Contribution from the Departments of Chemistry, Delaware State College, Dover, Delaware 19901, University of Delaware, Newark, Delaware 19716, and State University of New York, Plattsburgh, New York 12901

Preparation, Structure, and Magnetic Properties of $Na_{10}Fe_4Cu_2W_{18}O_{70}H_6{\cdot}29H_2O$, Containing the Double Keggin Anion $[Fe_4Cu_2W_{18}O_{70}H_6]^{10-}$

Sadiq H. Wasfi,*[1a] Arnold L. Rheingold,*[1b] Gerald F. Kokoszka,*[1c] and Alan S. Goldstein[1c]

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The sodium salt of the double Keggin anion $[Fe_4Cu_2W_{18}O_{70}H_6]^{10-}$ has been prepared from $Na_2WO_4{\cdot}2H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, and $Cu(CH_3COO)_2{\cdot}H_2O$ in water and isolated in cystalline form as $Na_{10}Fe_4Cu_2W_{18}O_{70}H_6{\cdot}29H_2O$: monoclinic, $P2_1/n$, $a = 13.079$ (3) Å, $b = 17.772$ (4) Å, $c = 21.104$ (7) Å, $\beta = 93.46$ (2)°, $V = 4896$ (2) Å^3, $Z = 2$, D(calcd) = 3.75 g cm^{-3}. This is the first polytungstate ion to contain six paramagnetic centers and the first with four paramagnetic centers bridged by a single oxygen atom. The anion contains two octahedral Cu(II) sites, two octahedral Fe(III) sites, and two tetrahedral Fe(III) sites forming a $Cu_2Fe_4O_{21}$ core. The cationic portion of the structure consists of two $[Na_5O_{22}]^{5+}$ oxygen-bridged structures draping the anion in necklace fashion. The magnetic susceptibility of the salt was determined for the temperature range 4–374 K; it exhibits strong antiferromagnetic interaction at low temperature. $\chi_M T$ shows a pronounced decrease at about 100 K and approaches a constant value at 20 K. The EPR spectrum in the 77–300 K range consists of a broad feature (1000 G) with little structure centered at about $g = 2.2$ and a weaker second line at about $g = 4.4$. The broad line suggests that the six central metal ions participate in the magnetism in this temperature range.

Introduction

Heteropolyoxoanions of groups 5 and 6 form a large class of complexes with an extraordinary array of interesting properties.[2] To a large extent, these discrete inorganic complexes may be viewed as fragments of close-packed metal oxide lattices, and they provide well-defined models for examining many of the properties of such lattices, including magnetic interaction, electron delocalization, and heterogeneous catalysis. The study of spin–spin interactions with multinuclear centers is gaining increasing attention.[3] Several systems of coupled spins have been reported. These systems include pairs,[4,5] triads,[6,7] and some finite chains[8] with similar and dissimilar spins and g values. In 1972, Baker[9] et al. reported six heteropoly complexes in which a pair of paramagnetic centers of different spins and g values are coupled.

The double Keggin structure anion[10,11] we now report, $[Fe_4Cu_2W_{18}O_{70}H_6]^{10-}$, provides a well-characterized system to study the magnetic interaction of four Fe(III) sites (two tetrahedral, two octahedral) and two Cu(II) sites (octahedral) in an oxygen-bridged network. Such systems are analogous to the redox center of the cytochrome oxidase molecule.[12]

Experimental Section

Preparation of $Na_{10}Fe_4Cu_2W_{18}O_{70}H_6{\cdot}29H_2O$. A solution of 17 g (42.1 mmol) of $Fe(NO_3)_3{\cdot}9H_2O$ in 200 mL of distilled water was combined with 30 mL of a saturated sodium acetate solution and added to a solution containing 10 g (50.1 mmol) of $Cu(CH_3COO)_2{\cdot}H_2O$ in 100 mL of distilled water. The resulting solution containing Cu^{2+} and Fe^{3+} was added dropwise to a solution of 112 g (339.6 mmol) of sodium tungstate, $Na_2WO_4{\cdot}2H_2O$, in 500 mL of distilled water. After the completion of the addition, the solution was boiled for 1 h and left to cool to room temperature. After filtration, the filtrate was left to crystallize; crystals of $Na_{10}Fe_4Cu_2W_{18}O_{70}H_6{\cdot}29H_2O$ formed overnight.

Fe was determined by precipitation as Fe_2O_3, Cu by precipitating it as Cu-benzoin oxime, and W by precipitation either as tungstic acid or cinchonin tungstate followed by conversion to tungstic oxide by ignition at 750 °C.[13,14] Sodium and H_2O (Karl Fischer) were determined by Galbraith Laboratories, Knoxville, Tn. Anal. Calcd for $Na_{10}Fe_4Cu_2W_{18}O_{70}H_6{\cdot}29H_2O$: Na, 4.15; Fe, 4.03; Cu, 2.29; W, 59.78; H_2O, 10.09. Found: Na, 4.95; Fe, 3.41; Cu, 2.34; W, 57.05; H_2O, 10.17.

Table I. Crystal and Data Collection Parameters

(a) Crystal Parameters			
formula	$Na_{10}Fe_4Cu_2W_{18}O_{70}H_6{\cdot}29H_2O$		
fw	5536.13		
cryst syst	monoclinic		
space group	$P2_1/n$		
a, Å	13.079 (3)		
b, Å	17.772 (4)		
c, Å	21.104 (7)		
β, deg	93.46 (2)		
V, Å^3	4896 (2)		
Z	2		
color	brown		
cryst dimens, mm	0.21 × 0.21 × 0.43		
temp, °C	23		
μ, cm^{-1}	234.2		
D(calcd), g cm^{-3}	3.75		
D(obsd), g cm^{-3}	3.70		
F(000)	4966		
(b) Data Collection			
diffractometer	Nicolet R3		
radiation	Mo Kα		
wavelength, Å	0.71073		
monochromator	oriented graphite		
scan limits, deg	$4 \leqslant 2\theta \leqslant 45$		
scan technique	ω		
scan speed, deg min^{-1}	4–10, variable		
no. of reflcns collcd	6670		
no. of unique data	6140		
no. of unique data, $F_o \geqslant 3\sigma(F_o)$	4944		
std reflcns	3 std/197 reflcns		
decay	<1%		
T_{max}/T_{max}	1.53		
(c) Refinement			
R_F, %	6.87	GOF	1.373
R_{wF}, %	7.32	g^a	0.0025
N_o/N_v	7.6	Δ/σ	0.054

[a] $w^{-1} = \sigma^2(F_o) + gF_o^2$.

