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Synthesis and Magnetic Properties of Some Chiral Tetranuclear Imino-Alkoxy Complexes of Copper(II)

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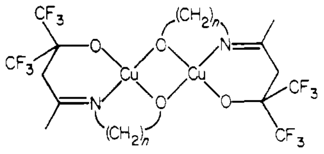
Received July 28, 1980

Template condensations of 5,5,5-trifluoro-4-(trifluoromethyl)-4-hydroxy-2-pentanone, $CH_3COCH_2C(CF_3)_2OH$, with a variety of β-substituted aminoethanols NH_2CHRCH_2OH [R = H, CH_3, C_2H_5, C_6H_5, $(CH_3)_2CH$] in the presence of Cu^{2+} lead to stable, neutral, imino-alkoxy complexes with a 1:1 metal:ligand ratio; these appear to be associated into tetranuclear units, and magnetic susceptibilities are best fitted to an equation describing the overall structure as a Cu_4O_4 core. The effect of chirality and the variation of R on the degree of superexchange between Cu^{2+} ions is discussed.

Introduction

A large number of dinuclear and tetranuclear copper complexes[2] are known for which magnetic susceptibility measurements show some degree of spin pairing between copper atoms via bridging oxygen atoms,[3-7] and a number of studies have been made of the influence of structural parameters on these interactions.[8-12]

We have previously shown[12] that 5,5,5-trifluoro-4-hydroxy-4-(trifluoromethyl)-2-pentanone (hexafluorodiacetone alcohol, HFDA) will readily condense with primary amino alcohols in the presence of Cu^{2+} to form complexes of the type

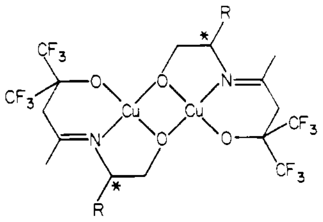


1 (n = 2-4)

Variable-temperature magnetic susceptibility studies on this group of compounds show the influence of chelate ring size on molecular structure[13] and magnetic properties.[12] Whereas with $n = 2$ the compound obeys the Curie-Weiss law down to 77 K, when $n = 3$ or 4, the compounds are essentially diamagnetic through antiferromagnetic coupling. It was further found by molecular weight measurements that, in solution, the $n = 2$ complex is associated into tetranuclear units, while those with $n = 3$ or 4 are only dinuclear.

Structural studies have demonstrated the existence of a Cu_4O_4 "cubane" core in tetranuclear complexes of this type,[10,14,15] and different geometrical models have been used to account for the observed magnetic interaction.[16-18]

In view of the known sensitivity of these magnetic interactions to small changes in ring geometry, we have prepared a series of substituted tetranuclear complexes based on the system



2 [R = H, CH_3, C_2H_5, C_6H_5, $(CH_3)_2CH$]

In this paper, we discuss their magnetic properties.

Experimental Section

General Data. Infrared spectra were recorded on a Perkin-Elmer 621 instrument, visible-UV spectra on Cary 14 and 118 spectrometers, and mass spectra on a Varian MAT 311A instrument. Microanalysis were performed by Malissa-Reuter Laboratories, West Germany; all analytical data are in Table I.

Variable-temperature magnetic susceptibilities were determined by Dr. A. B. P. Lever, York University, using the Faraday method. Diamagnetic corrections were made with use of the Pascal constants of Figgis and Lewis,[19] and the temperature-independent paramagnetism, N_α, was taken as 60×10^{-6} cgsu/Cu atom. Experimental susceptibility data were fitted to the appropriate theoretical susceptibility equations with use of a nonlinear regression by the Gauss-Newton method, employing a least-squares objective function $\sum(\chi_{\text{calcd}} - \chi_{\text{obsd}})^2$ as the fitting criterion.

5,5,5-Trifluoro-4-(trifluoromethyl)-4-hydroxy-2-pentanone (HFDA) was prepared by the condensation of hexafluoroacetone with acetone as described previously.[20]

Imino Complexes. In a typical preparation, anhydrous copper(II) chloride (1.34 g, 10 mmol) in warm ethanol was added to (R)-(-)-2-amino-1-butanol (0.89 g, 10 mmol) followed by HFDA (2.24 g, 10 mmol) and KOH (1.12 g, 20 mmol), also in ethanol. The solution was heated at reflux for 6 h and cooled to 0 °C, and KCl was removed by filtration. Concentration of the resulting blue solution and recrystallization yielded the imino complex **2** (R = C_2H_5), blue crystals from ethanol.

