K. The larger magnetic moments for the CF_3-, CH_3-substituted complex may be the result of the electronic effect of these groups compared to the effect of the phenyl groups in $Co_2(DBA)_2(py)_4$. Due to the paucity of data it is not possible to comment further at this time.

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Registry No. $Cu_2(HXFDAA)_2(CH_3OH)_2$, 74096-91-6; $Ni_2(TFDAA)_2(py)_4$, 74113-00-1; $Cu_2(HXFDAA)_2(H_2O)_2$, 74113-01-2; $Cu_2(TFDAA)_2(CH_3OH)_2$, 74096-92-7; $Ni_2(HXFDAA)_2(H_2O)_4$, 62560-16-1; $Co_2(TFDAA)_2(py)_4$, 74096-93-8.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes (10 pages). Ordering information is given on any current masthead page.

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Metal-Ion Recognition by Macrocyclic Ligands. Synthetic, Thermodynamic, Kinetic, and Structural Aspects of the Interaction of Copper(II) with 14- to 17-Membered Cyclic Ligands Containing an O_2N_2-Donor Set

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As part of a general study of the use of mixed-donor macrocycles as metal-ion-specific reagents, the interaction of copper(II) with a series of 14- to 17-membered macrocycles containing an O_2N_2-donor set has been investigated. The investigation parallels previous studies involving nickel complexes of this series of ligands. Copper complexes having both 1:1 and 1:2 metal to ligand ratios form under appropriate conditions. The kinetics of dissociation of the 1:1 complexes in HCl ($I = 0.1$) in 95% methanol have been studied, and the respective thermodynamic stabilities have been determined potentiometrically by the pH titration method. In contrast to the nickel complexes which show a peak in both the kinetic and thermodynamic stabilities at the 16-membered ring complex, the copper complexes show no definite ring-size discrimination effects; this different behavior is discussed in terms of the respective structures of these two sets of complexes. Solution studies indicate that all the macrocycles form five-coordinate complexes of type $[Cu(macrocycle)Cl]^+$, and the solid-state structure of the perchlorate salt of one such complex (containing the 15-membered macrocycle) has been determined by X-ray diffraction. The coordination sphere of the copper consists of the four donor atoms of the macrocycle together with a chloride ion. The copper ion sits above the hole of the macrocycle which is coordinated in a bent conformation.

Introduction

Typically, macrocyclic ligands containing nitrogen donors (including several natural macrocycles) show strong tendencies to complex transition-metal ions.[2] In contrast, those incorporating only oxygen donor atoms (the crown polyethers) prefer non transition metal ions such as the alkali or alkaline earth ions.[3,4]

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