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Table II. Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10³)

	x	*y*	*z*	*U*[a]		*x*	*y*	*z*	*U*[a]
W(1)	9472 (1)	−1711 (1)	5545 (1)	52 (1)	O(20)	11963 (15)	−2791 (12)	6688 (9)	56 (7)
W(2)	10637 (1)	−4470 (1)	7110 (1)	49 (1)	O(21)	11000 (19)	−1882 (13)	7534 (11)	78 (9)
W(3)	7793 (1)	−4446 (1)	6880 (1)	55 (1)	O(22)	10796 (15)	−3769 (12)	4452 (10)	61 (7)
W(4)	10670 (1)	−2601 (1)	7009 (1)	50 (1)	O(23)	9670 (15)	−2568 (10)	4056 (9)	51 (7)
W(5)	10840 (1)	−2784 (1)	4610 (1)	51 (1)	O(24)	11638 (17)	−2988 (10)	5404 (10)	61 (7)
W(6)	7819 (1)	−2564 (1)	6731 (1)	53 (1)	O(25)	11786 (17)	−2486 (12)	4151 (11)	63 (8)
W(7)	8330 (1)	−2794 (1)	4428 (1)	49 (1)	O(26)	7411 (17)	−1819 (12)	7202 (11)	67 (8)
W(8)	6686 (1)	−3658 (1)	5612 (1)	56 (1)	O(27)	6646 (16)	−2727 (13)	6202 (12)	76 (9)
W(9)	12043 (1)	−3652 (1)	6069 (1)	50 (1)	O(28)	8501 (17)	−3764 (12)	4311 (9)	63 (8)
Cu	11897 (3)	−4643 (2)	4616 (2)	53 (1)	O(29)	7286 (14)	−2999 (10)	5017 (9)	51 (7)
Fe(1)	10504 (3)	−5380 (2)	5593 (2)	41 (1)	O(30)	7510 (15)	−2506 (11)	3770 (11)	60 (7)
Fe(2)	10627 (3)	−6270 (2)	4251 (2)	44 (1)	O(31)	5421 (18)	−3551 (14)	5336 (10)	74 (9)
Na(1)	9601 (11)	−608 (8)	3020 (7)	77 (5)	O(32)	7116 (17)	−4501 (12)	5222 (11)	67 (8)
Na(2)	9426 (12)	−3812 (8)	1826 (8)	88 (6)	O(33)	13353 (18)	−3612 (15)	6050 (10)	75 (9)
Na(3)	9690 (10)	878 (7)	1824 (8)	79 (5)	O(34)	11707 (20)	−4458 (11)	5577 (11)	72 (9)
Na(4)	9620 (10)	−2508 (7)	2870 (6)	64 (4)	O(35)	10642 (15)	−5335 (10)	4684 (10)	55 (7)
Na(5)	11395 (11)	2286 (8)	964 (7)	82 (6)	O(36)	13224 (16)	−3952 (12)	4659 (11)	64 (8)
O(1)	10602 (17)	−1743 (12)	4979 (12)	72 (9)	O(37)	10538 (20)	554 (12)	2892 (11)	72 (9)
O(2)	9492 (15)	−2915 (10)	5212 (9)	51 (7)	O(38)	10914 (17)	−1590 (13)	3066 (11)	72 (9)
O(3)	9420 (17)	−731 (12)	5627 (10)	65 (8)	O(39)	9690 (17)	−575 (12)	1917 (11)	70 (8)
O(4)	8363 (17)	−1976 (11)	6061 (10)	59 (7)	O(40)	8265 (18)	−1506 (12)	2883 (12)	72 (9)
O(5)	10366 (16)	−1996 (11)	6240 (10)	61 (8)	O(41)	9791 (23)	−630 (14)	4090 (13)	95 (11)
O(6)	8485 (16)	−1787 (10)	4798 (10)	58 (7)	O(42)	8178 (22)	263 (19)	3197 (18)	125 (15)
O(7)	10786 (18)	−3428 (11)	7535 (10)	65 (8)	O(43)	7911 (28)	−3434 (16)	975 (16)	116 (14)
O(8)	10484 (13)	−3636 (10)	6376 (9)	47 (6)	O(44)	9729 (17)	−2481 (13)	1710 (11)	73 (9)
O(9)	9180 (17)	−4332 (11)	7184 (8)	58 (7)	O(45)	10605 (18)	−3612 (13)	2816 (11)	71 (9)
O(10)	12028 (16)	−4247 (13)	6867 (9)	64 (8)	O(46)	8218 (22)	−3367 (14)	2538 (17)	106 (13)
O(11)	10458 (16)	−5196 (11)	6510 (11)	62 (8)	O(47)	11496 (20)	1326 (13)	1697 (13)	83 (10)
O(12)	10955 (19)	−4980 (12)	7785 (11)	74 (9)	O(48)	7899 (18)	667 (14)	1638 (13)	82 (10)
O(13)	7530 (16)	−3401 (11)	7245 (11)	62 (8)	O(49)	9930 (23)	315 (16)	719 (13)	96 (11)
O(14)	11870 (15)	−6395 (11)	3853 (9)	53 (7)	O(50)	9539 (19)	2086 (18)	1044 (14)	99 (12)
O(15)	11927 (16)	−4799 (12)	3660 (12)	74 (8)	O(51)	10887 (24)	2748 (16)	−68 (13)	98 (12)
O(16)	6511 (17)	−4215 (12)	6401 (11)	67 (8)	O(52)	11124 (26)	3293 (20)	1660 (18)	125 (15)
O(17)	11099 (33)	−4154 (29)	1381 (21)	178 (23)	O(90)	6876 (19)	4459 (13)	670 (18)	113 (14)
O(18)	7288 (18)	−4905 (12)	7503 (11)	72 (9)	O(91)	7195 (34)	5624 (21)	75 (19)	154 (19)
O(19)	9244 (15)	−2598 (11)	7066 (9)	53 (7)	O(92)	8525 (28)	4035 (23)	1065 (15)	128 (16)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