The same method, using aminoethanol (0.61 g, 10 mmol), gave **2** (R = H, blue crystals from ethanol); (R,S)-(±)-2-amino-1-propanol (0.75 g, 10 mmol) gave **2** (R = CH_3, racemic, blue crystals from methanol); (S)-(+)-2-amino-1-propanol gave **2** (R = CH_3, optically pure, blue crystals from methanol); (S)-(+)-2-amino-3-methyl-1-butanol gave **2** (R = $(CH_3)_2CH$, blue crystals from ethanol); (R)-(-)-2-amino-2-phenylethanol gave **2** (R = C_6H_5, blue crystals from chloroform).

Results and Discussion

Each compound studied showed an increase in magnetic susceptibility with a decrease in temperature. The copper-copper interactions were determined from the χ_A vs. tem-

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(1) In this context, the term template condensation is used to describe a reaction that will only occur in the presence of the metal ion.
(2) Throughout this paper, we use the terms mono-, di-, or tetranuclear with reference to the number of copper atoms present in one unit of the complex.
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Table I. Analytical and Mass Spectral Data for **2**

R	molecular formula	% C		% H		% N		mp, °C	dimer parent ion *m/e*[a]
		calcd	found	calcd	found	calcd	found		
H	$C_{32}H_{36}Cu_4F_{24}N_4O_8$	29.2	29.1	2.74	2.75	4.26	4.12	220–235 dec	628
CH_3	$C_{36}H_{44}Cu_4F_{24}N_4O_8$	31.5	31.2	3.24	3.59	4.09	3.97	200–210 dec	684
C_2H_5	$C_{40}H_{52}Cu_4F_{24}N_4O_8$	33.7	33.8	3.68	3.80	3.96	4.00	100–105	712
C_6H_5	$C_{56}H_{52}Cu_4F_{24}N_4O_8$	41.5	41.5	3.24	3.24	3.49	3.44	128–130	808
$(CH_3)_2CH$	$C_{44}H_{60}Cu_4F_{24}N_4O_8$	35.6	35.6	4.08	4.04	3.81	3.80	118–120	740

[a] Mass numbers for complexes are for the peak containing $^{63}Cu_2$.

Table II. Infrared[a] and Visible Spectra[b] for **2**

R	ν(C=N), cm^{-1}	visible band maxima, nm (ϵ)
H	1672 (s)[c]	640 (178)
CH_3	1672 (s)	638 (167)
C_2H_5	1672 (s)	634 (163)
C_6H_5	1670 (s)	620 (149)
$(CH_3)_2CH$	1670 (s)	614 (80)
CH_3 (racemic)	1672 (s)	636 (174)

[a] As Nujol mulls. All compounds also show strong (C-F) absorptions in the region 1150–1200 cm^{-1}. [b] All spectra run in dichloromethane. [c] s = strong.

Table III. Calculated Parameters from Best Fit to Equations for Magnetic Susceptibility for **2**

T_d Geometry

R	*g*	2*J*	*s*[a]
H	2.06	+29.4	0.25
CH_3	2.00	−55.6	2.1
C_2H_5	2.00	−28.9	0.69
C_6H_5	2.00	−49.4	1.5
$(CH_3)_2CH$	2.00	−65.9	0.71
CH_3 (racemic)	2.15	−10.7	0.13

D_{2d} Geometry

R	*g*	J_L	J_S	*s*
H	2.00	+1.47	+27.9	0.26
CH_3	2.00	−25.8	−10.6	5.9
C_2H_5	2.00	−14.5	−14.5	0.67
C_6H_5	2.00	−18.6	−29.4	2.3
$(CH_3)_2CH$	2.01	−35.1	−35.1	0.67
CH_3 (racemic)	2.01	+44.0	−39.9	0.01

[a] $s = 10^7[\Sigma(\chi_{\text{calcd}} - \chi_{\text{obsd}})^2]$.