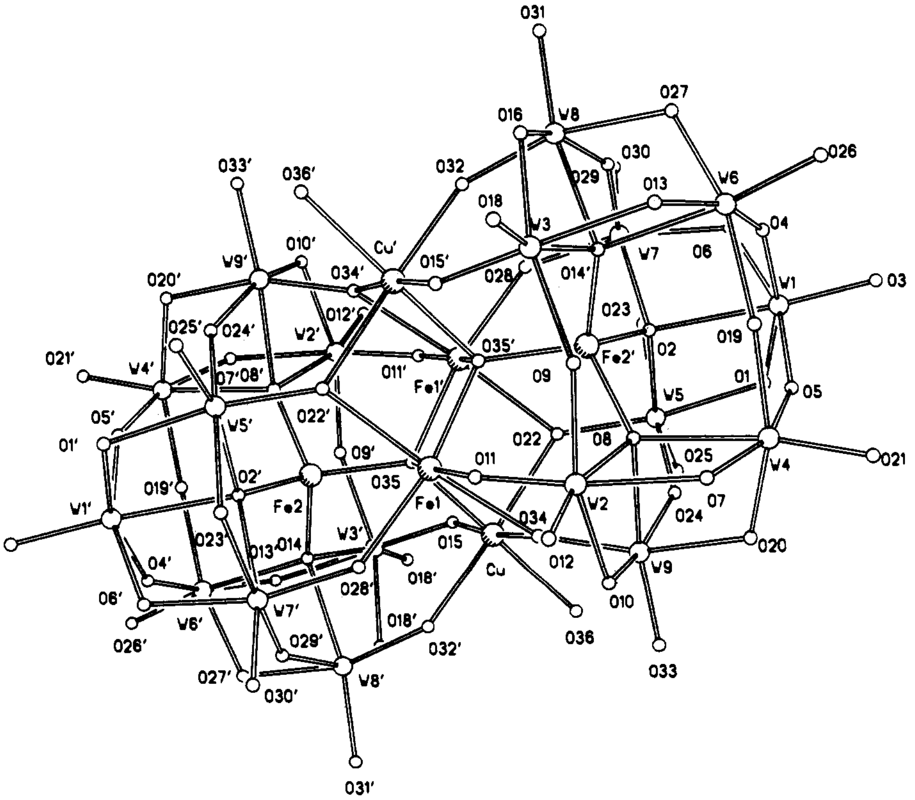

Figure 1. Anion structure and labeling scheme. A center of symmetry relates the labeled and unlabeled atoms.

Table III. Selected Interatomic Distances (Å) and Angles (deg) for $Na_{10}Fe_4Cu_2W_{18}O_{70}H_6 \cdot 29H_2O$

(a) W–O Anion Distances (±0.02 Å)

(i) Axial Exterior

W(1)–O(3)	1.75	W(6)–O(26)	1.76
W(2)–O(12)	1.72	W(7)–O(30)	1.78
W(3)–O(18)	1.71	W(8)–O(31)	1.73
W(4)–O(21)	1.73	W(9)–O(33)	1.72
W(5)–O(25)	1.70		

(ii) Axial Interior[c]

W(1)–O(2)	2.25	W(6)–O(14)	2.27
W(2)–O(8)	2.15	W(7)–O(2)	2.19
W(3)–O(14)	2.22	W(8)–O(14)	2.14
W(4)–O(8)	2.28	W(9)–O(8)	2.18
W(5)–O(2)	2.25		

(iii) Equatorial

W(1)–O(1)	1.96	W(5)–O(23)	1.91
W(1)–O(4)	1.93	W(5)–O(24)	1.95
W(1)–O(5)	1.89	W(6)–O(4)	1.93
W(1)–O(6)	1.98	W(6)–O(13)	1.89
W(2)–O(7)	2.06	W(6)–O(19)	1.95
W(2)–O(9)	1.94	W(6)–O(27)	1.87
W(2)–O(10)	1.96	W(7)–O(6)	1.96
W(2)–O(11)[b]	1.81	W(7)–O(23)	2.01
W(3)–O(9)	1.90	W(7)–O(28)[b]	1.76
W(3)–O(13)	2.05	W(7)–O(29)	1.94
W(3)–O(16)	1.95	W(8)–O(16)	1.96
W(3)–O(15a)[a]	1.81	W(8)–O(27)	2.07
W(4)–O(5)	1.97	W(8)–O(29)	1.92
W(4)–O(7)	1.84	W(8)–O(32)[a]	1.73
W(4)–O(19)	1.88	W(9)–O(10)	1.99
W(4)–O(20)[a]	1.89	W(9)–O(20)	2.02
W(5)–O(1)	2.04	W(9)–O(24)	1.89
W(5)–O(22)[a,b]	1.78	W(9)–O(34)[a]	1.81

(b) Fe–O Anion Distances (±0.02 Å)

Fe(1)–O(11)	1.97	Fe(1)–O(35a)	2.02
Fe(1)–O(34)	2.27	Fe(2)–O(14)	1.89
Fe(1)–O(35)	1.94	Fe(2)–O(35)	1.90
Fe(1)–O(22a)	2.29	Fe(2)–O(2a)	1.85
Fe(1)–O(28a)	2.01	Fe(2)–O(8a)	1.91

(c) Cu–O Anion Distances (±0.02 Å)