perature data by employing the Heisenberg–Dirac–Van Vleck model for the effective Hamiltonian with total spin *S* (eq 1).

$$\mathcal{H} = 2\sum_{i>j} J_{ij}S_iS_j \qquad (1)$$

All imino complexes were fitted to the Bleaney–Bowers equation (eq 2) for a dinuclear system,[21] as well as to equations

$$\chi_A = \frac{N\beta^2g^2}{3kT}\left[1 + \frac{1}{3}\exp(-2J/kT)\right]^{-1} + N\alpha \qquad (2)$$

for two different tetranuclear geometries, to initially determine the degree of aggregation.

None of the complexes in this series gave a satisfactory fit to the equation for a dinuclear system,[22] suggesting the existence of the tetranuclear Cu_4O_4 unit suspected from previous solution molecular weight measurements.[12]

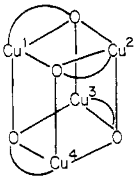
The susceptibility equation used to fit the four-center spin-$^1/_2$ system is dependent upon the local symmetry of the Cu_4O_4 core.[23] All complexes were fitted to the equation for T_d geometry[16] (eq 3) where $x = \exp(-2J/kT)$ and to the

$$\chi_A = \frac{Ng^2\beta^2}{2kT}\,\frac{J + 3x^2}{5 + 9x^2 + 2x^2} + N\alpha \qquad (3)$$

equation for D_{2d} geometry[17] (eq 4) where $x = J_L/kT$, $y =$

$$\chi_A = \frac{Ng^2\beta^2}{2kT}\,\frac{5e^{2x} + e^{-2x} + 2e^{-2y}}{5e^{2x} + 3e^{-2x} + e^{-4x} + 6e^{-2y} + e^{-4y}} + N\alpha \qquad (4)$$

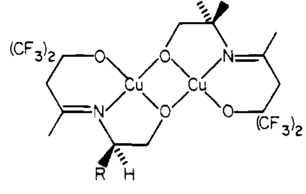
J_S/kT, χ_A is per Cu^{2+} atom, and all other symbols have their usual significance. Coupling constants in the Cu_4O_4 core may be represented as $J_{12} = J_{34} = J_S$ and $J_{13} = J_{14} = J_{23} = J_{24} = J_L$. The exchange coupling constants J_S and J_L and *g* values were calculated from a best fit of the observed data to the appropriate equations and are summarized in Table III. The relative difference in the fits between the two four-center geometries was small, although the fits were both considerably better than those for the simple dimer model.[22] Future references are limited to the D_{2d} model using exchange coupling constants J_L and J_S, since discussions are in terms of a distorted form of the ideal Cu_4O_4 core.



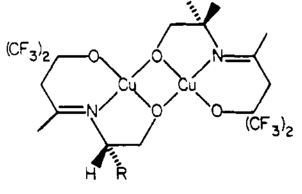
All ligands employed in this study (except R = H) contain a chiral center at the site of substitution. Thus more than one diastereomeric form is possible upon complexation and aggregation to a di- or tetranuclear species. To determine whether the optical purity of the ligand would affect the magnetic properties of the complexes, we undertook a comparison between the optically pure and racemic complexes **2** (R = CH_3).

Figure 1 shows the magnetic susceptibility vs. temperature plots for these two complexes fitted to the equation describing the core as D_{2d} geometry. The optically pure complex has J_L and J_S both negative, which is indicative of an antiferromagnetic interaction, while J_L and J_S are of opposite signs for the racemic complex, and, overall, a slight ferromagnetism is observed.

For a dinuclear complex derived from optically pure amino alcohol, only one diastereomer is possible, the *R–R* (or *S–S*) combination, whereas a racemic mixture of amino alcohols may give rise to two diasteriomeric forms, the *R–R/S–S* enantiomeric pair or the achiral *R–S* form.