Cu–O(15)	2.04	Cu–O(35)	2.06
Cu–O(22)	2.13	Cu–O(36)	2.13
Cu–O(34)	2.08	Cu–O(32a)	2.01

(d) Na–O Cation Distances (±0.03 Å)

Na(1)–O(37)	2.42	Na(3)–O(49)	2.58
Na(1)–O(38)	2.45	Na(3)–O(50)	2.71
Na(1)–O(39)	2.34	Na(3)–O(2a)	2.44
Na(1)–O(40)	2.37	Na(4)–O(23)	2.50
Na(1)–O(41)	2.26	Na(4)–O(38)	2.37
Na(1)–O(42)	2.47	Na(4)–O(40)	2.51
Na(2)–O(17)	2.51	Na(4)–O(44)	2.46
Na(2)–O(43)	2.68	Na(4)–O(45)	2.35
Na(2)–O(44)	2.41	Na(4)–O(46)	2.46
Na(2)–O(45)	2.55	Na(5)–O(47)	2.30
Na(2)–O(46)	2.38	Na(5)–O(50)	2.47
Na(2)–O(12a)	2.36	Na(5)–O(51)	2.39
Na(3)–O(37)	2.52	Na(5)–O(52)	2.36
Na(3)–O(39)	2.59	Na(5)–O(25a)	2.44
Na(3)–O(47)	2.52	Na(5)–O(36a)	2.63
Na(3)–O(48)	2.38		

(e) Nonbonded Distances

Fe(1)···Cu	3.120 (5)	Fe(2)···Cu	3.399 (6)
Fe(1)···Fe(2)	3.257 (6)		

(f) O–W–O Anion Angles with Greater than 10° Deviations from Octahedral Angles (±1°)

O(1)–W(1)–O(4)	164	O(8)–W(2)–O(12)	166
O(2)–W(1)–O(3)	168	O(9)–W(2)–O(10)	158
O(2)–W(1)–O(6)	73	O(9)–W(2)–O(12)	101
O(3)–W(1)–O(5)	103	O(11)–W(2)–O(12)	103
O(5)–W(1)–O(6)	161	O(9)–W(3)–O(16)	158
O(7)–W(2)–O(8)	72	O(9)–W(3)–O(18)	101
O(7)–W(2)–O(11)	161	O(13)–W(3)–O(14a)	72
O(8)–W(2)–O(10)	74	O(13)–W(3)–O(15a)	162
O(16)–W(3)–O(14a)	72	O(2)–W(7)–O(6)	75
O(18)–W(3)–O(14a)	164	O(2)–W(7)–O(23)	74
O(18)–W(3)–O(15a)	103	O(2)–W(7)–O(30)	168
O(5)–W(4)–O(7)	160	O(6)–W(7)–O(28)	160
O(7)–W(4)–O(8)	73	O(23)–W(7)–O(29)	163
O(7)–W(4)–O(21)	101	O(28)–W(7)–O(30)	104
O(8)–W(4)–O(20)	73	O(16)–W(8)–O(29)	159
O(8)–W(4)–O(21)	171	O(16)–W(8)–O(31)	101
O(19)–W(4)–O(20)	160	O(16)–W(8)–O(14a)	74
O(1)–W(5)–O(2)	75	O(27)–W(8)–O(32)	162
O(1)–W(5)–O(22)	164	O(27)–W(8)–O(14a)	73
O(2)–W(5)–O(22)	75	O(31)–W(8)–O(32)	105
O(2)–W(5)–O(25)	168	O(31)–W(8)–O(14a)	165
O(22)–W(5)–O(25)	102	O(8)–W(9)–O(10)	72
O(23)–W(5)–O(24)	158	O(8)–W(9)–O(20)	73
O(4)–W(6)–O(3)	160	O(8)–W(9)–O(33)	164
O(13)–W(6)–O(26)	101	O(10)–W(9)–O(24)	161
O(13)–W(6)–O(14a)	74	O(20)–W(9)–O(34)	162
O(19)–W(6)–O(27)	161	O(24)–W(9)–O(33)	101
O(2)–W(6)–O(27)	101	O(33)–W(9)–O(34)	103
O(27)–W(6)–O(14a)	74		

(g) O–Cu–O and O–Fe–O Anion Angles (±1°) with Greater Than 10° Deviations from Octahedral Symmetry (Cu and Fe(1)) and Tetrahedral Symmetry (Fe(2))

O(11)–Fe(1)–O(35)	168	O(28a)–Fe(1)–O(35a)	166
O(35)–Fe(1)–O(35a)	78		

(h) W–O–W Anion Bond Angles (±1°)

W(1)–O(1)–W(5)	114	W(2)–O(10)–W(9)	113
W(1)–O(2)–W(5)	96	W(3)–O(14a)–W(6)	97
W(1)–O(2)–W(7)	97	W(3)–O(14a)–W(8)	98
W(5)–O(2)–W(7)	122	W(6)–O(14a)–W(8)	98
W(1)–O(4)–W(6)	151	W(3)–O(16)–W(8)	114
W(1)–O(5)–W(4)	151	W(4)–O(19)–W(6)	155
W(1)–O(6)–W(7)	115	W(4)–O(20)–W(9)	117
W(2)–O(7)–W(4)	117	W(5)–O(23)–W(7)	114
W(2)–O(8)–W(4)	98	W(5)–O(24)–W(9)	150
W(2)–O(8)–W(9)	99	W(6)–O(27)–W(8)	116
W(4)–O(8)–W(9)	97	W(7)–O(29)–W(8)	150
W(2)–O(9)–W(3)	152		

(i) W–O–Cu Anion Angles (±1°)

Cu–O(15)–W(3a)	138	Cu–O(2a)–W(8a)	140
Cu–O(22)–W(5)	132		

(j) W–O–Fe Anion Angles (±1°)

W(2)–O(11)–Fe(1)	143	W(7a)–O(2a)–Fe(2)	118
W(5a)–O(22a)–Fe(1)	133	W(2a)–O(8a)–Fe(2)	118
W(7a)–O(28a)–Fe(1)	145	W(4a)–O(8a)–Fe(2)	122
W(1a)–O(2a)–Fe(2)	123	W(9a)–O(8a)–Fe(2)	119
W(5a)–O(2a)–Fe(2)	122		

(k) Cu–O–Fe Anion Angles (±1°)

Cu–O(22)–Fe(1a)	91	Cu–O(35)–Fe(1a)	101
Cu–O(34)–Fe(1)	91	Cu–O(35)–Fe(2)	118
Cu–O(35)–Fe(1)	102		

(l) Fe–O–Fe Anion Angles (±1°)

Fe(1)–O(35)–Fe(1a)	102	Fe(2)–O(35)–Fe(1a)	116

(m) Anion–O–Cation Angles (±1°)

W(2)–O(12)–Na(2a)	136	W(7)–O(23)–Na(4)	115
W(4)–O(21)–Na(3a)	144	W(5)–O(25)–Na(5a)	139
W(5)–O(23)–Na(4)	126	Cu–O(36)–Na(5a)	130

(n) Na–O–Na Anion Angles (±1°)

Na(1)–O(37)–Na(3)	96	Na(2)–O(45)–Na(4)	81
Na(1)–O(38)–Na(4)	90	Na(2)–O(46)–Na(4)	83
Na(1)–O(39)–Na(3)	96	Na(3)–O(47)–Na(5)	107
Na(1)–O(40)–Na(4)	88	Na(3)–O(50)–Na(5)	97
Na(2)–O(44)–Na(4)	82		

(o) O–Na–O Anion Angles (±1°) with Greater Than 10° Deviations from Octahedral Symmetry

O(37)–Na(1)–O(38)	105	O(43)–Na(2)–O(45)	155
O(37)–Na(1)–O(40)	159	O(43)–Na(2)–O(12a)	107
O(38)–Na(1)–O(42)	167	O(44)–Na(2)–O(12a)	165
O(39)–Na(1)–O(42)	103	O(37)–Na(3)–O(39)	73
O(17)–Na(2)–O(43)	116	O(37)–Na(3)–O(47)	79
O(17)–Na(2)–O(46)	161	O(37)–Na(3)–O(48)	119
O(43)–Na(2)–O(44)	79	O(37)–Na(3)–O(49)	131

Table III (Continued)

O(37)–Na(3)–O(50)	138	O(47)–Na(3)–O(48)	162
O(39)–Na(3)–O(47)	109	O(47)–Na(3)–O(50)	74
O(39)–Na(3)–O(49)	71	O(47)–Na(3)–O(21a)	102
O(39)–Na(3)–O(50)	147	O(48)–Na(3)–O(21a)	79
O(39)–Na(3)–O(21a)	133	O(49)–Na(3)–O(50)	76
O(49)–Na(3)–O(21a)	149	O(44)–Na(4)–O(46)	79
O(50)–Na(3)–O(21a)	75	O(47)–Na(5)–O(51)	151
O(23)–Na(4)–O(46)	104	O(47)–Na(5)–O(36a)	73
O(38)–Na(4)–O(45)	101	O(51)–Na(5)–O(52)	105
O(40)–Na(4)–O(45)	168		

[a] Forms link to Cu. [b] Forms link to Fe(1). [c] All form links to Fe(2).

Table IV. Magnetic Susceptibilities of $Na_{10}Fe_4Cu_2W_{18}O_{70}H_6{\cdot}29H_2O$[a]

T, K	$10^6\chi_g$	$10^6\chi_M{}^C$	$T\chi_M{}^C$	$(\chi_M{}^C)^{-1}$
373	3.18	18776.2	7.00	53.25
350	3.23	19055.7	6.67	52.47
323	3.27	19279.3	6.23	51.86
300	3.35	19726.5	5.92	50.69
279	3.39	19950.1	5.56	50.13
250	3.50	20565	5.14	48.62
210	3.66	21459	4.51	46.60
180	3.90	22801	4.10	43.86
140	4.35	25317	3.54	39.49
110	5.04	29174	3.20	34.28
90	5.61	32360	2.91	30.90
75	6.28	36105	2.70	27.69
60.4	7.44	42590	2.57	23.48
50.9	8.51	48571	2.47	20.59
40.4	10.23	58186	2.35	17.19
30.3	13.19	74732	2.26	13.38
20.4	19.03	107377	2.19	9.31
10.65	35.92	201793	2.14	4.95
7.20	53.04	297494	2.14	3.36
5.10	76.62	429306	2.19	2.33
4.59	84.53	473523	2.17	2.11

[a] Units: χ_g, cm^3 g^{-1}; χ_M, cm^3 mol^{-1}.

Visible spectra were recorded on a Perkin-Elmer Lambda 3 spectrophotometer.

X-ray Structural Determination. Table I contains crystal data and the parameters of data collection and refinement. Crystals suitable for an X-ray diffraction structural determination were obtained directly from the reaction mixture. The unit-cell parameters were obtained from the least-squares fit of the angular settings of 25 well-centered reflections ($20° \leqslant 2\theta \leqslant 28°$). The space group was uniquely assigned from systematic absences. A profile fitting procedure was used to improve the accuracy of the intensities of weak reflections. An empirical absorption correction was applied to the intensity data (256 data, six-parameter pseudoellipsoid).

The structure was solved by direct methods (SOLV), and completed by a series of difference Fourier syntheses. The identities of the three independent, first-row metal atoms was confirmed by site occupancy (K) refinement. If an Fe site was misassigned to Cu, K was 0.90 (1); if a Cu site was misassigned to Fe, K was 1.12 (1). All current assignments yielded K = 1.00 (1). The final model included anisotropic contributions for all non-hydrogen atoms. No attempt was made to include hydrogen atom contributions. The final difference map was devoid of chemically relevant peaks although a background "noise" level of 1.2–1.6 e Å^{-3} was present in the vicinity of the W atoms. All computations and sources of scattering factors are contained in the SHELXTL (4.1) program library (Nicolet Corp., Madison, WI).