R-R or *S-S*



R-S

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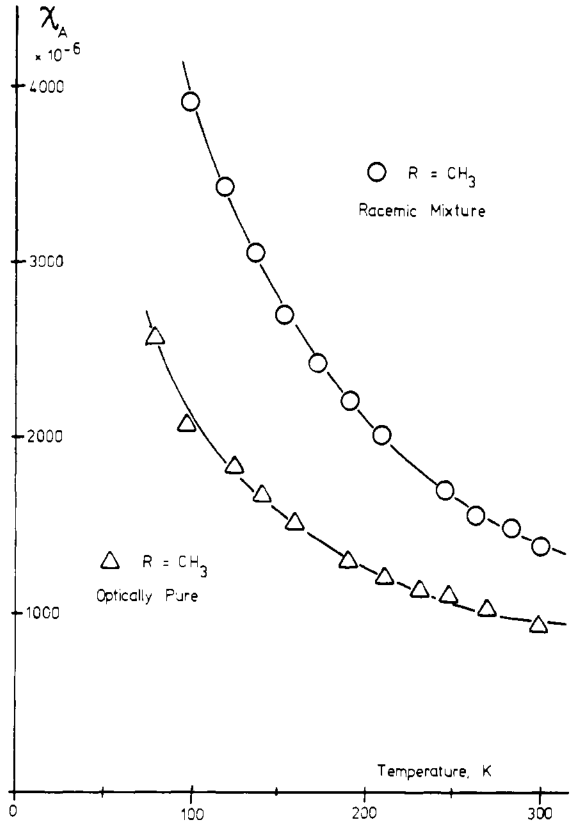


Figure 1. Magnetic susceptibility data for racemic and optically pure complexes of **2** (R = CH_3). Solid lines are calculated by eq 4, and values of g, J_L, and J_S are in Table III.

Clearly, the relative positions of the two substitutent R groups will be of importance in determining the ring conformations and hence magnetic properties, when two of these dinuclear units come together to form a tetranuclear unit. Differing properties would therefore result from the *R–R/S–S* or *R–S* diastereomeric forms.

To avoid the problem of obtaining structural Cu_4O_4 cores of different diastereomers, we used optically pure ligands for the study on the variation of magnetic properties in series **2** [R = H, CH_3, C_2H_5, C_6H_5, $(CH_3)_2CH$]. This series of five tetranuclear complexes was synthesized in order to investigate the effect on the Cu–Cu exchange interactions of varying the bulk of the alkyl group substituted on the five-membered chelate ring.

In general, the size and sign of the coupling constant offers a ready indication of the overall type and degree of magnetism present. An overall positive coupling constant indicates the presence of a net ferromagnetic interaction in the complex, and in this series this is displayed by complex **2** (R = H). By contrast, an overall negative coupling constant is indicative of a net antiferromagnetic interaction in the complex, exemplified by complex **2** [R = $(CH_3)_2CH$].

Exchange parameters for this series of compounds (Table III) show a general trend in which the bulkier substituents on the ring produce a higher degree of antiferromagnetic coupling, although the complex with R = CH_3, optically pure, is anomalously high. A similar trend is apparent in the shift to lower energy of the absorption band at 600–650 nm in the visible spectra (Table II), large shifts being observed for $(CH_3)_2CH > C_6H_5 > C_2H_5$ and barely significant shifts for R = CH_3.