Atomic coordinates are provided in Table II, and bond distances and angles are provided in Table III. Additional crystallographic data are available (see paragraph regarding supplemental material at the end of this paper).

Magnetic Measurements. Susceptibility measurements were determined by the SQUID method (superconducting quantum interference detector) between the He(l) temperature ~4 K and 374 K. The diamagnetic corrections were those given by Selwood based on work by Klemm.[15,16] The results are summarized in Table IV. EPR spectra were obtained at the X-band with a reflection cavity spectrometer in the temperature range 77–300 K. The broad features were centered below DPPH, which was used as an internal standard.

Results and Discussion

Determination of the Composition of $Na_{10}[Fe_4Cu_2W_{18}O_{70}H_6]{\cdot}29H_2O$. Analytical and crystallographic characterization showed that the atomic ratio for the metals, Cu:Fe:W, is 1:2:9. The Fe and Cu sites were crystallographically unambiguous; the visible and EPR spectra indicated tetragonal sites for Cu(II) and the strong antiferromagnetic coupling indicated the placement of the two Fe(III) sites. The pattern and degree of oxygenation about each W(VI) site is precisely known by crystallography. The anion charge is completed by six H^+ ions, the locations of which are unknown. The 10 Na^+ ions were crystallographically confirmed. The assignment of 29 "waters of hydration" is confirmed by Karl Fischer titration data and by crystallographic location of otherwise unassigned oxygen atoms. Overall, the composition $Na_{10}[Fe_4Cu_2W_{18}O_{70}H_6]{\cdot}29H_2O$ is supported by the close agreement between the calculated (3.75 g cm^{-3}) and experimental (3.70 g cm^{-3}) densities.

Structure of $Na_{10}Fe_4Cu_2W_{18}O_{70}H_6{\cdot}29H_2O$. The anionic and cationic portions of the structures are interlinked through five bridging oxygen atoms (O(12), O(21), O(23), O(25), and O(36)) to form an infinitely extended three-dimensional array. Figure 1 shows the $[Fe_4Cu_2W_{18}O_{70}H_6]^{10-}$ anion in a ball-and-stick representation with its labeling scheme. A stereoview is given in Figure 2. The anion structure is essentially that of a doubled and interpenetrating Keggin ion structure,[11] the halves being related by a crystallographic inversion center. Linking of the halves occurs through Cu–O bridges at the octahedrally coordinated Fe(1) and Fe(1′) sites as shown in Figure 3. The Fe(1) octahedron is distorted by elongation of the O(34)–Fe(1)–O(22′) axis whose Fe–O bonds average 2.28 (2) Å compared to an equitorial plane average of 1.98 (2) Å. All six Fe(1)–O bonds form links to other oxymetalate polyhedra. The structure is closely related to that reported by Weakley for the anion $(P_2Co_4W_{18}O_{70}H_4)^{10-}$.[2c,10]

The six oxygen atoms at Cu(1) form a fairly regular octahedral coordination site with an average Cu–O distance of 2.08 (2) Å; one of the six oxygen atoms, O(36), is a water molecule (cf., the average Cu–O distance in $Cu_4Mo_6O_{20}$ of 2.05 Å and in $NaCu(OH)(MoO_4)$ of 2.13 Å[17]). The Fe–O distances and angles at Fe(2) show a relatively undistorted tetrahedral environment but with Fe–O distances (average 1.89 (2) Å) considerably shorter than those at Fe(1); all four bonds to Fe(2) are linking.

The bond parameters of the nine independent W(VI) octahedra surrounding the $Cu_2Fe_4O_{21}$ core are within normal ranges[2d,2e] for individual bond types as grouped in Table III.

The cationic portion of the salt (Figure 4) consists of five Na^+ ions linked by oxygen atoms of water molecules to form a nearly semicircular cradle around each end of the anion with oxygen links to the cradled anion and also to adjacent anions. The structure is completed by six lattice water molecules for each double anion, which form many hydrogen-bonded contacts, the shortest being either to each other, e.g., O(90)–O(92) = 2.39 (4) Å, or to the cationic structure, e.g., O(90)–O(41) = 2.27 (5) Å.

The magnetic susceptibility measurements (Figure 5) show a strong antiferromagnetic coupling of the spins. However, at the highest temperature (374 K) some spin–spin coupling remains, while in the lower range the product χT approaches a constant value (see Table IV). The magnetic moment in the temperature region below about 20 K may be estimated from the equation of $\mu = 2.84(\chi_M T)^{1/2}$ and produces a result of about 3.2. The value is approximately that for two unpaired electrons per formula unit. The lowest state would seem to be paramagnetic and the excited spin states depopulated by 20 K. Spin–spin coupling constants of 10–100 K would not seem unreasonable in view of the simple bridging geometry found in the central metal core (see Figure 3). The paramagnetism that remains below 20 K is not understood

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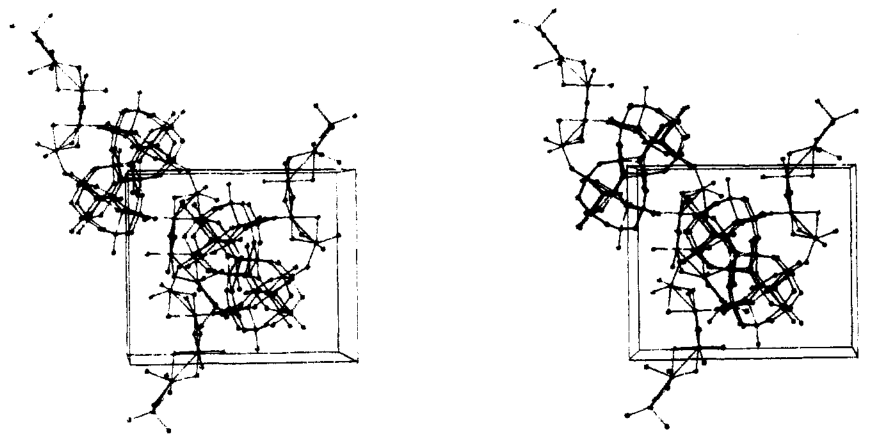

Figure 2. Stereoview of the unit-cell packing.