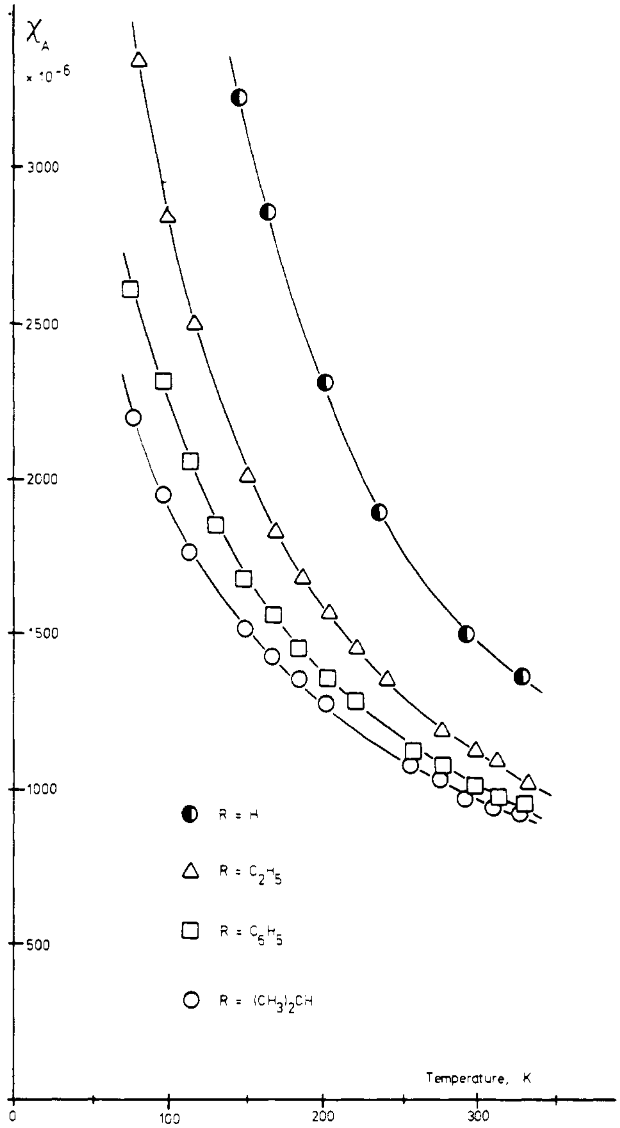
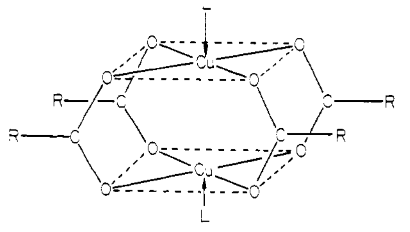


Figure 2. Magnetic susceptibility data for complexes of **2** [R = H, C_2H_5, C_6H_5, $(CH_3)_2CH$]. Solid lines are calculated by eq 4, and values of g, J_L, and J_S are in Table III.

Sacconi and Ciampolini[24] have shown that, in accordance with theoretical considerations, absorption bands in the region 555–1250 nm in copper complexes with bidentate salicylaldimines shift to lower energy as the ligand environment about the Cu^{2+} tends from planar to tetrahedral. Similarly, Edmundson and Lever[25] have shown that, for a number of dinuclear copper(II) vinyl acetate complexes, addition of a donor molecule L axial to the CuO_4 square plane produces a decrease in the energy of the visible absorption band (670–750 nm, CuO_4 + L) with the increased donor strength of L.



Thus the observed trends could be rationalized by either distortions of the Cu^{2+} square plane in each dinuclear unit or as different dimer–dimer interactions which alter the exchange pathways. It is well established that, if an exchange pathway

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involving the Cu^{2+} $d_{x^2-y^2}$ and oxygen p_x orbitals is important, distortion from planarity toward tetrahedral geometry would reduce overlap of the orbitals and weaken antiferromagnetic exchange.[26–28]

In this tetranuclear series a larger R produces a stronger antiferromagnetic interaction, and thus it would seem that variations in spectral and magnetic properties must be explained as a systematic variation in the dimer–dimer interaction. The change in central atom geometry from four- to five-coordinate by the introduction of a fifth donor in the apical position of the vinyl acetate dimer also occurs in the aggregation of two imino–alkoxy dinuclear units to form a tetranuclear species. Since, in general, short bond distances lead to greater overlap of metal d orbitals with orbitals of bridging oxygens leading to stronger interactions, a decrease in overlap of the copper d orbitals and sp hybrid orbitals on the bridging oxygens must occur with an increase in the bulk of R.

Therefore, as the bulk of R increases and the Cu–O (axial) overlap decreases, we see an increase in the antiferromagnetic behavior of the complex (Figure 2). This may be ascribed to less distortion of the dinuclear exchange system due to less dimer–dimer interaction and a dominance of the intradimer exchange pathway over the interdimer exchange pathway. Although coupling constants are small and small structural changes could easily affect their values, we believe this systematic variation of the magnitude of the coupling constants with the nature of R demonstrates that, in an imino complex of this type, the nature of a substitutent group in the chelate ring containing the bridging oxygen atom has an important effect on the degree and type of magnetic interaction between the four Cu^{2+} ions. The effect is clearly steric in nature, in agreement with earlier results in which the size and confirmation of this ring has been varied.[12,13] In particular, we show that even such an apparently trivial change as the use of resolved rather than racemic ligands may have a significant effect on interactions in the solid state.

Acknowledgment. Financial support for this work was provided by the National Science and Engineering Research Council of Canada. We are much indebted to Dr. A. B. P. Lever, York University, for measurement of variable-temperature magnetic susceptibilities.

Registry No. **2**, R = H, 77744-95-7; **2**, R = CH_3, 77744-96-8; **2**, R = C_2H_5, 77744-97-9; **2**, R = C_6H_5, 77744-98-0; **2**, R = $(CH_3)_2CH$, 77744-99-1; **2**, R = CH_3 (racemic), 77841-55-5.

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Magnetic and Spectroscopic Studies on *N*-(Picolinamido)salicylaldimine Complexes of Some Bivalent 3d Metal Ions

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Received June 26, 1980

Adducts as well as deprotonated complexes of *N*-(picolinamido)salicylaldimine (H_2PIS) of the types $MCl_2\cdot 2H_2PIS$ [M = Mn(II), Co(II), Ni(II)], $M(HPIS)_2$ [M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II)], and $M(PIS)\cdot nH_2O$ [M = $V^{IV}O$, Mn(II), Co(II), Ni(II), Cu(II), Zn(II); n = 1 for $V^{IV}O$, 2 for other metal ions] have been prepared. In the case of Cu(II) a partially deprotonated $Cu(HPIS)Cl\cdot H_2O$ has also been obtained. Molar conductivities indicate nonelectrolytic behavior of deprotonated complexes and some ionic dissociation of the adducts in 10^{-3} M DMF solution. Magnetic and electronic spectral studies suggest octahedral geometry for all the complexes except those of Cu(II), which are distorted octahedra. The distorted octahedral geometry for Cu(II) complexes is further shown by the solid-state ESR spectra. X-ray powder diffraction studies of $Cu(PIS)\cdot 2H_2O$ suggest that this complex belongs to the tetragonal crystal system with a = 8.6059 Å, c = 17.7 Å, and Z = 4. The infrared spectral studies indicate that H_2PIS acts as a bi-, ter-, or quadridentate ligand in the complexes.

Introduction

Recently a number of papers[1,2] have been published from our laboratories on 3d metal complexes of acetone isonicotinoyl-, nicotinoyl-, and picolinoylhydrazones and salicylaldehyde isonicotinoylhydrazone This work has now been extended to the hitherto uninvestigated *N*-(picolinamido)- and *N*-(nicotinamido)salicylaldimine complexes of 3d metal ions because there are as many as five potential donor sites and a possibility of keto–enol tautomerism in these ligands, which may be expected to lead to varied bonding and stereochemical behavior in the complexes. The present paper describes the results of our investigation on the synthesis and structural studies of *N*-(picolinamido)salicylaldimine complexes of $V^{IV}O$, Mn(II), Co(II), Ni(II), Cu(II), and Zn(II).

Experimental Section

Materials. All the chemicals used in this study were of BDH or equivalent quality. *N*-(Picolinamido)salicylaldimine was prepared as described by Sacconi;[3] mp 172 °C (lit.[3] mp 173–75 °C).

Synthesis and Analysis of the Complexes. Dichlorobis(*N*-picolinamido)salicylaldimine)metal(II) complexes, $M(H_2PIS)_2Cl_2$ [M = Mn(II), Co(II), Ni(II)], were obtained by mixing ethanolic solutions of H_2PIS and the appropriate metal chloride in ~2:1 molar ratio and refluxing the reaction mixture for about 6 h. The resulting solution was concentrated to incipient crystallization.

Aquo(*N*-(picolinamido)salicylaldiminato)oxovanadium(IV), $VO(PIS)\cdot H_2O$, and chloroaquo(*N*-(picolinamido)salicylaldiminato)copper(II), $Cu(HPIS)Cl\cdot H_2O$, were prepared by mixing the methanolic or ethanolic solutions of H_2PIS and vanadyl sulfate or cupric chloride in a 1:1 molar ratio. The complexes precipitated almost immediately.

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