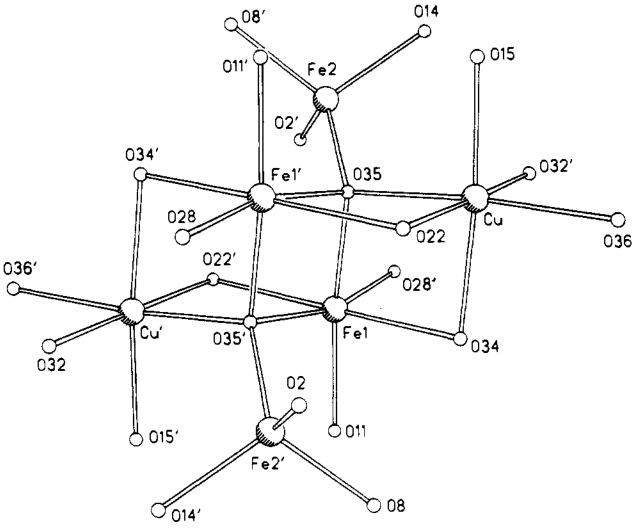

Figure 3. Central $Cu_2Fe_4O_{22}$ core of the anion.

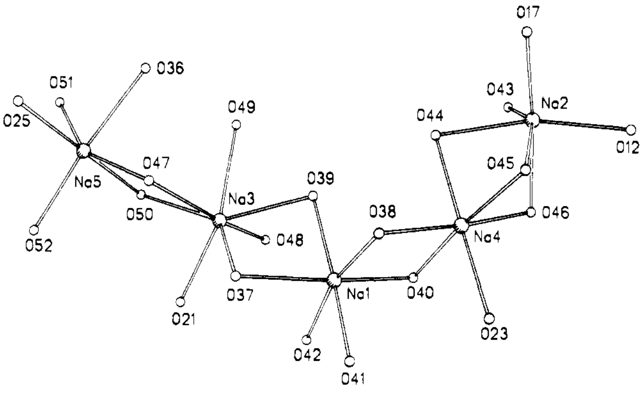

Figure 4. $[Na_5(H_2O)_{22}]^{5+}$ cation association.

but might be associated with spins predominantly on the two Cu(II) ions. Such a possibility would be consistent with the observed g values in the EPR spectrum and the low temperature χT product. Moreover, it would imply fairly strong antiferromagnetic Fe(III)-Fe(III) couplings in the $Cu_2Fe_4O_{22}$ core as found in the crystallography.

It is expected that the magnetic interaction will be quite complex and unique because all six paramagnetic centers are within reasonable distances for exchange interaction (see Table IV). The four bridged Fe^{+3} ions lie closer to each other than the bridged paramagnetic centers reported by Baker, et. al., of 3.3 Å.[9] The longest distance between two Fe^{+3} ions in the present complex anion is Fe(1')-Fe(2) = 3.259 Å.

The EPR spectra are consistent with the magnetic susceptibility data. A broad asymmetric peak centered about $g = 2.2$ with a width of nearly 1000 G was the major feature in the 77-300 K temperature range. A half-field line was also observed. From the measured crystallographic data a linewidth estimate can be made. The Van Vleck isotropic approximation is

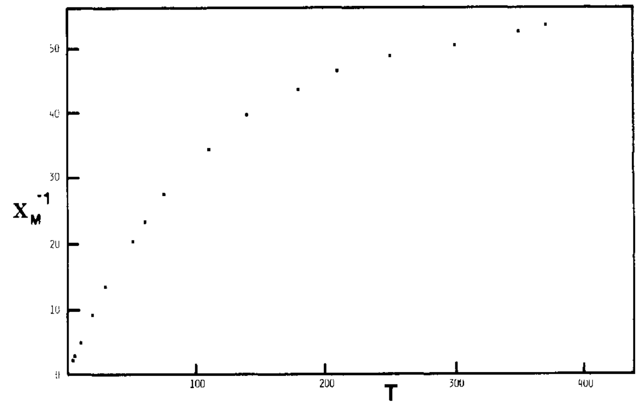

Figure 5. Plot of the inverse of the molar magnetic susceptibility vs. absolute temperature.

$$H_d = 4.72 \times 10^4[S(S + 1)]^{1/2}(d/m)$$

where d is the density, m is the molecular weight and S is taken as 5 for convenience in the calculation. This produces a line width of about 150 G, which is considerably smaller than the measured value. The observed line width may be associated with unresolved fine structure and possibly the superposition of various spin states. Dipole–dipole interactions within the cluster remains a possibility down to the lowest measured temperature.

The visible spectrum of a 5.69×10^{-4} M aqueous solution of the sodium salt of the anion is characterized by a wide absorption maximum around 830 μm (≡12 948 cm^{-1}) with an extinction coefficient of 80. A review of the spectra of copper(II) in different geometries indicates a tetragonal geometry for Cu(II). The hexaaquocopper(II) ion has a single, broad maximum at 12 000 cm^{-1} with an extinction coefficient of about 12, but it is clear that the envelope contains more than one transition.[18]

Regular tetragonal derivatives of Cu(II) are very common. In general, tetragonal copper(II) derivatives, if approximately regular, are expected to give a broad band (at room temperature) with a weak extinction coefficient.[19] However, spin–spin interactions can add appreciable intensity due to the magnetic dipolar transition probability supplementing the unusual electric dipolar mechanism.

In Cu(II) in 11:1 and 17:2 heteropoly complexes, Tourne[21] found the absorption band with a maximum at 10 690 cm^{-1} for $(GeCuW_{11}O_{40})^{8-}$, 11 240 cm^{-1} for $(PCuW_{11}O_{40})^{7-}$, and 11 230 cm^{-1} for $(P_2CuW_{17}O_{62})^{10-}$. The molar absorptivities for each of the complexes increased by a factor of 4 over that of $[Cu(H_2O)_6]^{2+}$. The increase in intensity is attributed to the deformation of the

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CuO_6 octahedron[20] as well as the enhancement due to increased magnetic dipole transition probability. The latter observation supports our contention that the metal ions are exchange coupled.

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Registry No. $Na_{10}[Fe_4Cu_2W_{18}O_{70}H_6]\cdot 29H_2O$, 109466-62-8; $Fe(NO_3)_3$, 10421-48-4; $Cu(CH_3COO)_2$, 142-71-2; Na_2WO_4, 13472-45-2.

Supplementary Material Available: Tables 2S–4S, listing bond distances and angles and anisotropic thermal parameters (7 pages); Table 1S, listing observed and calculated structure factors (29 pages). Ordering information is given on any current masthead page.

Contribution from the Laboratoire de Spectrochimie des Elêments de Transition, UA No. 420,
Universitê de Paris-Sud, 91405 Orsay, France, and Departament de Cristal.lografia i Mineralogia,
Universitat de Barcelona, 08007 Barcelona, Spain

Magnetic Interaction and Spin Transition in Iron(II) Dinuclear Compounds. Crystal Structure of (μ-2,2'-Bipyrimidine)bis[(2,2'-bipyrimidine)bis(thiocyanato)iron(II)]

Antonio Real,[1a,c] Jacqueline Zarembowitch,[1a] Olivier Kahn,*[1a] and Xavier Solans[1b]

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Three iron(II) dinuclear compounds of general formula $[FeL(NCS)_2]_2$bpym have been synthesized. Bpym is the bridging ligand 2,2'-bipyrimidine. L is bpym (**1**), bpy (2,2'-bipyridine; **2**), or bzp (bromazepan; **3**). The crystal structure of **1** has been solved. **1** crystallizes in the triclinic system, space group $P\bar{1}$, with a = 11.622 (3) Å, b = 9.138 (2) Å, c = 9.241 (2) Å, α = 118.74 (2)°, β = 74.39 (2)°, γ = 99.85 (2)°, and Z = 1. The structure consists of centrosymmetric dinuclear units with two NCS groups in a cis position, a terminal bpym, and two nitrogen donors of the bridging bpym around each iron. The magnetic properties of **1–3** have been investigated down to 4.2 K. In **1** and **2**, the iron(II) ions are high spin in the whole temperature range and interact in an antiferromagnetic fashion with $J = -4.1$ cm^{-1} in **1** and -4.9 cm^{-1} in **2** ($\mathcal{H} = -J\hat{S}_A\cdot\hat{S}_B$). In **3**, a gradual and incomplete spin transition occurs around 235 K. Below the transition, the compound consists of roughly 52% of the diamagnetic SS species, 40% of the antiferromagnetically coupled QQ species, and only 8% of the electronically dissymmetric SQ species (S = local singlet, Q = local quintet).

Introduction

The first report by Cambi on a metal complex exhibiting a temperature-induced low-spin ↔ high-spin transition appeared more than half a century ago.[2] Nevertheless, this field remains very active,[3,4] and great strides have been made in the last few years. The mechanism of the phenomenon is today reasonably well understood, at least qualitatively.[4,5] In particular, it has been conclusively pointed out that the abruptness of the transition is related to the cooperativity of the phenomenon within the crystal lattice.[6] Slichter and Drickamer have proposed a thermodynamic approach to an understanding of the spin transition in which this cooperativity is accounted for by an interaction Gibbs free energy.[6,7] This approach, similar to that utilized for the regular solutions, may fairly well reproduce the more or less abrupt nature of the transition, as well as the eventual hysteresis effect.[4,8,9] Another recent break-through in this area is the discovery of the LIESST (light-induced excited-spin-state trapping) phenomenon; Decurtins et al. have shown that it was possible to convert optically the low-spin phase into the high-spin phase in the very low temperature range where the low-spin phase is thermodynamically stable.[10,11]

The renewed interest brought to spin transitions is due, among other reasons, to the fact that this phenomenon is one of the most spectacular examples of bistability in inorganic chemistry. The spin transition may be very abrupt—the total conversion may occur within less than 1 K—and may exhibit an hysteresis. It follows that a spin transition system could potentially be utilized as an element of a molecular device able to store information. In other words, if we consider the low-spin/high-spin transformation

$$\underset{1-x}{\mathrm{LS}} \leftrightarrow \underset{x}{\mathrm{HS}} \tag{1}$$

which is assumed to be abrupt, where x is the molar fraction of high-spin form at a given temperature, the x vs. T plot (or the $\chi_M T$ vs. T plot, χ_M being the molar magnetic susceptibility) schematized in Figure 1 may be seen as a signal, in the general sense of the term.

A difficulty, however, arises along this line. For a mononuclear spin transition compound, the low-spin phase is always the stable phase below the critical temperature T_c. This situation may be understood on the basis of very simple thermodynamical considerations. At the temperature T_c, we have

$$\Delta G = \Delta H - T_c\Delta S = 0 \tag{2}$$

where the variations of Gibbs free energy $\Delta G = G_{HS} - G_{LS}$, of enthalpy $\Delta H = H_{HS} - H_{LS}$ and of entropy $\Delta S = S_{HS} - S_{LS}$ refer to the transformation (1). ΔS is positive. Indeed, the electronic degeneracy and hence the electronic entropy are higher in the HS phase than in the LS phase. Moreover, in the HS phase, the metal–ligand bond lengths are, on average, longer, so that the internal vibrational entropy, which is the main component of the total vibrational entropy,[3] is also higher in this phase than in the LS phase. Since ΔS is positive, from (2) ΔH is positive too. Below T_c, ΔG is positive and the LS phase is stable; above T_c, the reverse situation holds. To sum up this point, we can say that with a mononuclear compound exhibiting a spin transition, the most likely type of signal is that schematized in Figure 1; above T_c, we have a strong response and below T_c, a weak response. An exception would be possible with a compound presenting either two spin

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